



Institut für Chemie und Dynamik der Geosphäre
Institut V: Sedimentäre Systeme

***Geochemical Significance of Heterocompounds
in Petroleum Systems, Offshore Norway***

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Abbreviations

Amu	atomic mass unit
API gravity	$^{\circ}\text{API} = [141.5/\text{density of oil at } 60^{\circ}\text{F (g/cm}^3\text{)}]-131.5$
BCU	Base Cretaceous Unconformity
CPI	Carbon Preference Index (Bray and Evans, 1961)
E	East
ENE-WSW	Eastnortheast to Westsouthwest direction
EPC	Electronic Pressure Control
eV	Electron Volt (1.602×10^{-19} Joule)
FID	Flame Ionisation Detector
FZ Jülich	Forschungszentrum Jülich
GC	Gas Chromatography
GOR	‘Gas-Oil-ratio’
GC-MS	Gas chromatography – Mass spectrometry
HC	Hydrocarbons
HI	Hydrogen Index (mg HC/g TOC)
i.d.	internal diameter
<i>m/z</i>	mass/charge
Ma	Million years
md	millidarcy ($9.87 \times 10^{-10} \text{ m}^2$)
MDR	Methyldibenzothiophene ratio
MPLC	Medium Pressure Liquid Chromatography
N	North
NE	Northeast
NE-SW	Northeast to Southwest direction
N-S	North to South direction
NSO	organic compounds containing Nitrogen, Sulfur
and	Oxygen
NW	Northwest
OEP	Odd : Even Preference (Scalan and Smith, 1970)
OI	Oxygen Index (mg CO ₂ /g rock)

OM	Organic Matter
OWC	oil-water contact
PAH	Polycyclic Aromatic Hydrocarbons
PI	Production Index ($S_1/(S_1+S_2)$)
pr/ph	Pristane/Phytane ratio
R _c	Calculated Vitrinite Reflectance, extrapolated from
a	geochemical parameter
S	South
SE	Southeast
SW	Southwest
S ₁	(mg HC/g rock) - Rock-Eval data
S ₂	(mg HC/g rock) - Rock-Eval data
S ₃	(mg CO ₂ /g rock) - Rock-Eval data
TC	Total Carbon
T _{max}	Temperature at greatest HC generation - Rock-Eval
data	
TOC	Total Organic Carbon
TS	Total Sulfur
W	West
wt%	weight percent

Kurzfassung

Die vorliegende Arbeit fasst die Ergebnisse organisch-geochemischer Untersuchungen im *offshore*-Bereich Norwegens zusammen. Der Schwerpunkt dieser Studie liegt auf der geochemischen Signifikanz von Stickstoff-, Schwefel- und Sauerstoffverbindungen (NSO-Verbindungen) in Erdölsystemen. Neben Erdölen und potentiellen Erdölmuttergesteinen aus den *offshore*-Gebieten wird eine künstliche Reifesequenz, die mittels wässriger Pyrolyseexperimente erhalten wurde, zur Untersuchung der Reife- und Expulsionseffekte herangezogen. Im Rahmen dieser Arbeit wird zum ersten Mal das Vorkommen von Xanthonen in Erdölen beschrieben, und es werden die Retentionszeiten dieser Verbindungen bestimmt. Anhand der Kohlenwasserstoffgeochemie werden die Erdölproben bezüglich Fazies, Reife und Biodegradation klassifiziert, und darauf basierend wird das Verhalten von drei Verbindungsgruppen, nämlich der Carbazole, Fluorenone und Xanthone, hinsichtlich geochemischer Prozesse detailliert untersucht.

Die zwei potentiellen Erdölmuttergesteine sind anhand der Verteilungen der Carbazole und Fluorenone unabhängig von Reifeeffekten faziell unterscheidbar. Als Parameter dienen die relativen Konzentrationen der Verbindungsgruppen, mehrere Verhältnisse der alkylierten Carbazole und Fluorenone und auch die Verteilung von Benzocarbazolen und Benzofluorenonen. Die absoluten Konzentrationen der beiden Verbindungsgruppen sind eindeutig reifeabhängig, was anhand der natürlichen Erdölmuttergesteine und der Reifungsexperimente demonstriert wird. Einen Einfluss der Reife auf einige Verhältnisse alkylierter Carbazole und Fluorenone und auf die Verteilung der Benzoisomeren kann ebenso anhand der Extraktanalysen gezeigt werden. Während Fazies und Reife eindeutig die Verteilung dieser Verbindungsgruppen in den Erdölmuttergesteinen kontrollieren, ergeben Korrelationen mit den korrespondierenden Erdölen anhand der Verbindungsgruppen kaum Hinweise auf ihren Ursprung und die Reife. Diese Diskrepanz zwischen den Erdölen und ihrer Quelle, die Ergebnisse der künstlichen Reifesequenz und die Korrelationen mit Migrationsdistanzen der akkumulierten Erdöle zeigen, dass Partitionierungsprozesse einen bedeutenden Einfluss auf die Zusammensetzung dieser polaren Verbindungen in den Erdölen haben. Die Ergebnisse dieser Studie weisen auf verschiedene Szenarien für diese drei Verbindungsgruppen hin:

Der größte Teil der generierten Carbazole wird während der Expulsion im Erdölmuttergestein aufgrund der moderaten Polarität zurückgehalten. Abgeschirmte

Carbazole reichern sich gegenüber nicht abgeschirmten Isomeren in den Erdölen an. Die Auswirkungen der primären Migration werden durch sekundäre Migrationsprozesse verstärkt.

Im Vergleich zu Carbazolen werden die polareren Fluorenone stärker am Verlassen des Erdölmuttergesteins gehindert. Niedrigpolare Fluorene, die mit dem Erdöl migrieren, werden aufgrund der durch die beiden benachbarten Benzolringe aktivierten Methylenbrücke während der Migration durch Öl-Wasser und/oder Öl-Mineralwechselwirkungen zu den korrespondierenden Ketonen oxidiert. Eine Anreicherung der nicht geschützten Methylfluorenone relativ zu dem geschützten Isomer mit zunehmender Migrationsdistanz ist auf eine reduzierte Reaktivität des 1-Methylfluorens für die Oxidation aufgrund sterischer Hinderung zurückzuführen.

Im Gegensatz zu den hohen Konzentrationen der Carbazole und Fluorenone sind die der hochpolaren Xanthone in den Erdölmuttergesteinen nur sehr gering, oder die Konzentrationen liegen unterhalb der Nachweisgrenze. Dennoch sind ähnlich hohe Konzentrationen wie die der anderen beiden Verbindungsgruppen in den Erdölen enthalten. Dies deutet darauf hin, dass Xanthone während der sekundären Migration aus aromatischen Vorläufern geosynthetisiert werden und daher vielversprechend als Indikatoren für organisch-anorganische Wechselwirkungen im Trägergestein sind. Diese Vermutung wird dadurch unterstützt, dass die Konzentrationen der Xanthone mit zunehmender Migrationsdistanz zunehmen. Ähnlich wie bei den Carbazolen reichern sich die geschützten Isomere mit zunehmender Migrationsdistanz an, was durch Berechnungen der molekularen Dynamik bestätigt wurde.

Biodegradation kann gleichfalls die Verteilung dieser Erdölbestandteile in der Erdöllagerstätte verändern. Die nicht geschützten Isomere der Carbazole und Xanthone werden im Vergleich zu den geschützten Isomeren aufgrund einer höheren Affinität zu der Wasserphase bevorzugt biologisch abgebaut. Im Gegensatz dazu nimmt die Konzentration des 1-Methylfluorens mit zunehmendem Grad der Biodegradation im Vergleich zu seinen Isomeren ab. Die Ursache für die relative Abnahme des 1-Methylfluorens kann das Resultat des biologischen Abbaus von Fluorenen sein, da der biologische Abbau von Fluorenen über die Produktion von Fluorenonen führt. Durch die Methylgruppe des 1-Methylfluorens ist eine Oxidation zum korrespondierenden Keton sterisch gehindert.

Eine detaillierte deutsche Zusammenfassung der Arbeit ist auf den Seiten 202-206 zu finden.

Abstract

This thesis presents the results of an organic geochemical investigation of 72 oils, nine source rock samples and two core samples from the main petroleum systems located offshore Norway. The main focus of the study was on the geochemical significance of nitrogen, sulphur and oxygen (NSO) compounds in relation to source facies and maturity, primary and secondary migration, and biodegradation. Samples comprising an artificial maturity sequence, obtained by hydrous pyrolysis of an immature source rock, were also used for an investigation of the effects of maturity and expulsion on polar compound composition. During the course of this study, the occurrence of xanthenes in crude oils was detected and their gas chromatographic elution order was measured for the first time. The crude oils were initially classified into broad facies, maturity and biodegradation categories on the basis of their hydrocarbon geochemistry. The geochemical behaviour of three heterocompound classes, i.e. carbazoles, fluorenones and xanthenes, was then investigated in detail, and the data were interpreted within the context of these important geochemical controls and processes.

The two potential source rocks from the Haltenbanken area could be differentiated by the distribution of carbazoles and fluorenones, independent of maturity. The discrimination parameters include the relative concentrations of the compound groups, several ratios of alkylated carbazoles and fluorenones, and the distributions of benzocarbazoles and benzofluorenones. The absolute concentrations of these compound classes are strongly dependent on maturity, and this is convincingly demonstrated by the analysis of the natural source rock and the recovered rock extracts from the artificial maturation experiment. A maturity influence is observed for some ratios of alkylated carbazoles and fluorenones, and for the distribution of the benzo-isomers in the extracts. Whereas facies and maturity clearly control the distribution of these constituents in source rocks partitioning processes are thought to be the main control on the composition of these polar compounds in oils.

The results of this study indicate different scenarios for the three compound classes in crude oils. During petroleum expulsion, most of the carbazoles generated are retained within the source rock due to their moderate polarity. There is, however, an isomeric fractionation during primary migration such that shielded carbazoles are enriched relative to non-shielded carbazoles in the expelled crude oils. The effects of primary

migration are enhanced during secondary migration due to the interaction between carbazoles and the aqueous, organic and mineral phases of the carrier system.

In comparison to carbazoles, fluorenones are generally more strongly retained by the source rock during expulsion due to their higher polarity. Low-polarity fluorenes which are released during expulsion are easily oxidised to the corresponding ketones during migration through interaction with water and/or mineral matter. This susceptibility to oxidation is due to the activation of the methylene bridge by the two adjacent benzene rings. An observation of relative enrichment of the non-shielded methylfluorenones with increasing petroleum secondary migration distance is attributed to the reduced susceptibility of 1-methylfluorenone to oxidation due to steric hindrance.

In contrast to high concentrations observed for the carbazoles and fluorenones in the source rocks, the highly-polar xanthenes were detected either in minor amounts or were absent. However, concentrations of xanthenes similar to those of the other two compound classes were detected in the crude oils. This indicates that xanthenes probably originate by geosynthesis from suitable aromatic precursors within carrier systems. Xanthenes therefore show great promise as indicators of the degree of organic-inorganic interaction in carrier systems. This assumption is supported by an increase in the concentration of xanthenes in oils with increasing migration distance. The ratio of the shielded methylxanthenes to the non-shielded isomers increases with increasing migration distance in the same way as for the carbazoles. This observation conforms to oil-water partition behaviour as determined by molecular dynamics calculations.

Biodegradation of petroleum within the reservoir can also influence the occurrence and distribution of these polar constituents in oils. The non-shielded isomers of carbazoles and xanthenes are preferentially biodegraded compared to the shielded isomers due to their higher affinity for water. In contrast, the concentration of partially shielded 1-methylfluorenone decreases with increasing degree of biodegradation compared to its non-shielded isomers. The reason for the decrease in relative abundance of the 1-methylfluorenone may be related to biological degradation of fluorenes, as biological degradation of fluorene results in the production of fluorenone as a stable intermediate. The oxidation of 1-methylfluorene to its corresponding ketone is sterically hindered by the methyl group adjacent to the methylene bridge.

1. Introduction

Crude oils and soluble organic matter (bitumen) within petroleum source rocks are complex mixtures of ‘molecular fossils’ derived from once living organisms. Although crude oils originate from source rock bitumen, their physical properties and chemical compositions can differ significantly due to primary migration/expulsion from the source rock, secondary migration and in-reservoir processes. Advances within gas chromatography in the 1960’s and within gas chromatography-mass spectrometry in the 1970’s led to a quantum leap in the insight into molecular organic geochemistry. Due to their relatively high abundance in oil and their ease of analysis the hydrocarbon fractions were the main focus of early organic geochemistry studies. The hydrocarbon constituents of oils and bitumens provided information on the type and origin of organic matter in the source rock (e.g. steranes, oleanane), the environmental conditions during deposition and burial (e.g. pristane/phytane, gammacerane), the thermal maturity (e.g. steranes, hopanes, CPI) and the degree of biodegradation (e.g. pristane/*n*-heptadecane). As the biological markers occur in both source rock bitumens and oils, they provide a tool for oil-source rock correlation and they can be used to identify/differentiate oil families (oil-oil correlation), thus improving the understanding of reservoirs and petroleum migration pathways, and indicating possible new exploration plays. Earlier works that review biomarkers, their origins and applications include those by Connan (1981), Philp (1982), Mackenzie (1984), Tissot and Welte (1984), Johns (1986), Petrov (1987), Waples and Machihara (1991) and Peters and Moldowan (1993).

The non-hydrocarbon fraction (comprising nitrogen, sulphur and oxygen (NSO)-containing compounds) can make up a significant proportion of petroleum. Although the importance of the heterocompounds has been recognised in all of the processes involved in the origin and alteration of petroleum (Hunt, 1995; Tissot and Welte, 1984), their geochemistry is poorly understood. Their potentially significant value for the description and understanding of geochemical processes such as migration, biodegradation and water-washing, reflecting the great range in physico-chemical properties exhibited by these compounds, has prompted intense research activity especially over the past few years.

-Sulphur compounds-

Most of the sulphur present in crude oils and bitumens is organically bound. The abundance of these organic sulphur compounds (OSC) depends primarily on the composition of the original kerogen and on its maturity (Orr, 1986; Sinninghe Damsté and de Leeuw, 1990). Ho et al. (1974) subdivided the OSC into six classes, namely nonthiophenic sulphur, thiophenes, benzothiophenes, dibenzothiophenes, benzo-naphthothiophenes and “sulphur not recovered”, and classified crude oils into three ‘maturity groups’ on the basis of the content and distribution of OSC. More recently, increasing interest has been shown in the distributions of dibenzothiophenes (DBT) and methyl dibenzothiophenes (MDBT) due to their variation with increasing maturity (Radke et al., 1982; Hughes, 1984; Radke et al., 1986; Leythaeuser et al., 1988; Radke and Willsch, 1991).

-Oxygen-containing compounds-

The first detailed investigation of oxygen compounds in crude oils was made by Snyder et al. (1968). In addition to aliphatic carboxylic acids, phenols, benzo-, dibenzo- and benzo-naphthofurans and phenylketones, they identified compound classes with an additional heteroatom (sulphur or nitrogen) such as sulfoxides, pyridones and quinolones. Since this initial study many detailed characterisations of oxygen compound classes in crude oils and source rocks have been carried out at the molecular level. For example, a review of the occurrence of carboxylic acids in crude oils and sediments was reported by Seifert (1975). Jaffé and Gardinali (1990) described the generation and maturation of carboxylic acids in ancient sediments from the Maracaibo Basin, and Jaffé and Gallardo (1993) proposed these compounds as indicators of crude oil biodegradation and migration. Extended saturated and monoaromatic tricyclic terpenoid carboxylic acids have been found in Tasmanian tasmanite (Azevedo et al., 1994), and Barakat and Rullkötter (1995) reported the occurrence of extractable and bound fatty acids in sediments from the Nördlinger Ries in Germany. Chromans have been identified in a number of sediment extracts and oils ranging in age from Pleistocene to Permian, and it has been suggested that these compounds may be useful as palaeoenvironmental indicators (Sinninghe Damsté et al., 1987, 1993). Aliphatic ketones and aldehydes were identified in the Green River Formation oil shale (Anders et al., 1975; Wang and Rullkötter, 1997) and the Cretaceous black shale deposits of the Fardes Formation (Grimalt et al., 1990), in bitumen from the Proterozoic dolerite sill

from the McArthur Basin (George and Jardine, 1994) and in hydrothermal petroleum and sediment extracts from the Guaymas Basin (Leif and Simoneit, 1995). A detailed account of the distribution of several types of aromatic ketones and aldehydes such as indanones, tetralones, naphthaldehydes, acetylnaphthalenes, benzaldehydes and acetophenones in the low-polarity NSO compound fractions of Posidonia Shale bitumens was provided by Wilkes et al. (1998b).

Alkylated fluoren-9-ones were first identified in Wilmington petroleum by Latham et al. (1962) and were subsequently found in Athabasca oil sand bitumen (Mojelsky and Strausz, 1986) and Posidonia Shale bitumen (Wilkes et al., 1998a). The last study demonstrated that the concentrations of these compounds increase with increasing maturity and it was suggested that fluorenones and benzofluorenones could originate from functionalised biphenyls and phenylnaphthalenes by cyclisation reactions. In contrast, Bennett and Larter (2000) expressed concern that these compounds may, under some circumstances, be formed sporadically as a result of post-sampling oxidation.

Low molecular weight (C_0 - C_3) alkylphenols are ubiquitous constituents of crude oils and formation waters of petroleum systems (Ioppolo et al., 1992; Ioppolo-Armanios et al., 1994, 1995; Bennett et al., 1996). Alkylphenols are both oil- and water-soluble and their absolute and relative abundances in oils and associated formation waters are predictably determined by their partition coefficients, and the degree of oil/water interaction in the subsurface. Consequently, alkylphenols have been proposed as potential parameters for delineating secondary migration pathways (Larter et al., 1996b; Bennett and Larter, 1997; Taylor et al., 1997; Taylor et al., 2001).

-Nitrogen-containing compounds-

The nitrogen-containing tetrapyrrole pigments (porphyrins and the vanadyl and nickel metalloporphyrins) have been known for many years as maturity and redox indicators (Baker and Palmer, 1978; Mello et al., 1988).

Carbazoles, benzocarbazoles and dibenzocarbazoles are ubiquitous constituents of crude oils and source rock extracts (Helm et al., 1960; Frolov et al., 1989). It has been conjectured that their possible biological origin could be alkaloids, proteins and pigments in terrestrial plants and algae (Snyder, 1965; Kapil, 1971; Hesse, 1974). In the last few years these compounds have received considerable attention because of their potential use as primary and secondary migration indicators, this being related to their partition behaviour between oil and mineral phase in the subsurface (Larter et al.,

1996a). On the one hand, alkyl substituents adjacent to the N-H functional group inhibit sorption by hydrogen bonding, resulting in preferential enrichment of these 'NH-shielded' isomers in crude oils, whereas the relative concentrations of the so-called 'non-shielded isomers', with no alkyl substituents directly adjacent to the heteroatom, were reported to be higher in (non-expelled) source rock bitumens (Larter et al., 1995; Li et al., 1994, 1995). The absolute and relative abundance of the rod-shaped benzo[a]carbazole and the subspherical benzo[c]carbazole have been proposed as a tool to infer distances travelled by crude oils along carrier systems from the source to the trap (Larter et al., 1996a).

More recent investigations of the occurrence of carbazoles in oils indicate that maturity and facies may play a major role in controlling the distribution of this compound class under certain tectonostratigraphic settings. For instance, C₁-carbazole concentrations in both Tithonian source rocks and their expelled crude oils from the Sonda de Campeche (Mexico), a vertically drained petroleum system, first increase and then decrease during maturation, with 1-methylcarbazole being the dominant isomer (Horsfield et al., 1998). Studies of clastic and carbonate source rocks from Germany, western Canada and the North Sea support these results (Stoddart et al., 1995; Clegg et al., 1997; Li et al., 1997; Wilkes et al., 1998a). These authors also observed the same maturity-related trend for the benzo[a]carbazole/(benzo[a]carbazole + benzo[c]carbazole) ratio. Artificial maturation effects on carbazole distributions, as revealed by hydrous pyrolysis of an organic-sulphur-rich source rock from the Ghareb Formation, Jordan, also showed a maturity dependence of the carbazole and benzocarbazole isomers (Clegg et al., 1998a). The influence of different facies (reflecting deposition under transgressive and regressive events) within carbonates in the Keg River Formation (Western Canada) on the distribution of carbazoles was described by Clegg et al. (1997). More recently, Bakr and Wilkes (2002) showed that the benzocarbazole and alkyl carbazole ratios in crude oils from the Gulf of Suez were strongly dependent on source facies and depositional environment. All these studies suggest that facies and maturity, rather than partitioning, play a dominant role in the distribution of carbazoles.

2. Goals and Approach

It was within the context of this background on heterocompound geochemistry that the current research project was conceived, the overall aim being to obtain new insights into the geochemical significance of NSO compounds in crude oils from the Norwegian shelf. The scope of the project was intentionally broad, especially at the outset of the work, such that oils from all of Norway's petroleum systems were studied. Sample subsets were initially placed into broad maturity, facies, migration and biodegradation frameworks on the basis of information provided by the sponsors and from published literature, but could be modified as the work proceeded. Hydrocarbon analysis constituted the first step in the analytical programme, followed by an investigation of the low-polar NSO compounds. Concerning the latter, full-scan GC-MS data were gathered so as to allow quantitatively significant new compound classes to be evaluated. The methodological approach of the project can be summarised as follows:

- characterise crude oils (and some source rocks) using conventional/established hydrocarbon-based parameters;
- identify new molecular NSO compound classes in crude oils and source rocks, and examine their significance in petroleum systems in terms of source indicators and maturity parameters;
- investigate the influence of migration and water-washing on the occurrence of NSO compounds;
- recognise biodegradation by monitoring changes in NSO compound distributions;
- test for primary migration effects on NSO compound distributions using hydrous pyrolysis experiments.

3. Sampling Framework

The Norwegian Offshore Hydrocarbon System can be divided into four proven petroleum provinces (Fig. 3.1).

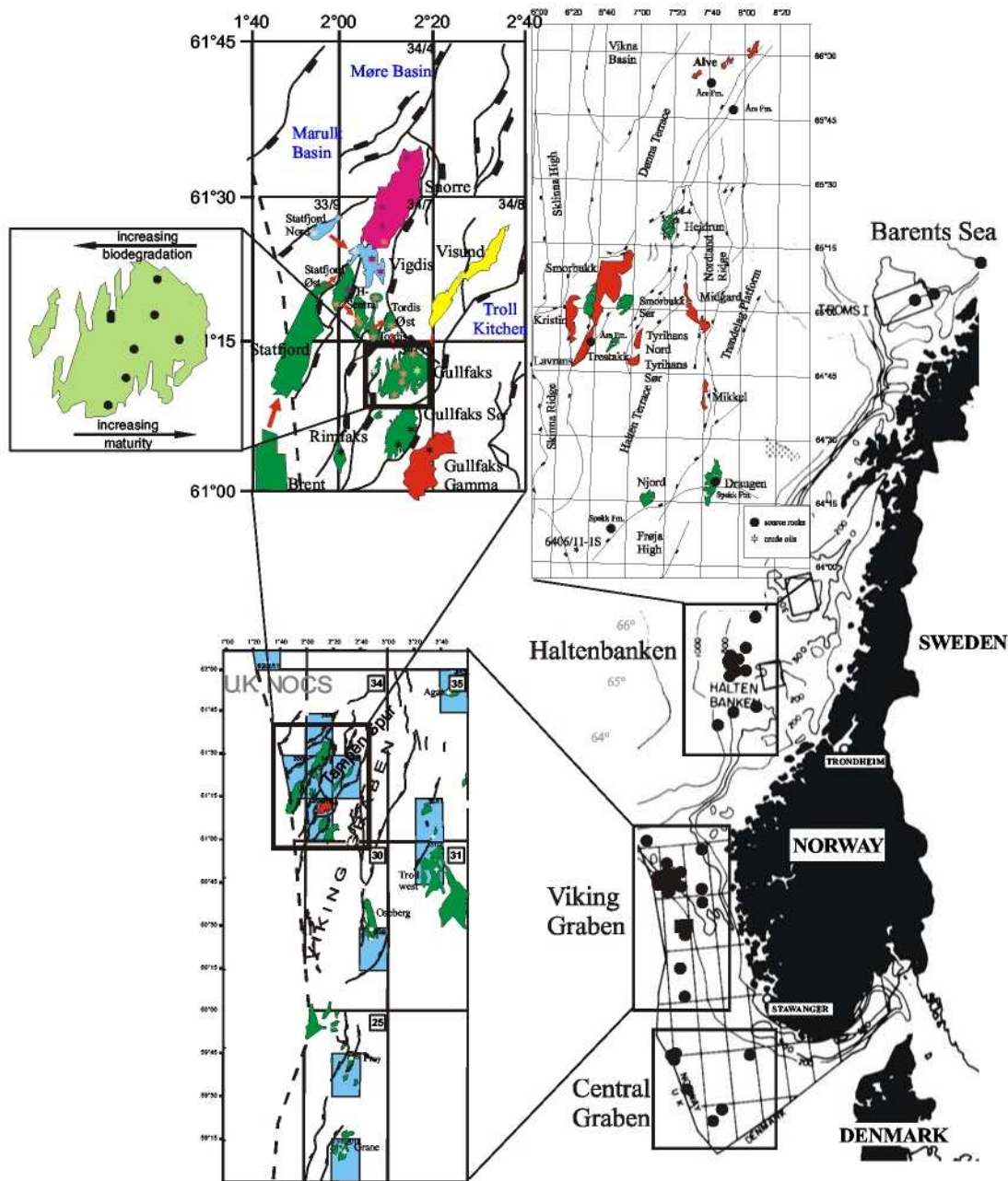


Fig 3.1: Regional map, with dots indicating the general location of the crude oils analysed in this study

Two of the provinces are located in the North Sea: the *Central Graben* to the south and the *Viking Graben* to the north. Both are mature petroleum provinces. The other two provinces are the *Haltenbanken* area in the Norwegian Sea and the area in the southernmost portion of the *Barents Sea* (Fig. 3.1). The Phanerozoic history of all four

areas is essentially similar in that all underwent rifting movements in late Jurassic to early Cretaceous times, prior to further major subsidence in the Late Cretaceous. When the Atlantic Ocean widened, Tertiary thermal subsidence took place along the North Sea and Norwegian Sea sectors, whilst widespread uplift affected the Barents Sea (Fig. 3.2). For more details of the

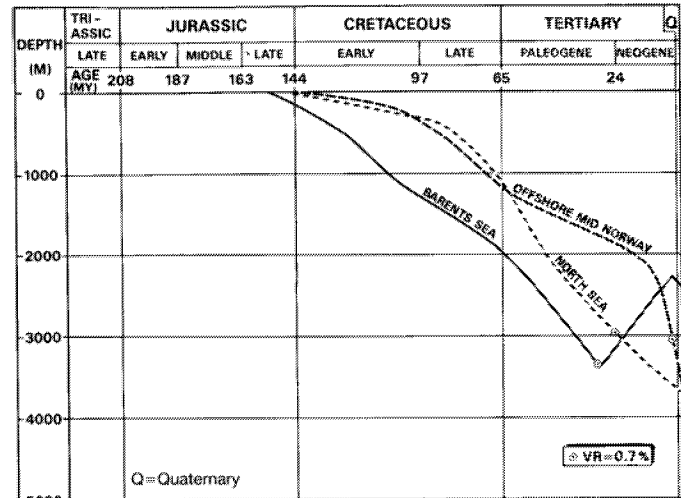


Fig. 3.2: Generalised burial history graphs for the Upper Jurassic shales offshore Norway (after Fjaeran and Spencer, 1991)

geological history the reader is referred to Berglund et al. (1986), Gage and Doré (1986), Heum et al. (1986) and Ziegler et al. (1986). The major source intervals for the Norwegian petroleum provinces are located in the Jurassic formations (Barnard and

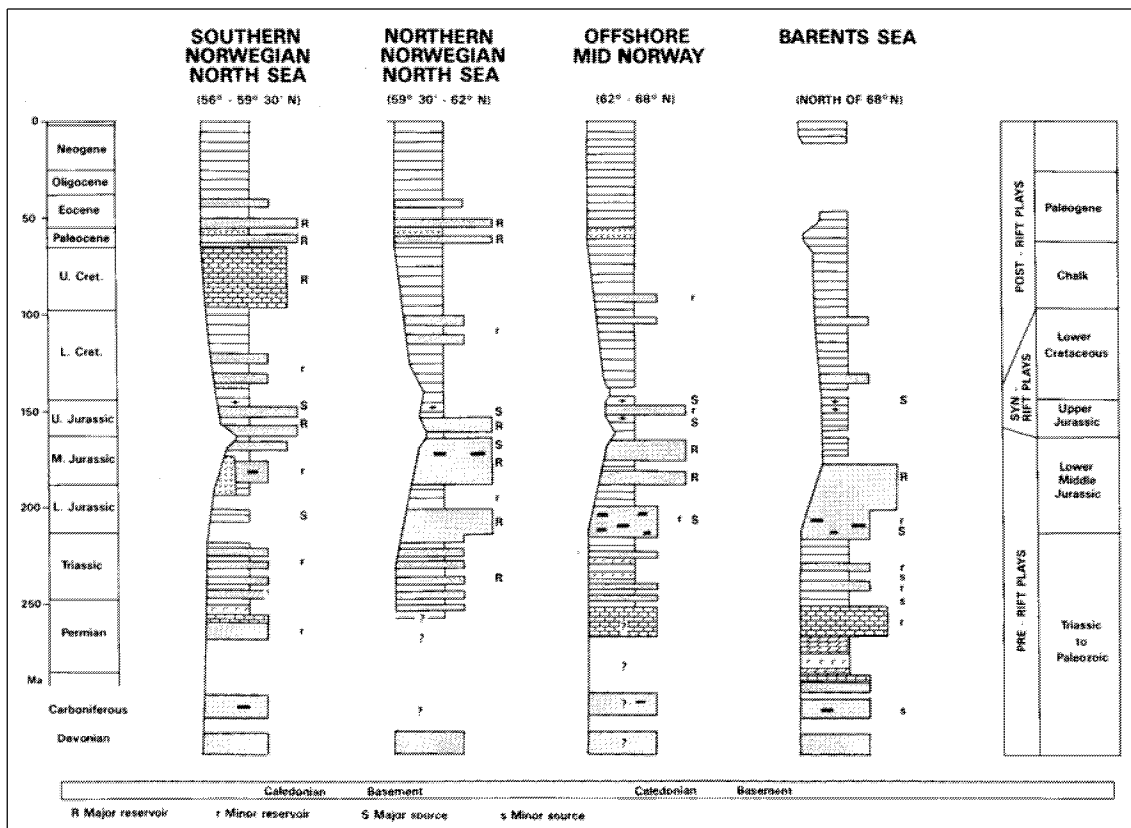


Fig. 3.3: Generalised stratigraphy offshore Norway and classification of source rocks and reservoirs by age (after Fjaeran and Spencer, 1991)

Cooper, 1981; Goff, 1983; Field, 1985; Fjaeran and Spencer, 1991) (Fig. 3.3). Of these formations, the Kimmeridge Clay Formation lateral equivalents are the sources of the major oil accumulations in these areas (Schou et al., 1985; Cornford et al., 1986; Karlsen et al., 1995).

The work described in this thesis is based on the analysis of seventy-two representative crude oils from these four proven petroleum provinces, and a tar mat sample, an oil leg rock sample and nine source rock samples from the Haltenbanken area. The sampling locations for these oils and rocks are described in a regional context below.

3.1 Viking Graben (VG)

The Viking Graben is situated in the northern part of the North Sea. The major oil provinces are located on the Tampen Spur which is in the middle of the northern North Sea, between Norway and the Shetland Islands. The Tampen Spur forms part of a system of rotated fault blocks dipping towards the west and is a Late Jurassic to Cretaceous structure. The area has been subjected to several pre-Upper Jurassic tectonic episodes. These episodes are associated with rifting and regional subsidence and took place during most of the Triassic and Lower and Middle Jurassic (Badley et al., 1988; Charpentier et al., 1992). The area of Block 34/7 in the Norwegian sector was exposed to erosion in late Jurassic time. The erosion of the Triassic, Lower and Middle Jurassic strata took place during several uplift episodes in the Kimmeridgian to Portlandian, probably caused by footwall uplift in response to the large displacement of the Inner Snorre Fault. The late Jurassic uplift was followed by Cretaceous subsidence of the Snorre Block, plunging towards the NNW, causing the Cretaceous to onlap the Base Cretaceous Unconformity (BCU) surface from north to south (Solli, 1995).

The main oil source rocks in the Viking Graben province are the Upper Jurassic Draupne Formation (Kimmeridge Clay equivalent) and the Heather Formation. Whereas the Draupne Formation is almost accepted as the main source rock in the northern North Sea, the Heather Formation is also a viable source of oils with a more terrestrial signature, e.g. well 35/11 and the Agat Field (Chung et al., 1992; Gormly et al., 1994). These two formations exhibit significant vertical heterogeneities in kerogen

composition (Huc et al., 1985) and in kerogen pyrolysate composition (Bailey et al., 1990). Lateral organic-facies heterogeneities in the Viking Graben system and in other regions were reported by Grantham et al. (1980), Bailey et al. (1990) and Scotchman (1991). The major source-rock kitchens in the northern North Sea are the Marulk Basin, the Møre Basin, and the 34/5 Basin to the north of the Tampen Spur high, the Troll Kitchen to the east and the Oseberg Kitchen to the south of the Tampen Spur (Karlsson, 1986).

The main reservoirs in this area are the Middle Jurassic Brent Group, the Early Jurassic Cook Formation, the Late Triassic to Early Jurassic Statfjord Formation and the Triassic Lunde Formation (Kirk, 1980; Eynon, 1981; Karlsson, 1986; Erichsen et al., 1987; Graue et al., 1987; Roberts et al., 1987).

The Viking Graben was one of the main areas studied in this project, with a total of 39 crude oils and two core samples being analysed. Sample information and location are given in Table 3.1 and Figure 3.4, respectively. This sample set was subdivided into three groups:

- a. *VG isolated*; eight oils and two core samples from locations across the whole northern North Sea (Fig. 3.4),
- b. *Tampen Spur*; twenty-three oils, all from the Tampen Spur but excluding the oils from the Gullfaks Field (Fig. 3.5) and
- c. *Gullfaks Field*; eight oils from the Gullfaks Field which represent a biodegradation sequence (Fig. 3.6).

The VG isolated oils comprise a range in maturity and source facies, and some of them are biologically degraded. In the northern-most part of the North Sea one oil from well 6201/11-1 was investigated. Other samples included a condensate from the Agat Field and an oil from Block 35/11, described by Chung et al. (1992) to be of a more terrestrial nature, probably sourced from the Heather Formation. This was supported in a study by Gormly et al. (1994) who pointed out that, apart from the Draupne Formation as the primary source rock, the Heather Formation is also an important oil source, especially up on the Horda Platform. This was substantiated by the current oil generation potential of these shales of up to 25 mg/g rock in Block 35/11. Thus, based on geochemical investigations the authors suggested that at least part of the oils and condensates in Block 35/11, the Agat Field and Troll West Field and from the Oseberg complex are derived from the Heather Formation. Two oil samples from the Frøy Field

and Grane Field in the southern area of the Viking Graben and sourced by the marine Draupne Formation (e.g. Bhullar et al., 1998) were also investigated in this study. Two core samples, a tar mat sample and an oil leg sample, from the Oseberg Field were analysed to investigate differences in their heterocompound composition.

E.nr.	Well	Field		Depth [m]	Age	Lithostratigraphy	
E47548	25/5-1	Froy	oil	2987-3002	M. Jurassic	Vestland Gp	Sleipner Fm
E47612	25/11-T-21A	Garne	oil				
E48127	NSO-1Std	Oseberg	oil				
E35214	30/9-10	Oseberg	oil	2757-2776	U. Jurassic	Viking Gp	Draupne Fm
E47693	30/9-1[OL]	Oseberg	oil leg	2728.75			
E47694	30/9-1[TM]	Oseberg	tar mat	2741.3			
E47613	31/2-G-3H	Troll West	oil				
E43864	35/3-4	Agat	oil	3445-3472	L. Cretaceous	Cromer Knoll Gp	
E43866	35/11-4		oil	2284-2291	M. Jurassic	Viking Gp	Fensfjord Fm
E47557	6201/11-1		oil	2712.6-2716.7	L. Triassic	Hegre Gp	Lunde Fm
E47549	33/9-12	Statfjord Øst	oil	2505-2508	M. Jurassic	Brent Gp	Etive Fm
E28212	33/9-14	Statfjord Nord	oil	2718-2732	L. Jurassic	Viking Gp	Draupne Fm
E47568	34/4-6	Snorre	oil	2577-2585	Triassic	Hegre Gp	U. Lunde Fm
E43858	34/7-4	Snorre	oil	2547-2563	L. Jurassic	Hegre Gp	Statfjord Fm
E47550	34/7-6	Snorre	oil	2518.5-2522.5	L. Jurassic		Statfjord Fm
E47551	34/7-8	Snorre	oil	2359-2374	L. Jurassic		Statfjord Fm
E35213	34/7-10	Snorre	oil	2606.7-2610.7			
E47552	34/7-13	Vigdis West	oil	2500.6-2503.6	M. Jurassic	Brent Gp	Etive Fm
E48128	34/7-13	Vigdis West	oil				
E47553	34/7-14	Tordis	oil	2232.3-2241.3	M. Jurassic		Ness Fm
E47554	34/7-16	Vigdis	oil	2401-2414	M. Jurassic	Brent Gp	Etive Fm
E48129	34/7-16	Vigdis	oil				
E48130	34/7-18		oil				
E47555	34/7-21	H-Sentral	oil	2510.5-2537.5	U. Jurassic-Creta.	Viking Gp	Draupne Fm
E48131	34/7-22	Tordis Øst	oil				
E48132	34/7-23A		oil				
E48133	34/7-26A	H-Sentral	oil				
E43859	34/8-8R	Visund	oil	2921-2950	M. Jurassic		Ness/Tarbert Fm
E43861	34/10-17	Rimfaks	oil	2880-2890	M. Jurassic	Brent Gp	Ness Fm
E43862	34/10-30	Gullfaks Sør	oil	3297-3318	Triassic/Jurassic	Statfjord Fm (Rande Mbr)	
E47556	34/10-32R	Gullfaks Sør	oil	3345-3351	L. Jurassic/?Triassic		Statfjord Fm
E48584	34/10-34		oil				
E43863	34/10-35	Gullfaks Gamma	oil	4015-4025	L. Jurassic	Dunlin Gp	Cook Fm
E43860	34/10-1	Gullfaks	oil	1839-1844	M. Jurassic	Brent Gp	Etive Fm
E48134	34/10-3	Gullfaks	oil	1936-1948	M. Jurassic	Brent Gp	
E48135	34/10-3	Gullfaks	oil	1895-1900	M. Jurassic	Brent Gp	
E48136	34/10-7	Gullfaks	oil		M. Jurassic	Brent Gp	

E.nr.	Well	Field		Depth [m]	Age	Lithostratigraphy	
E48137	34/10-8	Gulfaks	oil		M. Jurassic	Brent Gp	
E48138	34/10-9	Gulfaks	oil		M. Jurassic	Brent Gp	
E48139	34/10-14	Gulfaks	oil		M. Jurassic	Brent Gp	
E48140	34/10-A-1H	Gulfaks	oil		M. Jurassic	Brent Gp	

Tab. 3.1: Sample information for crude oils and core samples from the Viking Graben

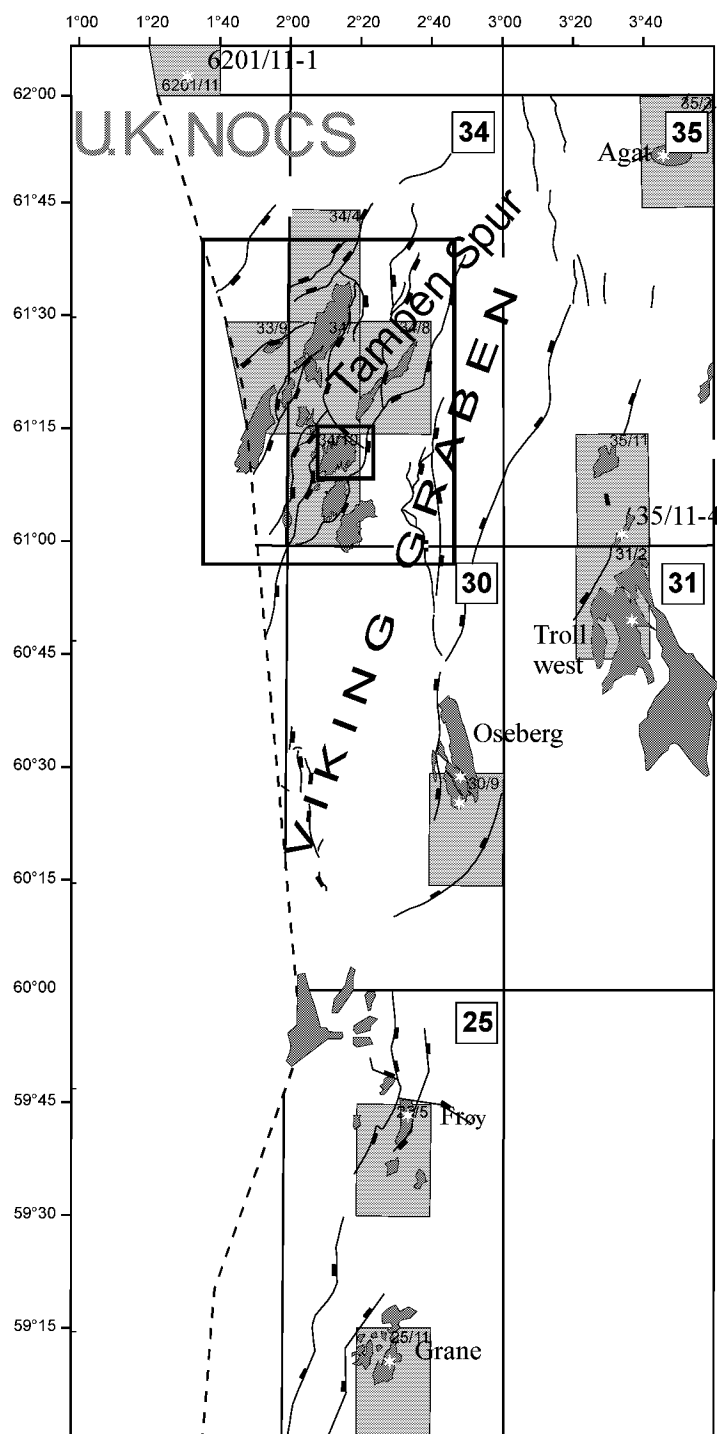


Fig. 3.4: Oil fields and sampling locations in the Viking Graben, North Sea; sampling locations for the 8 'VG isolated' oils are indicated by asterisks

3.2 Tampen Spur

Horstad et al. (1995) analysed the saturated and aromatic hydrocarbon fractions of 86 different test oils and c. 220 reservoir core extracts from 48 wells in the Tampen Spur area using GC-FID, GC-MS and stable carbon isotope analysis. The authors concluded from the extensive oil-source rock correlation studies and from quantitative considerations that most of the oils accumulated in the Tampen Spur area were generated in the Draupne Formation. Significant contributions from the Heather Formation or from coal sequences remain to be documented for the area: Both may represent important sources of the gas in the Gullfaks Gamma Field. Gormly et al. (1994) suggested that very mature, high-gravity oils and condensates from the Gullfaks Gamma Field originate from the Heather Formation. They also concluded that the oils from the Gullfaks Sør Field are mixed and sourced from both the Draupne and the Heather Formations.

Horstad et al. (1995) proposed five major petroleum charging systems within the Tampen Spur area and probable migration/fill scenarios for many of the oil fields. Oils from four of these proposed oil populations were analysed in the present study; sampling locations are shown in Figure 3.5. Mapping of the oil populations in the area demonstrated that the Tampen Spur has a more complex filling history than those proposed earlier by Thomas et al. (1985) and Karlsson (1986) and that it is possible to evaluate the filling of such a complex area by a combined geological and reservoir geochemical approach. The authors concluded that four of the five petroleum groups have similar ranges of maturities but significantly different 28,30-*dinor*-17 α ,18 α -hopane/30-*nor*-17 α -hopane ratios and stable carbon isotope signatures. The fifth petroleum group, comprising oils from the Visund Field, are more mature based on diahopane, C₂₇ 13 β ,17 α -diasteranes and C₂₉ 14 β ,17 β -steranes.

Horstad et al.'s (1995) 5 oil populations are indicated in Figure 3.5. The first oil population is located within the Brent Group of the Visund Field and in the Cook and Statfjord Formations of the Gullfaks Field. Horstad et al. (1995) suggested that the oil leg in the Visund Field probably spills to the southwest along the large fault towards the eastern part of the Gullfaks Field. Although the Visund Field may have been filled from several directions and the petroleum emplacement is complex, a spill route towards Gullfaks is in accordance with the proposed filling from the Cook and Statfjord Formations in the Gullfaks Field.

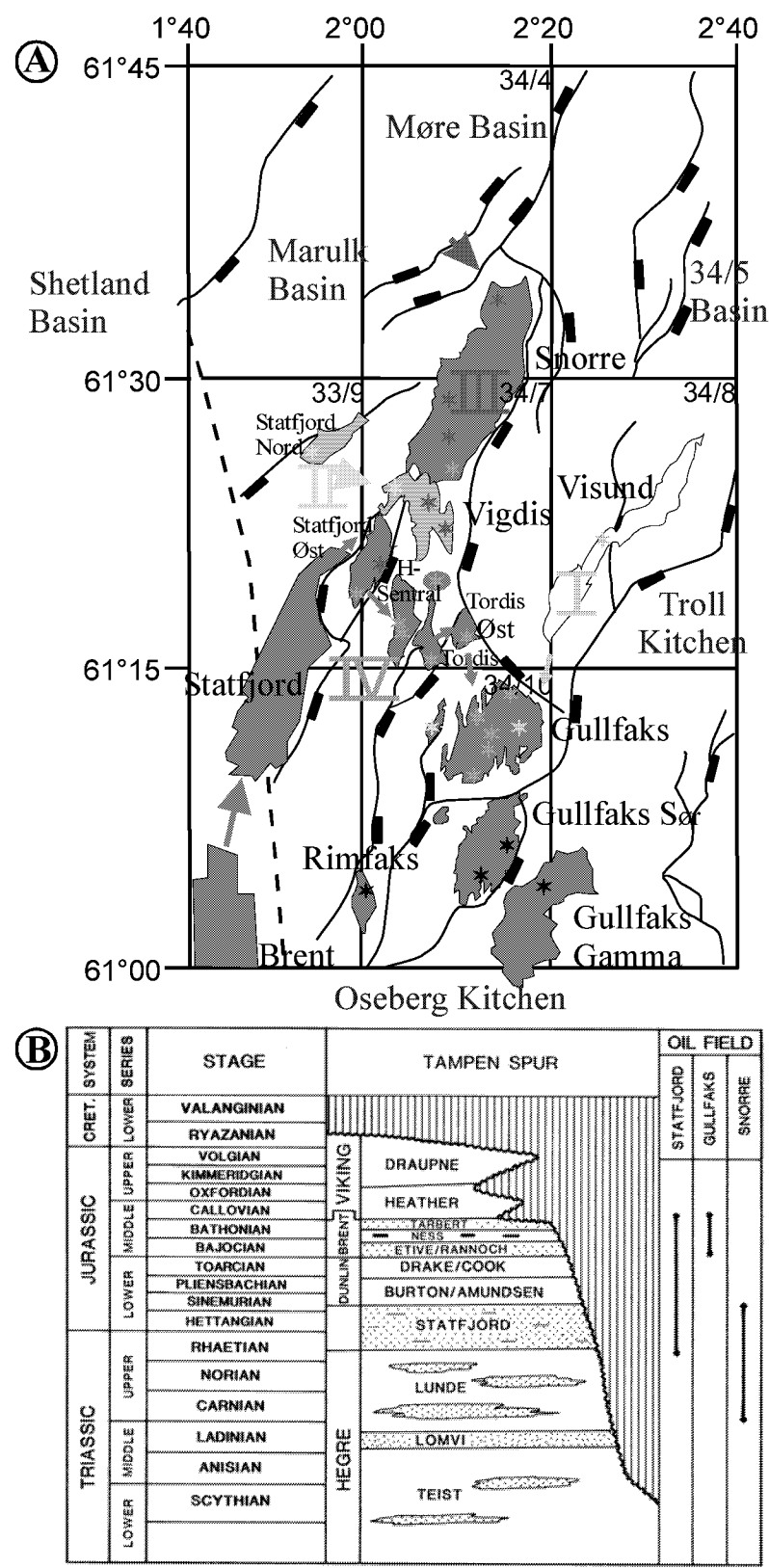


Fig. 3.5: Oil fields and sampling locations (marked by asterisks) in the Tampen Spur, North Sea; (A) map and (B) stratigraphy. Roman numerals I to V in (A) indicate 5 major petroleum populations proposed by Horstad et al. (1995).

Horstad et al. (1995) suggested a Statfjord Nord oil population, present within the Upper Jurassic sandstones and the Brent Group of the Statfjord Nord Field, and in the Brent Group of parts of the Vigdis Field.

The third oil population is named Snorre Field oil population because it is comprised of the oils within the Statfjord Formation and Lunde Formation of the Snorre Field and possibly in the Zeta Structure in the north of the Snorre Field.

The Statfjord Øst oil population is present in the Brent Group in the Statfjord Field, Statfjord Øst structure, Tordis Field and Gullfaks Field. This is almost the same major fill-spill route along the North Alwyn-Brent-Statfjord-(Snorre)-Gullfaks trend that was proposed previously for the whole Tampen Spur by Thomas et al. (1985) and Karlsson (1986).

The last oil population was described to be present within the Statfjord Formation in the Statfjord Field, but no samples of these accumulations were available for analysis in the present study.

3.3 Gullfaks Field

The Gullfaks Field (Block 34/10, Norwegian North Sea), a part of the very prolific area of the Tampen Spur, is documented as a good example of lateral variability in the degree of biological degradation of petroleum in a reservoir (Fig. 3.6 A). The geology of the Gullfaks Field was discussed in detail by Karlsson (1986), Erichsen et al. (1987) and Graue et al. (1987). The petroleum in the Gullfaks Field is contained within three formations: the Brent Group, the Cook Formation and the Statfjord Formation (Fig. 3.6

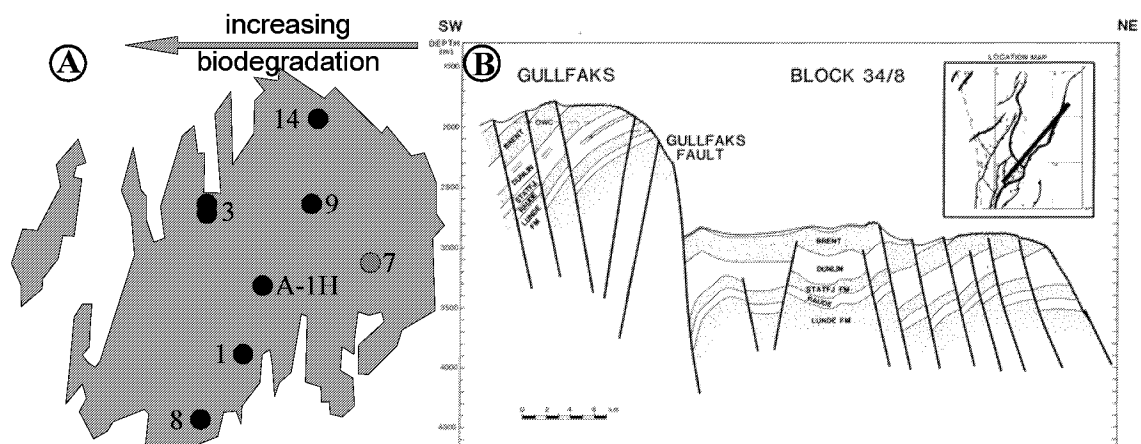


Fig. 3.6: Sampling locations of oils from the Gullfaks Field, North Sea

B). The petroleum within the Brent Group has different source characteristics and is less mature than the petroleum in the Cook and Statfjord Formations which are the reservoirs in the eastern part of the field (Horstad et al., 1990; Larter and Horstad, 1992). The authors suggested that the Brent Group was possibly filled from a westerly direction and this was confirmed by the fact that the most mature petroleum occurs in the western part of the Brent Group within the Gullfaks Field. The Tordis Field, located northwest of the Gullfaks Field, is filled to spillpoint and was proposed as the immediate supply point of the oil in the Gullfaks Brent reservoir. Horstad et al. (1990) concluded that the similarity between the biomarker distributions of the Gullfaks and Tordis oils support the proposed filling direction into the Brent Group reservoir in the Gullfaks Field.

The most severe biological degradation of oils in the Gullfaks Field took place within the uneroded Brent Group sediments in the western part of the field. The lack of erosion in the west suggests that this part of the reservoir has always been buried at greater depths than the eastern part of the field (Horstad et al., 1991).

A suite of variably degraded oils from the Gullfaks Field was analysed in order to investigate the effect of biological degradation on heterocompound geochemistry.

3.4 Central Graben

The Central Graben is a long-proven hydrocarbon province situated in the southern part of the Norwegian continental shelf, bordering the offshore exploration waters of Denmark in the southeast and the UK in the west/southwest. The organic facies and geological setting of the Central Graben depositional system have been described in

E.nr.	Well	Field		Depth [m]	Age	Lithostratigraphy	
47542	2/2-5		oil	3666.25-3670.5	Jurassic		Intra Farsund
28816	2/4-14		oil	4700	Jurassic		
47543	6/3-1		oil	3015-3023	U. Triassic		Skagarrak Fm
47544	7/7-2		oil	3348-3350	Triassic/U. Jurassic	Hegre Gp	Smith Bank Fm
47545	9/2-1	Yme	oil	3177-3210	M. Jurassic	Vestland Gp	Sandnes Fm
47546	15/12-5	Fenris	oil	2937	U. Jurassic	Vestland Gp	Oxfordian SST
47547	15/12-6	Fenris	oil	2922-2930	U. Jurassic	Vestland Gp	Oxfordian SST

Tab. 3.2: Sample information for the crude oils from the Central Graben analysed in this study

several publications (van den Bark and Thomas, 1981; Growers and Sæbøe, 1985; Fraser et al., 1993). Briefly, restricted basinal conditions which prevailed during the Late Jurassic resulted in the deposition of thick organic-matter-rich shales (the Mandal/Farsund Formations), which are the major petroleum source in the area. Subsequent widespread basinal subsidence during the Late Cretaceous accompanied by eustatic and climatic changes resulted in the deposition of more than 1000 m of thick chalk sequences which comprise the major reservoir in the Central Graben. Continued tectonic activity and ongoing halokinesis resulted in an extensive remobilization, redistribution and reworking of the chalks in the graben. The Maastrichtian/Danian age Ekofisk and Tor Formations are the principal reservoir units in most of the oil fields in the Greater Ekofisk area. Seven crude oils from different areas of the Central Graben were collected for analysis; sample information and location are given in Table 3.2 and Figure 3.7, respectively.

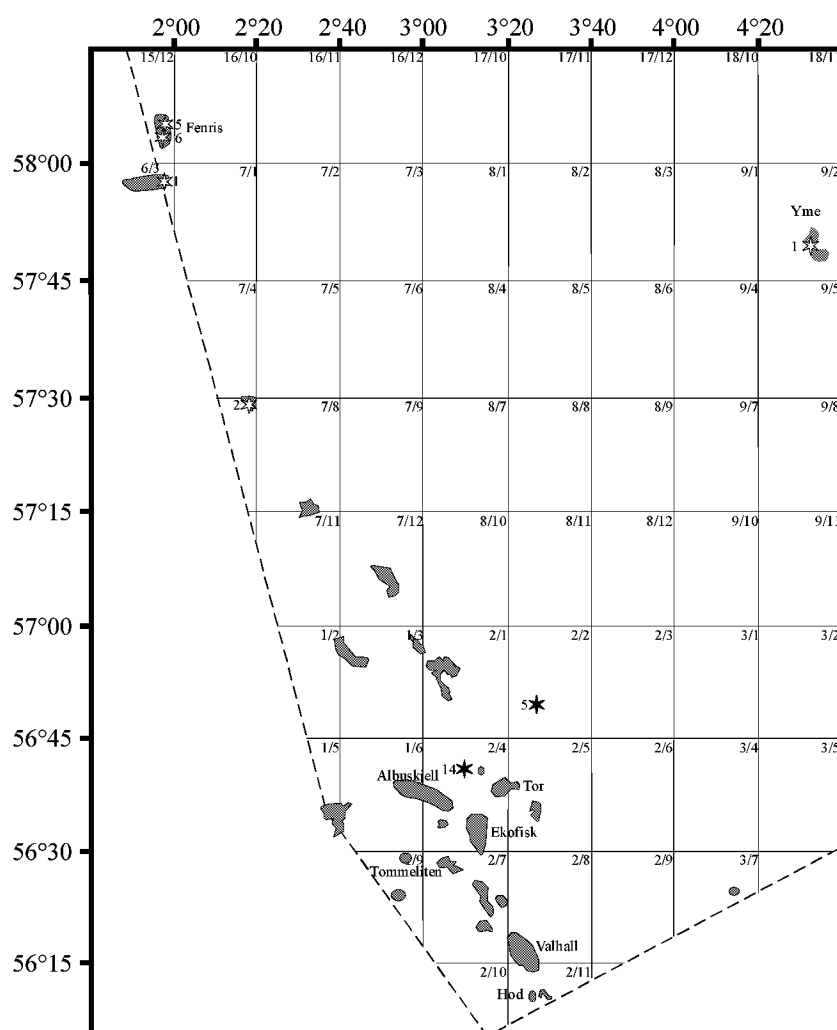


Fig. 3.7: Oil fields and sampling locations (marked by asterisks) in the Central Graben, North Sea.

Hughes et al. (1985) and Bjorøy et al. (1994) pointed out that the maturity of the Greater Ekofisk Cretaceous oils/condensates varies significantly in the area. A general trend of maturity increase from the south-east to the north-west is indicated by API gravity values of 31° to 35° in Hod and Valhall to the south and 45° to 50° in Tommeliten and Albuskjell in the north.

3.5 Haltenbanken and Barents Sea

The Mid-Norwegian Continental Shelf is located between latitudes 62°N and 69°N. It includes a landward platform area known as the Trøndelag Platform, west of which is the Mid-Norway Basin comprising the Træna Sub-Basin, the Vøring Basin and the Møre Basin (Fig. 3.8). Even further west, a complex transition zone between oceanic and continental crust can be found (Gabrielsen and Robinson, 1984). Situated in a tectonically active area between two stable plates (the Eurasian Plate and the North American Plate), the geological development of the Mid-Norwegian Shelf is characterised by three main episodes of global tectonics. These are the Caledonian orogenesis (Ordovician-Silurian), with subsequent erosion and transgression in Devonian-Permian times, the Ural orogenesis (Permian-Triassic) with subsequent tension and faulting during Late Triassic-Early Cretaceous times; and the opening of the Norwegian Sea (Tertiary), with faulting and subsidence of large areas and associated with strong volcanism (Hollander, 1984).

The oldest sediments penetrated in the Haltenbanken area are of Middle Triassic age. Red siltstones, shales and thin sandstone layers reflect continental conditions. Two intercalated halite sequences are believed to result from two marine incursions from the Barents area along the Atlantic rift system during Middle and Late Triassic. They are separated by dolomitic shales of Carnian age. From the Rhaetian to the Upper Sinemurian the climate became more humid, leading to the deposition of what are now fluvio-deltaic coals, sandstones and siltstones of the 300-500 m thick Åre Formation (Whitley, 1992). An Early Jurassic marine incursion interrupted the evolution of the coaly sequence in the Pliensbachian stage, generating a marginally marine to deltaic environment in the Haltenbanken area. As a consequence, 90-100 m of shallow-marine sand was deposited, known as the Tilje Formation (Gabrielsen and Robinson, 1984). This formation represents a heavily bioturbated, shallow-marine tidal flat sequence,

which comprises sand bar deposits as well as frequent storm surge sands with mud clasts and pebble-sized rock fragments (Karlsson, 1984). The marine transgression culminated during the Toarcian, and the marine clays and muds of the Ror Formation were deposited (Whitley, 1992). This period of deposition was locally interrupted by the temporary outpourings of a fan delta, causing the development of the sand-dominated Tofte Formation and reflecting a local uplift in the western part of Haltenbanken (Dalland et al., 1988). The upper Lower Jurassic and the Middle Jurassic were characterised by regional updoming, synsedimentary faulting and erosion, due to initial Cimmerian movements. This led to the deposition of the marine and fluvial sandy sequences of the Fangst Group, comprising the Ile, the Not and the Garn Formations (Whitley, 1992). The Ile Formation consists of tidally influenced nearshore marine sandstones and thinner bioturbated shale and siltstone intervals (Ehrenberg et al., 1992). Marine shelf deposits comprising the Not Formation were then laid down during the Aalenian, above which occurs a sharp erosional contact followed by the Middle Jurassic Garn Formation with sandy fan delta or braided delta deposits (Bajocian to Bathonian; Dalland et al., 1988). The whole area was inundated during Bathonian times and, as a consequence, the marine shales of the Melke Formation developed. During the Late Jurassic, the transgression with marine anoxic bottom water conditions culminated and led to the deposition of the shaly sequences of the Spekk Formation during Oxfordian and Ryazanian times (Whitley, 1992). Local erosion of the Spekk Formation was induced by a significant eustatic sea-level drop and the culmination of the Late Cimmerian tectonic phase during the Early Cretaceous (Hollander, 1984). The onlap of the succeeding calcareous marine shales and turbiditic sandstones of the Cromer Knoll Group, comprising the Lyr, the Lange and the Lysing Formation, onto the Cimmerian structures west of Haltenbanken reflects rapid subsidence during the Cretaceous (Whitley, 1992). The Lyr Formation consists of open-marine marls interbedded with carbonates and locally underlies the marine claystones, carbonates and sandstones of the Lange Formation. The submarine fan deposits of the Lysing Formation were deposited from the Late Cenomanian to Coniacian (Dalland et al., 1988).

Of these different formations the main source rock in the Haltenbanken region is the Upper Jurassic Spekk Formation (Kimmeridge Clay equivalent). This formation is markedly heterogeneous, both laterally and vertically (i.e. according to Walters law) with respect to its geochemistry and the depositional and early diagenetic environment

(Karlsen et al., 1995). The organic matter in the Spekk Formation is immature to the east of the Halten Terrace and overmature to the west, but the pristane/phytane ratio in the western Vøring Basin is low relative to that of the Trøndelag Platform (immature organic matter) in the east, which reflects changes in organic facies (Cohen and Dunn, 1987; Hemmens et al., 1994). Generally, the Spekk Formation contains large amounts of high-quality (hydrogen-rich) kerogen with a hydrogen index of up to 700 mg HC/g TOC where immature (Mo et al., 1989). Total organic carbon (TOC) values between 4 and 13% are common and the kerogen, consisting of marine algae with a subsidiary terrigenous proportion, has a Type II composition (Hollander, 1984). Peak oil

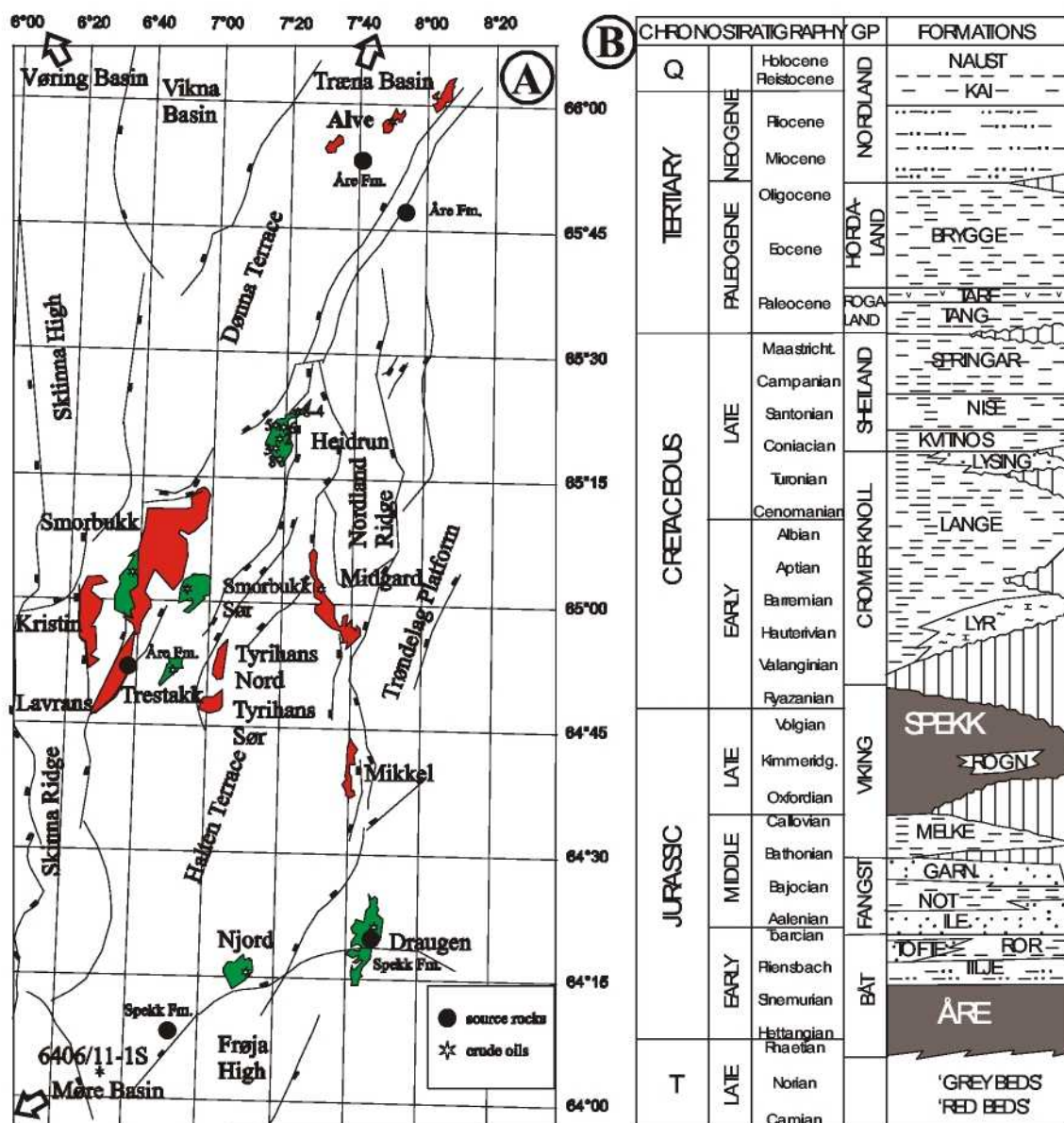


Fig. 3.8: Oil field (asterisks) and source rock (filled dots) sampling locations (A); and sedimentary stratigraphy (B) for the Haltenbanken area, Norwegian Sea.

generation is estimated to have occurred over large areas in the Halten Terrace during the Late Tertiary at about 3400 m burial depth (Leadholm et al., 1985). Cohen and Dunn (1987) considered that oil expulsion was initiated at 120°C, equivalent to 3100 m of burial in their dataset, whereas Heum et al. (1986) placed the initial oil expulsion from this formation at a vitrinite reflectance equivalence (VRE) of 0.7% which corresponds to 3900 m in their database - this depth was considered by Cohen and Milovanovic (1968) to be associated with initial oil to gas cracking ($T \approx 150^\circ\text{C}$). Based on a biomarker study, Karlsen et al. (1995) suggested that significant oil expulsion occurred from the Spekk Formation at a depth shallower than 3900 m. In addition to having been an effective petroleum source, the shales of the Spekk Formation now serve as an excellent cap rock (Fjaeran and Spencer, 1991).

The Middle Jurassic Melke Formation has an insignificant oil potential, since it is rated to release not more than 1.5 kg of petroleum/tonne rock (Heum et al., 1986; Cohen and Dunn, 1987).

The source rocks of the Lower Jurassic Åre Formation consist of alternating sandstones, shale and coaly lithologies which were deposited under paralic conditions. This formation contains Type III kerogen. The organic matter is more mature than that in the Spekk Formation and is considered to be an at least locally important petroleum source (Thompson et al., 1985; Heum et al., 1986; Forbes et al., 1991). Approximately 135 kg of petroleum/tonne rock (with about 30% gas, 50% condensate and 20% oil) were estimated to have been expelled from the Åre Formation during burial to 4% vitrinite reflectance (Heum et al., 1986). The maturity of the organic matter in the Åre Formation decreases towards the east and is generally in the order of 0.2-0.5% R_o higher than in the overlying Spekk Formation (Heum et al., 1986; Whitley, 1992). The Åre Formation has been modelled to be about six times more important volumetrically with respect to expelled C_{15+} hydrocarbons compared to the Spekk plus Melke Formations in the Smørbukk Sør accumulation area (Forbes et al., 1991). Likewise, Espitalié et al. (1991) rated the petroleum potential of the coals as four times higher than those of the Viking Group (Spekk and Melke Formation) based on pyrolysis experiments and modelling. However, Karlsen et al. (1995) saw no evidence in biomarker distributions for significant contributions from the Åre Formation to the reservoired petroleum. The main reservoirs in this area are the Middle Jurassic sandstones.

The main source rocks in the south of the Barents Sea are the Upper Jurassic Kimmeridge equivalent and the coal-bearing Lower Jurassic strata. These source rocks underwent uplift and erosion in the Neogene and never attained oil-window maturity (Fjaeran and Spencer, 1991). The major reservoirs are found in the Lower and Middle Jurassic. Minor reservoirs and source rocks range in age from the Permo-Carboniferous to the Tertiary.

The oils and source rocks from the Haltenbanken area and the Barents Sea investigated in this study are listed in Table 3.3. Refer to Figure 3.8 for sample locations.

E.nr.	Well	Field		Depth [m]	Period	Lithostratig.
E 47558	6406/11-1S		oil	3692-3705	Jurassic	Ile Fm.
E 47559	6406/3-2	Trestakk	oil	3937-3995	M. Jurassic	Tomma Fm.
E 47569	6407/7-4	Njord	oil	2999-3008	Jurassic	Tilje Fm.
E 47560	6407/9-1	Draugen	oil	1632-1638	U. Jurassic	Frøya Fm.
E 47561	6506/11-2	Smorbukk	oil	3373.5-3398	U. Cretaceous	Lysing Fm.
E 47562	6506/12-3	Smorbukk Sør	oil	3162-3174	U. Cretaceous	
E 47563	6507/3-1	Alve	oil	3611-3636	M. Jurassic	Garn Fm.
E 47910	6507/7-2 DST.2	Heidrun	oil			
E 47911	6507/7-2 DST.3	Heidrun	oil			
E 47912	6507/7-2 DST.4R	Heidrun	oil			
E 47913	6507/7-5 DST.1	Heidrun	oil			
E 47914	6507/7-5 DST.2	Heidrun	oil			
E 47915	6507/7-6 DST.1	Heidrun	oil			
E 47916	6507/7-6 DST.2	Heidrun	oil			
E 47917	6507/7-8 DST.1	Heidrun	oil			
E 47918	6507/7-8 DST.2	Heidrun	oil			
E 35212	6507/7-3	Heidrun	oil	2385-2400	M. Jurassic	Tomma Fm.
E 47564	6507/8-4 DST.2	Heidrun	oil	2200-2208	L. Jurassic	Åre Fm.
E 47919	6507/8-4 DST.3	Heidrun	oil			
E 47920	6507/8-4 DST.4	Heidrun	oil			
E 47921	6507/11-3 DST.1	Heidrun	oil			
E 47922	6507/11-3 DST.2	Heidrun	oil			
E 47923	6507/11-3 DST.3	Heidrun	oil			
E 48155	6406/2-1R		source rock	5647.15	L. Jurassic	Åre Fm.
E 48156	6406/2-1R		source rock	5647.6	L. Jurassic	Åre Fm.
E 48157	6406/12-2		source rock	3744.0	U. Jurassic	Speck Fm.
E 48158	6406/12-3		source rock	3749.0	U. Jurassic	Speck Fm.
E 48159	6507/3-2		source rock	1406.4	L. Jurassic	Åre Fm.
E 48160	6507/3-3		source rock	1406.5	L. Jurassic	Åre Fm.
E 48161	6407/9-3		source rock	1623.3	U. Jurassic	Speck Fm.
E 48162	6407/9-3		source rock	1627.5	U. Jurassic	Speck Fm.
E 48163	6407/9-3		source rock	1675.0	U. Jurassic	Speck Fm.

E.nr.	Well	Field		Depth [m]	Period	Lithostratig.
E 47565	7120/1-2	Barents Sea	oil	1879-1896	L. Cretaceous	Wedge Fm
E 47566	7121/5-1	Barents Sea	oil	2802-2825	L. Triassic	Aun Fm
E 47567	7124/3-1	Barents Sea	oil	1298	L. Triassic	Stø Fm

Tab. 3.3: Sample information for the crude oils and source rocks from the Haltenbanken area and from the Barents Sea analysed in this study

4. Methods

4.1 General analytical scheme

The sequence of analytical steps used in the characterisation of the oils and rock samples is illustrated in Figure 4.1.

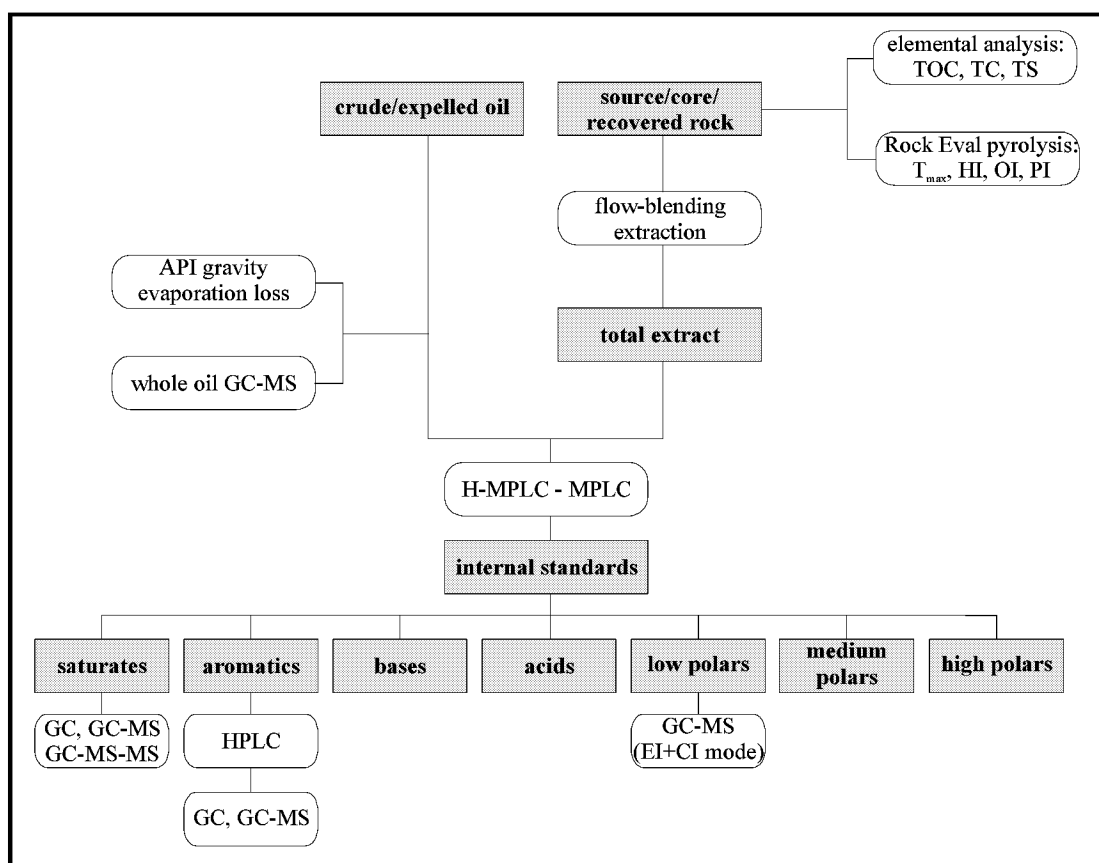


Fig. 4.1: Simplified scheme for sample preparation and fractionation of oils and rock extracts

4.2 Bulk parameters

Rock samples

The rock samples analysed in the project included potential source rock and core samples, and the recovered rock samples from the hydrous pyrolysis experiments. These were ground and homogenised using a RetschTM disc mill. For the determination of the total organic carbon (TOC) content the samples were initially wetted with ethanol and then carbonate was removed by treatment with 25% hydrochloric acid. The TOC content was determined using a LECOTM CS 225 elemental analyser. Combustion was

performed in oxygen at 1100°C and carbon was recorded as CO₂ using an infrared detector. Total sulfur (TS) and total carbon (TC) were determined on the same instrument using sample which had not been previously treated with hydrochloric acid. Inorganic carbon content was determined as the difference between total and organic carbon content.

For predicting bulk petroleum generation characteristics of source rocks a Rock Eval II[®] instrument from Delsi[™] was used (Espitalié et al., 1977). The thermal extract released at 300°C over a 3 min heating period was recorded as S1 (mg HC/g rock) using flame ionisation detection (FID). The residual organic matter was pyrolysed between 300 and 550°C at a heating rate of 25°C/min, the products yielded during this procedure being determined as S2 (mg HC/g rock) by FID. The CO₂ liberated up to 390°C was held in a molecular sieve trap until the pyrolysis was completed. It was then released and quantified as S3 (mg CO₂/g rock) using a thermal conductivity detector (TCD). Hydrogen (HI) and oxygen (OI) indices were calculated by normalising S2 and S3 yields to TOC (mg/g TOC). All reported values are the means of duplicate analysis and were calibrated using an international standard (IFP 55000) provided by the Institut Français du Pétrole.

Oil samples

The API gravity is an inverted density scale for oils devised by the American Petroleum Institute. The oil density was measured using a Heraeus[™] DMA 45 instrument. The API gravity was calculated as follows:

$$^{\circ}\text{API} = [141.5/\text{density of oil at } 60^{\circ}\text{F (g/cm}^3\text{)}]-131.5$$

For the determination of evaporative loss, 50 mg of oil were transferred to a 1.5 ml vial, which was then filled with dichloromethane and left open to the air for 28 hours at room temperature. The evaporative loss of the oils was determined as the difference in weight before and after evaporation.

4.3 Extraction, fractionation and standardization

Ground rock samples were extracted with an azeotropic mixture of acetone, methanol and chloroform (38 : 30 : 32 vol%) using a modified flow-blending technique described by Radke et al. (1978). After filtration using a micro-porous membrane filter,

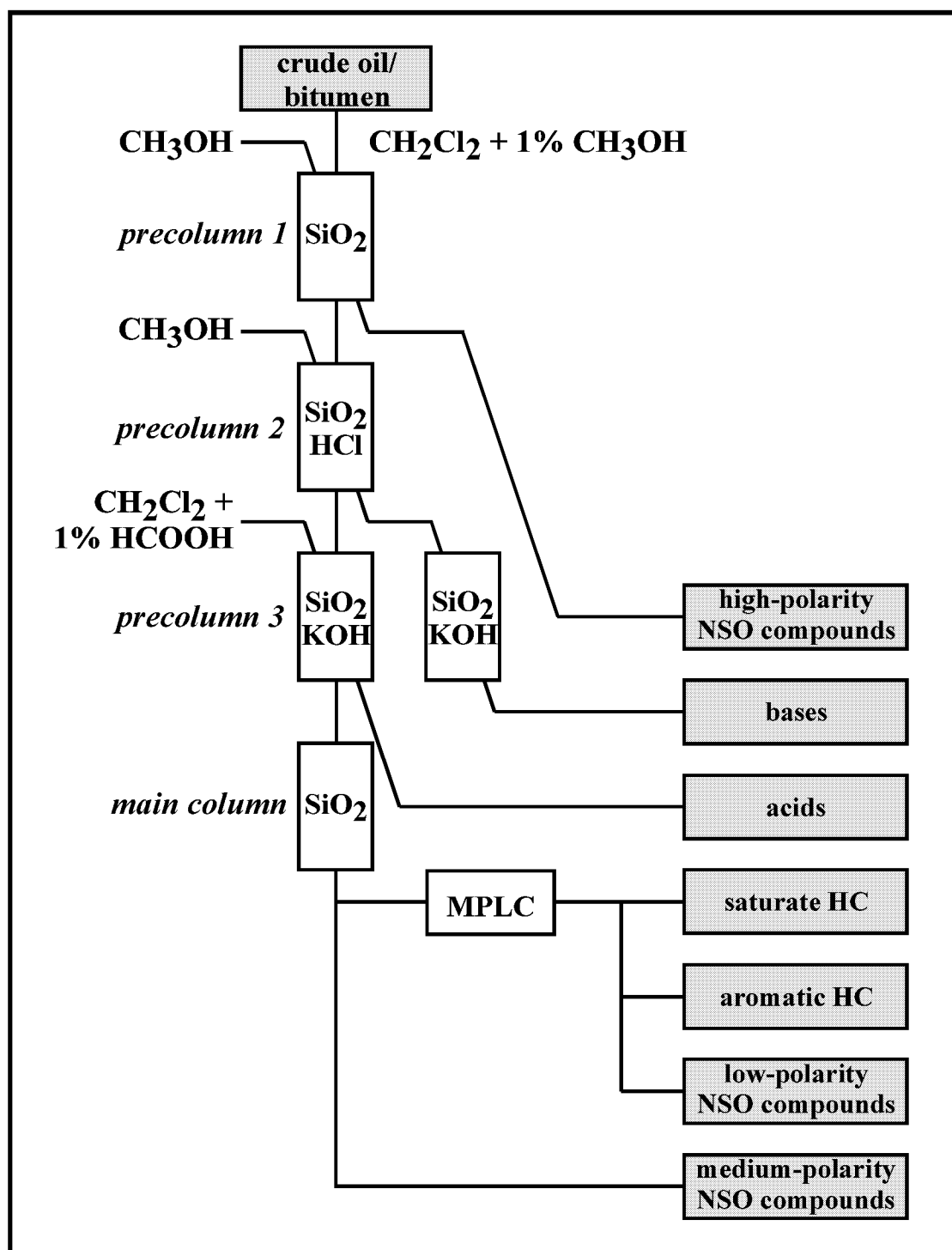


Fig. 4.2: Schematic diagram of the liquid chromatographic fractionation system, modified after Willsch et al. (1997)

the extract was concentrated by removing the solvent in a rotary evaporator (Turbovap[®]).

The rock extracts and oils were separated into seven fractions according to the method of Willsch et al. (1997). As illustrated in Figure 4.2 the extracts and oils were passed through silica gel, acidic silica gel, and basic silica gel to remove high-polarity NSO compounds, bases and acids. Chromatography on the main silica gel column separated the medium-polarity NSO compounds and a low-polarity fraction. The latter was then separated via medium pressure liquid chromatography (MPLC) (Radke et al., 1980b) on silica gel into saturated hydrocarbons, aromatic hydrocarbons and low-polarity NSO compounds. The latter fraction was the main focus of study and contained, among other compound classes, carbazoles, fluoren-9-ones and xanthenes. All fraction yields were determined gravimetrically after removal of solvent.

4.4 Authentic standards

Known amounts of internal standards were added to the saturated (5 α -androstane), aromatic (mixture of 32.9 : 25.2 : 16.6 : 8.7 : 8.3 : 8.3 wt% of 1-phenylhexane, 1-phenylheptane, 1,8-dimethylnaphthalene, 1-phenylnaphthalene, 1-ethylpyrene and 1-butylpyrene) and low-polarity (9-phenylcarbazole) fractions for quantification.

Xanthone was purchased from Aldrich (Steinheim, Germany). Prof. Frahm from the University of Freiburg, Germany, provided samples of the four methylxanthenes and the 2,4- and 3,4-dimethylxanthenes. All of these standard compounds were used for coinjection and confirmation of identification. Briefly, the alkylated xanthenes were synthesised by a two-step reaction, the first step being a condensation reaction of a benzoic acid and a cresol under Ullmann conditions. The alkylated xanthenes were then formed in a second step by intramolecular Friedel-Crafts acylation of the phenoxybenzoic acid as described by Pickert et al. (1998).

4.5 Gas chromatography (GC)

GC analysis of the saturated hydrocarbon fraction was performed using a Hewlett-Packard[™] (HP) 5890B gas chromatograph equipped with an on-column injector with electronic pressure control (EPC) and a standard flame ionisation detector (FID).

Hydrogen was used as carrier gas with a pressure of 1.6 bar at initial temperature. The gas chromatograph was fitted with an Ultra-1 fused silica capillary column (HP) of 50 m length, 0.2 mm i.d. and 0.33 μm film thickness. The oven temperature was programmed from 90°C (hold time, 4 min) to 310°C (hold time, 50 min) at 3°C/min. The aromatic hydrocarbon fractions were analysed using an HP 5890B instrument which was equipped with an on-column injector, EPC, FID and a sulphur-selective HALLTM electrolytic conductivity detector (HECD). Helium (4.4 bar at starting temperature) was used as the carrier gas. The gas chromatograph was fitted with a BPX-5 fused silica capillary column (SGE) of 50 m length, 0.15 mm i.d. and 0.25 μm film thickness. The oven temperature was programmed from 90°C (hold time, 4 min) to 120°C at 50°C/min (hold time, 1 min) and then to 310°C (hold time, 51 min) at 3°C/min.

4.6 Gas chromatography – mass spectrometry (GC-MS)

GC-MS analysis was performed on either a FinniganTM MAT 95SQ mass spectrometer coupled to an HP 5890B (GC) or a MagnumTM ion trap mass spectrometer coupled to a VarianTM 3100 GC. In both systems, the GC was equipped with a temperature-programmable injection system (GerstelTM KAS 3) and a BPX-5 fused silica capillary column (SGE) of 50 m length, 0.22 mm inner diameter and 0.25 μm film thickness. Helium was used as the carrier gas (EPC, flow rate 1 ml/min). The oven temperature was programmed from 60°C to 340°C (final hold time, 23 min) at 3°C/min.

In electron impact (EI) mode, the mass spectrometer was operated at an electron energy of 70 eV and a source temperature of 260°C. EI mass spectra were recorded over the mass range m/z 50-600 at a scan rate of 0.74 s/decade, an interscan time of 0.2 s and a scan cycle time of 1.0 s.

Whereas the identification of carbazoles (EI-mode: m/z 167, 181, 195 for carbazole, C₁ and C₂ carbazoles; m/z 217 for benzocarbazoles), fluoren-9-ones (EI-mode: m/z 180, 194, 208 for fluoren-9-one, C₁ and C₂ fluoren-9-ones; m/z 230 for benzofluoren-9-ones) and xanthenes (EI-mode: m/z 196, 210, 224 for xanthone, C₁ and C₂ xanthenes) was performed using GC-MS under EI conditions, the quantification of compounds was performed using data from chemical ionisation (CI) mass spectrometry. Using *i*-butane as the reactant gas, mass spectra were obtained which almost exclusively showed the

corresponding pseudomolecular ions $[M+H]^+$. In CI mode the mass spectrometer was operated at an electron energy of 50 eV and a source temperature of 260°C. CI mass spectra were recorded over the mass range m/z 100-600 at a scan rate of 1.03 s/decade, an interscan time of 0.2 s and a scan cycle time of 1.0 s.

For unequivocal identification, authentic reference standards of xanthone, the methylxanthenes and 2,4- and 3,4-dimethylxanthone were coinjected with a suitable natural sample under the GC-MS conditions described above. Coinjection experiments were also performed using an HP-1 fused silica capillary column of 50 m length, 0.2 mm inner diameter and 0.33 μ m film thickness under otherwise identical GC-MS operating conditions.

Biomarkers in the saturated hydrocarbon fraction were measured in EI mode on the Finnigan™ MAT 95SQ system using a GC oven temperature programme of 110°C - 340°C at 3°C/min. To increase the signal/noise ratio and to obtain better peak identification, multiple reaction monitoring (MRM) was performed using GC-MS-MS. The parent $\rightarrow$ daughter ion transitions monitored were the following for each structural family of compounds were as follows: steranes (C_{26} - C_{30} : m/z 358, 372, 386, 400, 414 $\rightarrow$ 217), methylsteranes (C_{27} - C_{31} : m/z 372, 386, 400, 414, 428 $\rightarrow$ 231); dinosteranes (C_{29} - C_{30} : m/z 400, 414 $\rightarrow$ 98), hopanoids (C_{27} - C_{35} : m/z 370, 384, 398, 412, 426, 440, 454, 468, $\rightarrow$ 191), oleanane and gammacerane (m/z 412 $\rightarrow$ 191).

The data obtained were processed using the ICIS-1 software package (ThermoQuest Finnigan, Egelsbach).

Whole-oil gas chromatography-mass spectrometry (GC-MS) was performed using a Fisons Quadrupole MD800 mass spectrometer. Full scan mass spectra were recorded over the mass range m/z 10-420 with 2.5 scans/s. The mass spectrometer was coupled to a Fisons GC 8000 equipped with a split/splitless injection system and an HP-1 fused silica capillary column of 50 m length, 0.31 mm i.d., and 0.5 μ m film thickness. The oven temperature was programmed from 40°C (hold time, 3 min) to 300°C (final hold time, 45 min) at 5°C/min. Helium was used as the carrier gas.

4.7 Biomarker parameters in petroleum systems

Biomarker distributions were used to characterise the crude oils in terms of source facies, depositional environment and maturity. The influence of these factors on the occurrence and distribution of heterocompounds (see chapters 5.2-5.4) could then be evaluated. The characterisation was based mainly on biomarker parameters which have been described in the literature as being successful for the oils and source rocks from offshore Norway. However, relatively little is known about the influence of primary/expulsion processes on the composition of the oils from this geologically complex area. In an attempt to improve our understanding of this aspect, several different terpane- and sterane-based biomarker parameters were investigated using this suite of oils and their significance. A review of all these parameters has been presented by Peters and Moldowan (1993).

Terpane and sterane parameters for geothermal maturity assessment

The relative abundances of most tetra- and pentacyclic terpanes depend on the source facies and the environment of deposition. In addition, some biogenic configurations of hopane and sterane isomers will be converted to thermodynamically more stable geogenic configurations during maturation. At higher stages of maturation (oil window) the relative abundances of the hopanes and steranes are increasingly controlled by their thermal stabilities. Therefore, parameters involving compounds of different thermal stability can be usefully applied to determine the degree of maturity.

a) Hopanes:

Typical mass chromatograms (GC-MS and GC-MS-MS) obtained in the analysis of the hopanes in oils from offshore Norway are shown in Figure 4.3. A key to peak labels is given in Table 4.1 and molecular structures are shown in Appendix 7a.

Relative thermal stability of hopanes:

- $17\alpha,21\beta$ -diahopanes > $18\alpha,21\beta$ -*neo*-hopanes > $17\alpha,21\beta$ -hopanes > $17\beta,21\alpha$ -hopanes > $17\beta,21\beta$ -hopanes
- epimerization of C_{31} - C_{35} $17\alpha,21\beta$ -hopanes at C-22; $22S > 22R$

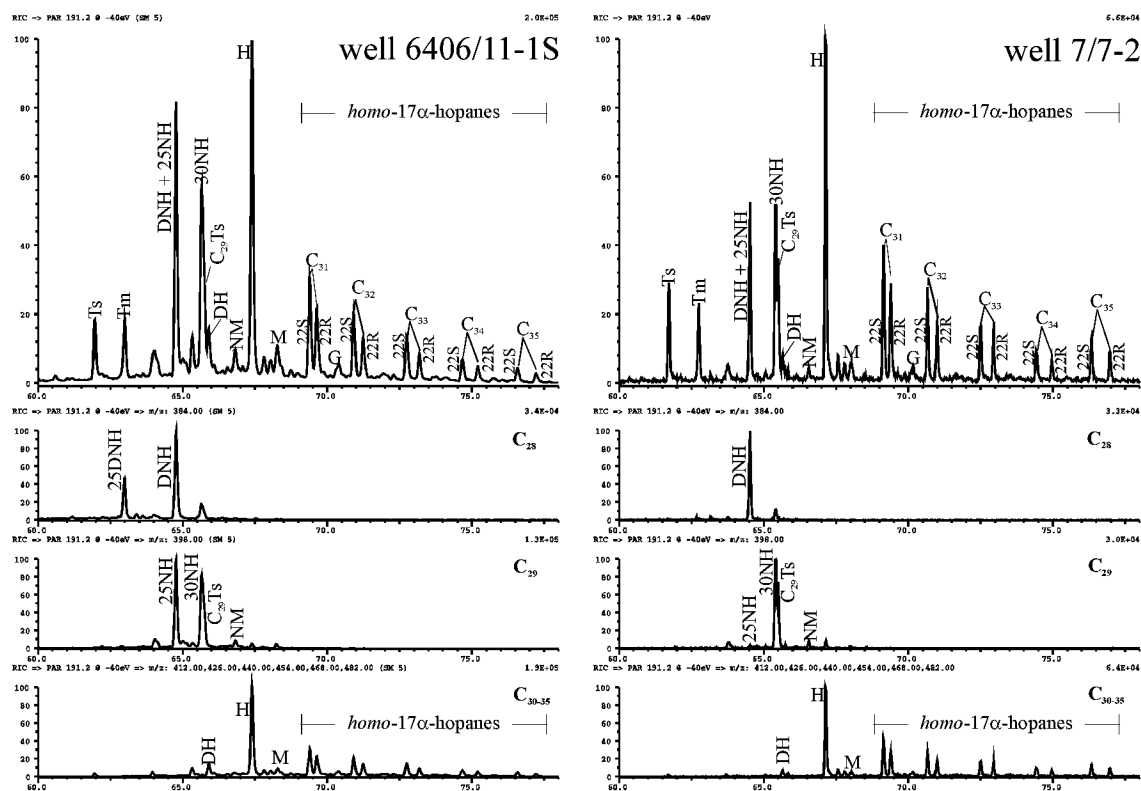


Fig. 4.3: Mass chromatograms of two oils from Haltenbanken and the Central Graben illustrating the hopane series (bottom: GC-MS-MS mass chromatograms; top: GC-MS m/z 191 mass chromatograms). See Table 4.1 for key to peak labels.

On the basis of the differences in thermal stability of the hopanes, the following parameters were used to provide a maturity assessment of the analysed oils and source rock extracts from offshore Norway (see Table 4.1 for key to compound abbreviations).

- $H/(H+M)$ (e.g. Seifert and Moldowan, 1980)
- $22S/(22S+22R)$ (for the C_{31} - C_{35} -hopanes) (e.g. Seifert and Moldowan, 1980)
- $DH/(DH+30NM)$ (e.g. Horstad et al., 1995)
- $DH/30NH$ (e.g. Horstad and Larter, 1997)
- $C_{29}Ts/30NH$ (e.g. Hughes et al., 1985)
- $Ts/(Ts+Tm)$ (e.g. Seifert and Moldowan, 1978)

Label	Compound
Ts	22,29,30- <i>trinorneo</i> -18 α -hopane
Tm	22,29,30- <i>trinor</i> -17 α -hopane
DNH	28,30- <i>dinor</i> -17 α ,18 α ,21 β -hopane
25DNH	25,30- <i>dinor</i> -17 α ,21 β -hopane
25NH	25- <i>nor</i> -17 α ,21 β -hopane
30NH	30- <i>nor</i> -17 α ,21 β -hopane
C ₂₉ Ts	30- <i>norneo</i> -18 α ,21 β -hopane
DH	15 α - <i>methyl</i> -27- <i>nor</i> -17 α ,21 β -hopane (17 α ,21 β - <i>diahopane</i>)
30NM	30- <i>nor</i> -17 β ,21 α -hopane (30- <i>nor</i> -moretane)
H	17 α ,21 β -hopane
M	17 β ,21 α -hopane (moretane)
G	gammacerane
C _x 22 <i>S</i> /22 <i>R</i> (x=31-35)	(22 <i>S</i> /22 <i>R</i>)- <i>homo</i> -17 α ,21 β -hopanes
$\beta\alpha$ - C _x (x=29-30)	17 β ,21 α -hopanes (for C ₂₉ – C ₃₀)
(22 <i>S</i> /22 <i>R</i>) $\beta\alpha$ - C _x (x=31-35)	(22 <i>S</i> /22 <i>R</i>)- <i>homo</i> -17 β ,21 α -hopanes (for C ₃₁ – C ₃₅)
$\beta\beta$ - C _x (x=28-30)	17 β ,21 β -hopanes (for C ₂₈ – C ₃₀)
$\beta\beta$ - C _x (x=31-34)	(22 <i>R</i>)- <i>homo</i> -17 β ,21 β -hopanes (for C ₃₁ – C ₃₄)
C _x -TT and TT-diene	triterpenoids
C _x -17(21)-ene	hop-17(21)-enes
C _x -13(18)-ene	hop-13(18)-enes
C ₂₉ - <i>neo</i> -13(18)-ene	30- <i>norneo</i> -hop-13(18)-ene
F	fernene

Tab. 4.1: Assignment of compounds to the peak labels in Figures 4.3 and 5.1.47 and the structures in Appendix 7a

b) Steranes

Relative thermal stability of steranes:

- $13\beta,17\alpha$ -diasteranes $> 5\alpha,14\beta,17\beta$ -steranes $> 5\alpha,14\alpha,17\alpha$ -steranes
- epimerization of C_{29} $5\alpha,14\alpha,17\alpha$ -steranes at C-20; $20S > 20R$
- epimerization of C_{29} $5\alpha,14\alpha,17\alpha$ -steranes at C-14 and C-17

On the basis of these maturity-related differences in the stability of steranes, the following parameters were used to provide a maturity assessment of the oils and source rock extracts from offshore Norway (for key to identification of compounds see Table 4.2).

- $5\alpha,14\beta,17\beta/(5\alpha,14\beta,17\beta + 5\alpha,14\alpha,17\alpha)$ ($20S$ and $20R$ epimers)
(e.g. Seifert and Moldowan, 1978)
- $20S/(20S+20R)$ ($5\alpha,14\alpha,17\alpha$ C_{29} -steranes)
(e.g. Seifert and Moldowan, 1978)
- $13\beta,17\alpha/(5\alpha,14\beta,17\beta + 5\alpha,14\alpha,17\alpha)$ (sum of C_{27} , C_{28} and C_{29} diasteranes and steranes ($20S + 20R$))
(e.g. Seifert and Moldowan, 1978)

Label	Compound
α,α,α - S (C_{27} - C_{30})	$5\alpha,14\alpha,17\alpha$ -sterane ($20S$) (C_{27} - C_{30})
α,α,α - R (C_{27} - C_{30})	$5\alpha,14\alpha,17\alpha$ -sterane ($20R$) (C_{27} - C_{30})
α,β,β - S (C_{27} - C_{30})	$5\alpha,14\beta,17\beta$ -sterane ($20S$) (C_{27} - C_{30})
α,β,β - R (C_{27} - C_{30})	$5\alpha,14\beta,17\beta$ -sterane ($20R$) (C_{27} - C_{30})
β,α - S (C_{27} - C_{30})	$13\beta,17\alpha$ -diasterane ($20S$) (C_{27} - C_{30})
β,α - R (C_{27} - C_{30})	$13\beta,17\alpha$ -diasterane ($20R$) (C_{27} - C_{30})
α,β - S (C_{27} - C_{30})	$13\alpha,17\beta$ -diasterane ($20S$) (C_{27} - C_{30})
α,β - R (C_{27} - C_{30})	$13\alpha,17\alpha$ -diasterane ($20R$) (C_{27} - C_{30})

Tab. 4.2: Assignment of compounds to the peak labels in Figure 4.4 and the structures in Appendix 7a (C_{27} = cholestane, C_{28} = 24-methylcholestane, C_{29} = 24-ethylcholestane, C_{30} = 24-*n*-propylcholestane, and corresponding diasteranes)

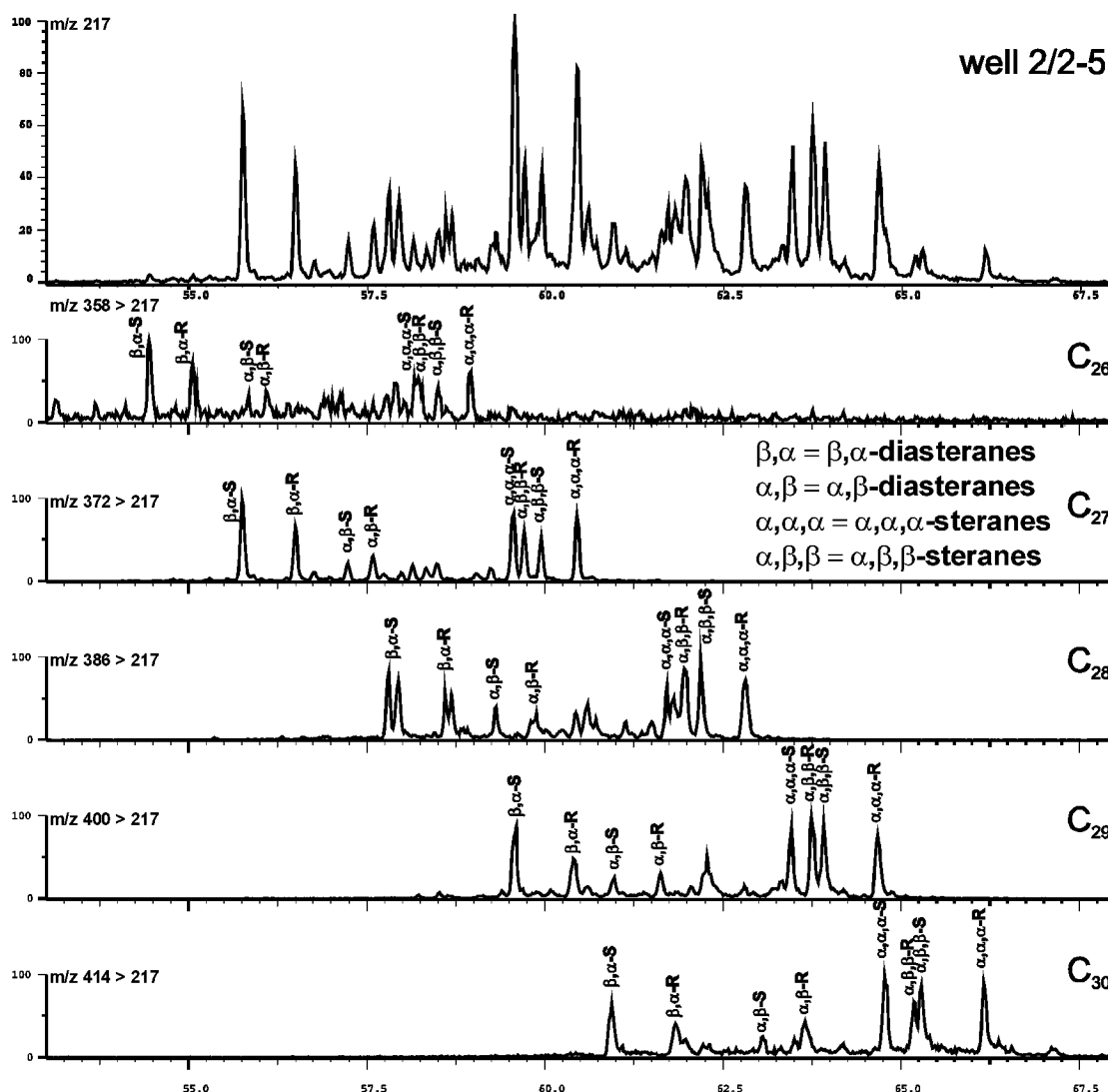


Fig. 4.4: Mass chromatograms of oils from the Viking Graben and the Central Graben illustrating the sterane and diasterane series (bottom: GC/MS/MS mass chromatograms; top: GC/MS m/z 217 mass chromatograms). For key to peak identification see Table 4.2.

Terpane and sterane parameters as indicators of facies and depositional environment

The relative abundances of many steranes and hopanes depend on the source (facies) and the depositional environment in sediments and can provide valuable information particularly for low maturity sediments or in comparative analysis of samples which have similar maturity. For example, the conversion of sterols to diasterenes during diagenesis is believed to be catalyzed by acidic sites on clays (e.g. Rubinstein et al., 1975). Diasterenes are ultimately reduced to diasteranes. Thus, diasterane/sterane ratios are commonly used to indicate whether a petroleum originates from carbonate source rocks or from clastic source rocks (e.g. Mello et al., 1988). However, at high levels of

thermal maturity, rearrangement of steroids to diasteranes may become possible, even in the absence of clays, due to hydrogen exchange reactions which are enhanced by the presence of water (Rullkötter et al., 1984a). In addition, diasteranes are more stable and survive thermal degradation better than steranes, as described above. Similar effects of variation in the main control of many different biomarker parameters from facies and the environment of deposition to maturity are known, but some parameters seem to be independent of maturity, or at least the influence of maturity change is less significant. In the following paragraphs, some biomarker parameters applied most successfully in the present study to assess facies and depositional environment influences in the offshore area of Norway will be described.

C₂₇-C₂₈-C₂₉ steranes

The principal use of C₂₇-C₂₈-C₂₉ sterane ternary diagrams is to distinguish between petroleum originating from different source rocks or from different organic facies of the same source rock. For this purpose, the relative abundance of the sum of the 5 α ,14 β ,17 β 20*S* and 20*R* peaks epimers of the C₂₇, C₂₈, and C₂₉ steranes obtained from GC-MS-MS analysis were used. High concentrations of C₂₉ steranes (24-ethylcholestanes) relative to the C₂₇ and C₂₈ steranes may indicate a land plant source; this is based on the work of Huang and Meinschein (1979), who observed a predominance of the C₂₉ sterol in higher plants and related sediments. However, many exceptions to this relationship have been described in the literature. C₂₉ sterols are also known to occur in marine sediments, and Volkman et al. (1981) showed that 24-ethylcholest-5-en-3 β -ol (a C₂₉ sterol) is a significant component in a mixed diatom culture. Such data must therefore be interpreted with caution and in conjunction with other diagnostic parameters where available.

Gammacerane Index

Gammacerane is a C₃₀ triterpane which appears to represent a marker for highly saline marine and non-marine depositional environments. This compound is a major biomarker in many lacustrine oils and bitumens of rocks deposited in various arid or semiarid lacustrine settings and in certain marine petroleum from carbonate or evaporite source rocks (e.g. Moldowan et al., 1985). Gammacerane may be derived by reduction of tetrahymanol (e.g. ten Haven et al., 1989), a lipid thought to replace steroids in membranes of certain protozoa (e.g. Ourisson et al., 1987), phototrophic

bacteria (Kleemann et al., 1990) and possibly other organisms. The gammacerane index (GI) $[G/H \times 100]$ (see Table 4.1) is commonly used to express the relative amount of gammacerane (Peters and Moldowan, 1993).

DNH/(DNH+30NH)

28,30-*dinor*-17 α ,18 α ,21 β -Hopane (DNH) is a desmethylhopane which is typically found in petroleum from highly reducing to anoxic depositional environments. This compound does not appear to be generated from kerogen, but is passed on from the original free bitumen in the source rock to the oil (e.g. Seifert et al., 1978). Therefore, the relative amount of 28,30-*dinor*-17 α ,18 α ,21 β -hopane normalised to 30-*nor*-17 α ,21 β -hopane in oil seems to be more dependent upon the facies of the source rock from which the oil was expelled than upon its maturity at the time of expulsion (Horstad et al., 1995). However, in studies where the maturity range of the analysed oils is very large, the relative concentration of 28,30-*dinor*-17 α ,18 α ,21 β -hopane may include a significant maturity component.

25NH/(25NH+30NH)

The 25-*nor*-17 α ,21 β -hopane series is typically found in many (but not all) heavily biodegraded oils (e.g. Seifert and Moldowan, 1979; Rullkötter and Wendisch, 1982). These compounds appear to result from the bacterial removal of the methyl group at C-10 in the regular 17 α -hopanes. Laboratory pyrolysis studies of kerogen have shown that 25-*nor*-17 α ,21 β -hopanes (and also 28,30-*dinor*-17 α ,18 α ,21 β -hopane) are not products of kerogen cracking. Consequently, Noble et al. (1985) suggested that 25-*nor*-17 α ,21 β -hopanes occur in sediments as isolated compounds, not as complete series as in biodegraded oils. In addition, Blanc and Connan (1992) contended that 25-*nor*-17 α ,21 β -hopanes are already present in petroleum at the expulsion stage and are 'unmasked', or concentrated, during biodegradation of the more labile hydrocarbon components. Horstad and Larter (1997) suggested that the relative abundance of 25-*nor*-17 α ,21 β -hopanes in oils from the Oseberg-Troll area, northern North Sea, represents an indicator of the depositional environment of the source rock rather than the extent of biological degradation. In addition, these authors showed that higher amounts of 25-*nor*-17 α ,21 β -hopanes are accompanied by lower relative concentrations of 28,30-*dinor*-17 α ,18 α ,21 β -hopane. However, this could also be an indication of biodegradation since

it is expected that 28,30-*dinor*-17 α ,18 α ,21 β -hopane should be degraded to 25,28,30-*trinor*-17 α ,18 α ,21 β -hopane.

The oils from offshore Norway, including both biodegraded oils and oils showing no indications of biodegradation, contain 25-*nor*-17 α ,21 β -hopane. Three reasons could explain the occurrence of 25-*nor*-17 α ,21 β -hopane in obviously non-degraded oils: first, this compound is a constituent of the free bitumen converted from unknown precursors during early diagenesis; second, this compound will be formed from the corresponding 17 α ,21 β -hopane by resedimentation of mature organic matter from eroded rocks or by impregnation of migrated hydrocarbons during deposition; or third, an oil was previously highly biodegraded in the reservoir and then mixed with fresh oil during recharge. The first two explanations would reflect the influence of facies and the depositional environment whereas mixed oils would be difficult to interpret. Therefore, the relative amount of 25NH normalised to 30NH seems to be dependent on the extent of biodegradation in biodegraded oils and more facies-related in non-biodegraded oils.

4.8 Molecular dynamics calculations

The molecular dynamics calculations briefly described below were carried out by Dr. Adri van Duin, NRG, Newcastle upon Tyne, U.K., as part of the present study.

Molecular dynamics simulations were performed to determine the relative heats of solvation of xanthone and the methylxanthone isomers in water and cyclohexane and these values were then used to derive the oil/water partition coefficients. The two solvent phases were simulated using 200 water molecules and 50 cyclohexane molecules. Each substrate/solvent system was equilibrated at temperature/pressure conditions of T=298K and P=10 bar until monotonic oscillating values for the system energy were obtained, using a time step of 2 femtoseconds. Temperature and pressure were controlled during these simulations with the algorithm described by Berendsen et al. (1984) using relaxation times for the temperature and pressure coupling of 100 and 1000 femtoseconds, respectively. A cutoff radius of 9.0 Å was used, and the system energy was corrected for van der Waals interactions beyond this cutoff range (Allen and Tildesley, 1987). A 7th order taper interaction was used, as described by de Vos Burchart (1992), to ensure a stable simulation of the Coulomb interactions. Molecular bonds were constrained using the RATTLE-approach (Andersen, 1983).

After equilibration, relative heat of solvation values for the methylxanthone isomers and xanthone in the water and cyclohexane phase were obtained by averaging system energies over an interval of 2 nanoseconds. These relative heats of solvation were used to calculate the methylxanthone and xanthone oil/water partition coefficients.

Charge distributions and forces for xanthone and the methylxanthones were calculated using the methods described by van Duin and Larter (1998). The water phase was simulated using the TIP3P water force field from Jorgensen et al. (1983). The cyclohexane phase was simulated using the united atom approach (in which the CH₂ groups are described as a single atom) using the parameters described by DeBolt and Kollman (1995).

4.9 Hydrous pyrolysis experiments

Dr. Michael Lewan (U.S. Geological Survey, Denver, U.S.A.) kindly placed expelled oils and recovered rocks from hydrous pyrolysis experiments on Ghareb Formation source rocks at our disposal. The samples were used to evaluate the effects of primary migration on the occurrence and distribution of carbazoles, fluorenones and xanthenes in oils.

A detailed description of the experimental procedures of a typical hydrous pyrolysis experiment was given by Lewan (1993). A one-litre Hastelloy-C276 reactor was filled with 300 g of rock chips and 350 g of distilled water. The remaining volume was purged and filled with helium at a pressure of 2.4 bar. In a series of six different experiments, rock chips were heated isothermally for 72 h at 310, 330, 345, 355, 360 and 365°C, respectively. The temperatures were monitored at 30 s intervals during the course of the experiments. Standard deviations in temperature were between ± 0.1 and $\pm 0.4^\circ\text{C}$ for all experiments. All experiments generated expelled oil which was recovered from the water surface with a pipette. The reactor walls and the rock chips were rinsed with benzene to recover any sorbed oil films which occurred in the experiments. The recovered rock chips were dried in a vacuum oven ($T \leq 50^\circ\text{C}$).

5. Results and Discussion

5.1 Geochemical framework for facies, maturity variations and biodegradation effects

A substantial literature already exists on the organic geochemistry of sedimentary rocks from offshore Norway and reveals a complex interplay of processes, varying from area to area. For this reason, the samples analysed in this study have been divided into the following groups in order to provide a more specific context for data interpretation and to facilitate discussion:

1. *VG (Viking Graben) isolated*; eight isolated oils and two core samples from locations covering the whole northern North Sea. This group of samples allows the effects of facies and maturity on geochemical composition to be introduced.
2. *Tampen Spur*; Twenty-three oils, all from the Tampen Spur area but excluding oils from the Gullfaks Field. These data are discussed mainly within the context of migration effects.
3. *Gullfaks Field*; eight oils from the Gullfaks Field representing a biodegradation sequence.
4. *Central Graben*; seven crude oils from the Central Graben, located in the southern North Sea.
5. *Haltenbanken and Barents Sea*; twenty-three crude oils from the Norwegian Sea and three oils from the Barents Sea.
6. *Haltenbanken source rocks*; nine samples of two potential source rocks (Spekk and Åre Formations) from the Haltenbanken area.
7. *Artificial maturation experiments*; six expelled oils and corresponding recovered rocks from a series of artificial maturation experiments using an immature source rock from the Ghareb Formation.

5.1.1 Viking Graben (VG) isolated oils

Several isolated oils from the northern North Sea (excluding the Tampen Spur area) were analysed (see Fig. 3.4 and Table 3.1 for sample information). It has been suggested that these oils have different maturities and originate from source rocks of different facies. In addition, two core samples, one from an oil leg and the other from a tar mat, were analysed in order to examine variations in the composition of organic matter at these two zones within the reservoir.

5.1.1.1 Bulk organic geochemical characteristics

Whole-oil characteristics

The oil from the northernmost location in the Viking Graben (well 6201/11-1) and the oil from the Frøy Field (well 25/5-1) have similar distribution patterns (whole-oil chromatogram; Appendix 2) dominated by short-chain *n*-alkanes. The northernmost oil is differentiated by very high amounts of isoprenoids relative to *n*-alkanes. The oils from the Oseberg Field (30/9-10; Norwegian Standard Oil (NSO-1)), the Agat Field (35/3-4) and from well 35/11-4 are also characterised by high concentrations of short-chain *n*-alkanes, suggesting that they are relatively non-biodegraded. Conspicuously different distribution patterns were found for the oils from the Troll West Field (31/2-G-3H) and the Grane Field (25/11-T21A). These oils are depleted in *n*-alkanes and appear to be biodegraded. The whole-oil chromatogram of the oil from the Grane Field shows a significant unresolved complex mixture (UCM) or “hump”, which rises significantly above the baseline, whereas the biodegraded character of the oil from the Troll West Field is manifest only in the lack of *n*-alkanes.

Gross compound composition

The ternary diagram in Figure 5.1.1 shows the relative abundance of saturated and aromatic hydrocarbons and NSO compounds in oils and extracts and reveals a great variability in their gross composition. The proportion of NSO compounds in these oils varies between 8.2% (well 35/11-4) and 28.5% (Grane Field) whereas the proportions of NSO compounds in the rock extracts were notably higher, at about 42%. The oils

from the Troll Field and the Grane Field, with proportions of saturated hydrocarbons less than 40%, are affected by biological degradation.

Although the tar mat sample and oil leg sample from well 30/9-1 are very similar with respect to bulk hydrocarbon/NSO composition, they differ significantly in terms of their TOC content (1.45% and 0.84%, respectively) and sulfur content (0.06% and 0.27%, respectively), in agreement with data reported by Wilhelms and Larter (1994a). Wilhelms and Larter (1994a) found a much higher proportion of asphaltenes in the tar mats compared with oil leg extracts but similar amounts of the resins. These authors used the Iatroscan TLC-FID technique with a solvent mixture (tetrahydrofuran : dichloromethane : methanol (50 : 46 : 4 vol%)). It is possible that the absence of a much higher relative abundance of NSO compounds in the tar mat sample analysed here is due to our separation method, because after extraction with an azeotropic mixture of acetone, methanol and chloroform (38 : 30 : 32 vol%) only the dichloromethane/methanol (99/1 vol%) soluble part of the extract was used for further fractionation into saturated and aromatic hydrocarbons and NSO compounds.

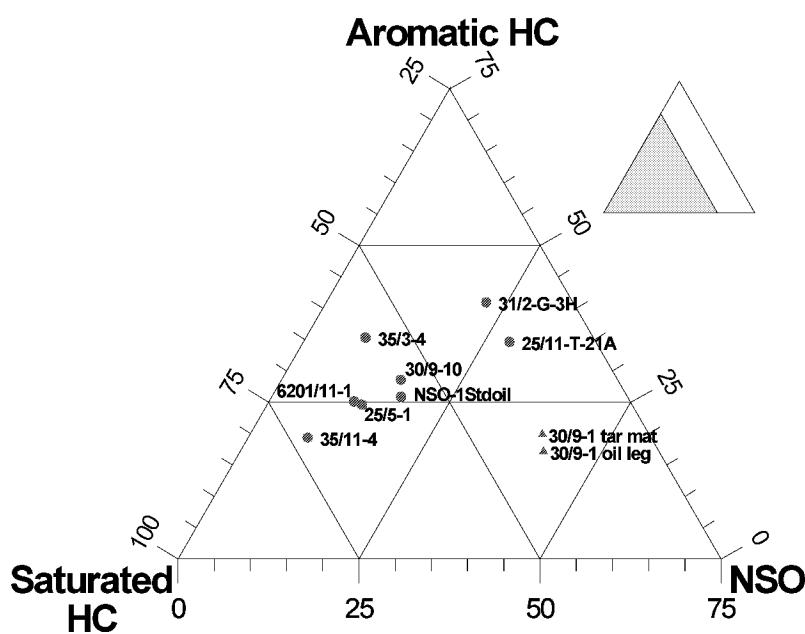


Fig. 5.1.1: Ternary diagram showing the gross composition (saturated and aromatic hydrocarbons, NSO compounds) of the crude oils and the two core rock samples from the Viking Graben

Gross heterocompound composition

Compound class fractionation using the liquid chromatographic method allowed a more detailed examination of the bulk compound class distribution. Figure 5.1.2 illustrates the distribution of heterocompound classes in the isolated crude oils and core samples from the Viking Graben. With the exception of the condensate from the Agat Field where the proportion of heterocompounds is naturally very low, the concentrations of heterocompounds in the crude oils were between 50 and 200 mg/g oil. The low-polarity NSO compound fraction of these oils constitutes the main heterocompound fraction.

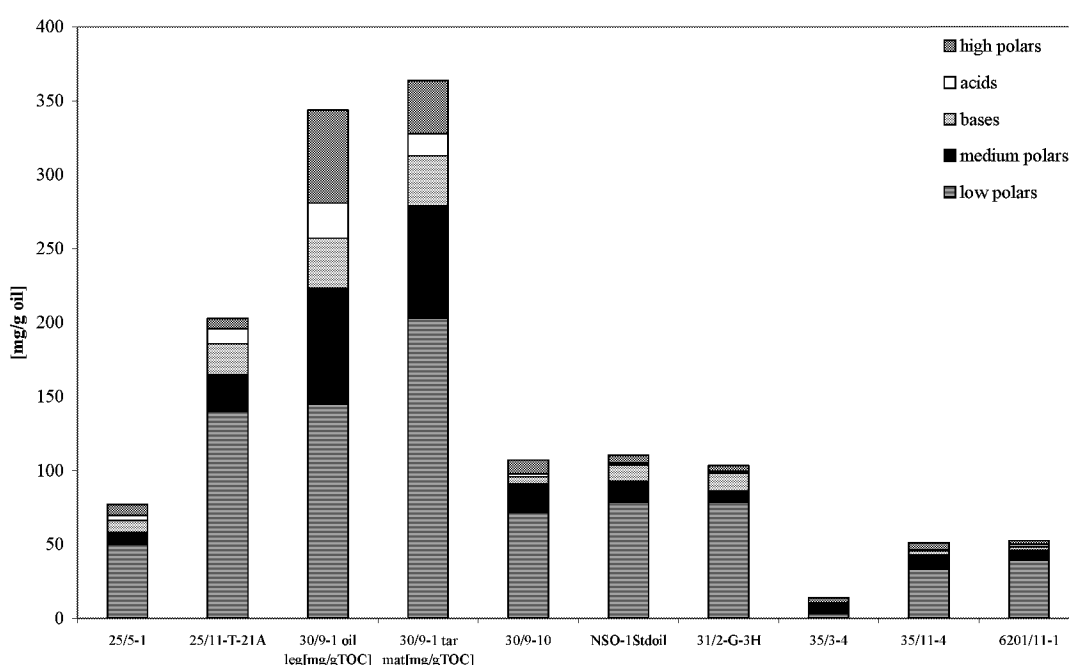


Fig. 5.1.2 Gravimetric composition of the heterocompound fractions of oils and core extracts from the Viking Graben

The biodegraded oil from the Grane Field is remarkable in that it contains the highest amount of heterocompounds (203 mg/g oil) and a higher content of acids than the other oils. An increase in the concentration of acids with biological degradation has been reported previously, e.g., Mackenzie et al. (1983), Behar and Albrecht (1984) and Jaffé and Gallardo (1993). Interestingly, the other (probably) biodegraded oil, from the Troll West Field, does not show an elevated amount of the acid fraction; this oil was characterised by a much less-pronounced UCM than the oil from the Grane Field and may be at a less-advanced stage of biodegradation.

The two core samples from well 30/9-1 contain high concentrations of all heterocompound fractions. A comparison of the two samples shows that the tar mat contains the highest concentration of low-polarity NSO compounds whereas the oil leg has higher amounts of the medium- and high-polarity NSO compound fractions and of the acid fraction. The lower amounts of highly polar compounds in the tar mat sample may reflect their retention by the insoluble part of the extract thereby excluding them from the separation procedure. The extraction was carried out with an azeotropic mixture of acetone, methanol and chloroform (1.9 : 1.5 : 1.6 vol%), whereas for separation the extracts were dissolved in a less polar mixture of dichloromethane and methanol (99 : 1 vol%) as described in Chapter 4.3.

API gravity

Determination of the API gravity of crude oils allows differentiation of petroleum fluids into condensates, oils and heavy oils. Whereas facies changes are reflected by the API gravity, the most important factors which can influence the chemical composition (and consequently the API gravity or the density) of a crude oil in the reservoir are alteration processes such as biodegradation, deasphalting etc. as described by Connan (1984). A correlation of API gravity with the percentage of less-than- C_{15} hydrocarbons, measured by topping, may also indicate the maturity level of fluids (Longman and Palmer, 1987; Karlsen et al., 1995). The API gravity of the Viking Graben oil series varies between 18° and 51°, as illustrated in Figure 5.1.3. The crude oil from well 35/3-4 (Agat) appears to be a condensate whereas the biodegraded oil from the Grane Field is a heavy oil. The oil from well 25/5-1 (Frøy) sourced by the marine Draupne Fm. (Bhullar et al., 1998) is

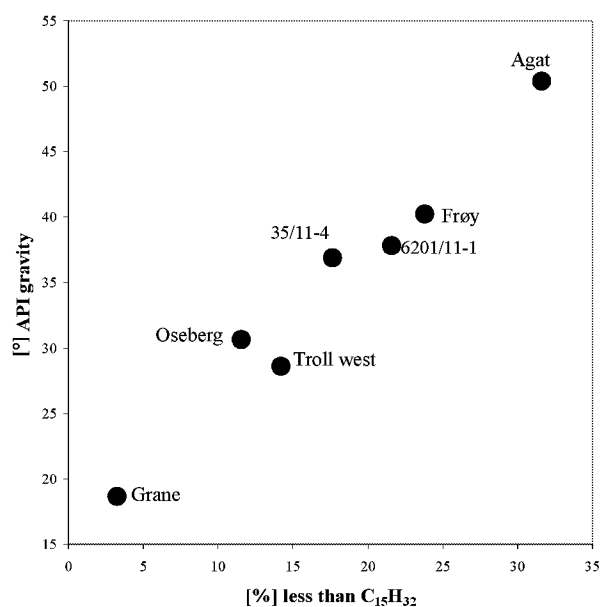


Fig. 5.1.3 Cross-plot of API gravity (calculated from density data) and evaporative loss of the Viking Graben isolated samples

a mature light oil, but Figure 5.1.2 shows that this oil contains slightly higher amounts of polar compounds compared to the other mature oils from wells 6201/11-1 and 35/11-4. Bhullar et al. (1998) attributed this phenomenon to the “sieving” of asphaltenes in the carrier bed sands, as proposed by Wilhelms and Larter (1994b). In this process, this sieving and the consequent formation of tar mats, in most cases in coarse-grained sandstones with vertical barriers, takes place by a migration-related mechanism. The reservoir sandstones in well 25/5-1 (Frøy) are coarse grained with heterogeneous lithologies and the presence of samples with higher contents of asphaltenes and resins indicates that the sands in this crestal well were probably conduits for migration of petroleum over an extended period of time. Although the content of asphaltenes was not determined by the classical precipitation method in the present study, the high-polarity fraction is considered to contain most of the proportion of asphaltenes in the oils/extracts.

5.1.1.2 Maturity and facies assessment using hydrocarbons

Alkanes

The alkanes of the 8 crude oils and two core samples from the Viking Graben were analysed quantitatively by gas chromatography. Due to variable loss of volatile compounds during the analytical separation method only the *n*-alkanes in the range from pentadecane and above (C₁₅₊) could be quantified reliably. The long-chain *n*-alkanes derive from epicuticular waxes of higher land plants or from highly aliphatic biopolymers of algae and other marine organisms. The *n*-alkane distributions from higher plant sources are typically characterised by an odd carbon-number dominance. During maturation the preference decreases due to the generation of new *n*-alkanes. Thus, the relative abundance of odd- and even-carbon-numbered *n*-alkanes can provide a crude estimate of the thermal maturity of petroleum. Carbon preference index (CPI) values (Bray and Evans, 1961) significantly above (odd carbon number preference) or below (even carbon number preference) 1.0 indicate that the oil or extract is thermally immature. Values of 1.0 suggest (but do not prove) that an oil or extract is thermally mature. In some cases, a significant proportion of the long-chain *n*-alkanes may be derived from other (non-terrestrial) sources, such as planktonic algae and bacteria. CPI values of less than 1.0 are typically associated with oils or bitumens from carbonate or hypersaline environments (Tissot and Welte, 1984; Peters and Moldowan, 1993).

The 8 crude oils and the two core samples from the Viking Graben do not show any significant odd or even carbon number predominance among the long-chain *n*-alkanes (CPI = 1.02-1.10; Appendix 3a). The CPI values of two oils and the two core samples from the Oseberg Field are very similar to each other whereas the more mature samples from the Agat and Frøy Fields and from well 6201/11-1 show slightly higher values of this parameter (Appendix 3a). However, the differences are very minor and essentially the CPI values show that all of the oils are mature.

Pristane/*n*-C₁₇ and phytane/*n*-C₁₈ ratios

The pristane/*n*-C₁₇ and phytane/*n*-C₁₈ ratios of crude oils are geochemical parameters commonly used to assess maturity, facies and/or biological degradation (du Rouchet and Dagens, 1976; Connan and Cassou, 1980). Figure 5.1.4 shows that most of the analysed oils from the Viking Graben have ratios of less than 1.0, a common feature of non-biodegraded oils (Connan and Cassou, 1980). These values are observed for the oils and rock extracts from the Oseberg Field and for the oils from the Frøy Field and

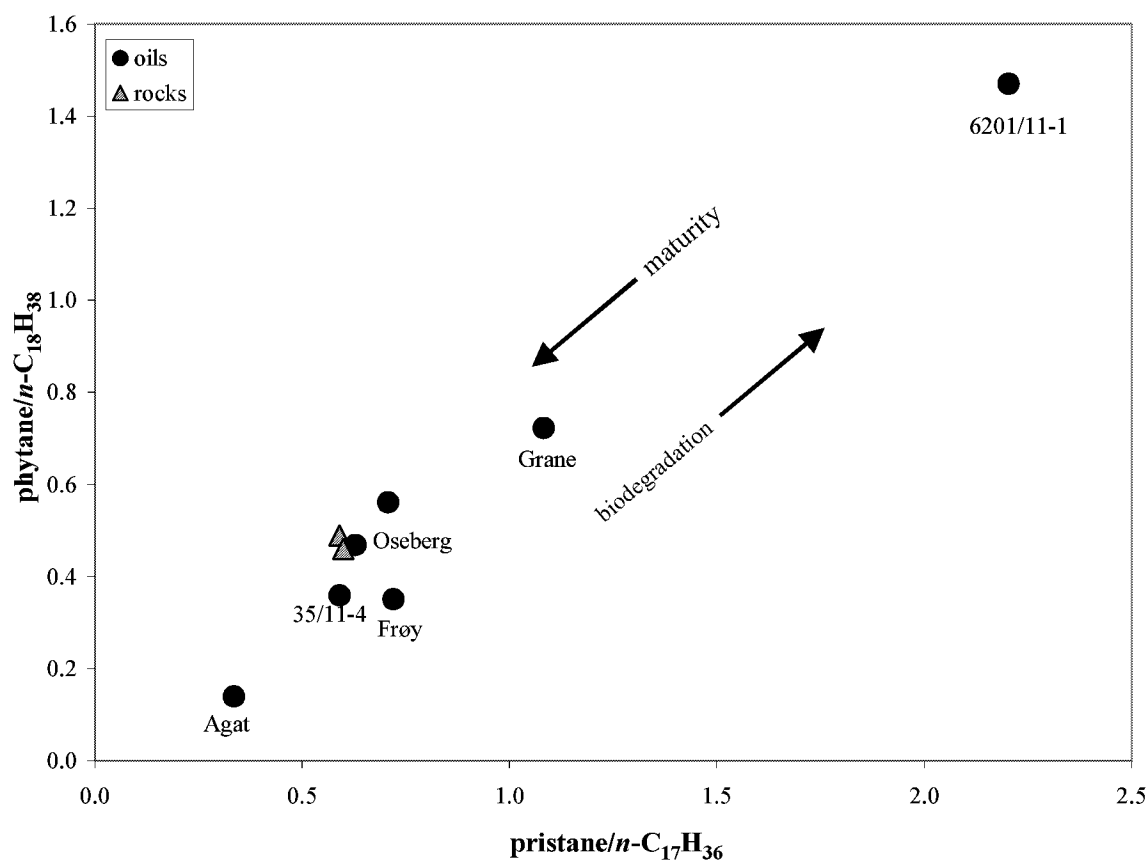


Fig. 5.1.4: Plot of pristane/*n*-C₁₇H₃₆ vs. phytane/*n*-C₁₈H₃₈ for the oils and rock extracts from the Viking Graben

well 35/11-4.

The lowest value in the data set was obtained for the very mature condensate from the Agat Field and this reflects the decrease in abundance of isoprenoids and increase in the formation of *n*-alkanes with increasing maturity. The oil from the Grane Field has relatively low isoprenoid/*n*-alkane ratios reflecting removal of *n*-alkanes during biological degradation. The data for the other probably biodegraded oil, from the Troll West Field, is not shown in this figure because no *n*-alkanes could be detected. The anomalously high concentrations of pristane and phytane in the non-biodegraded oil from well 6201/11-1 indicate a very immature oil. This seems to be in conflict with the high API gravity of 38° and the high evaporation loss in this sample. According to Connan et al. (1980) this apparent contradiction could point to an immature condensate.

A facies-related differentiation of the crude oils in this suite could not be established on the basis of the isoprenoid/*n*-alkane data.

Pristane/phytane

The pristane/phytane ratios of oils and bitumens have been used to indicate the redox potential of the source sediments (Didyk et al., 1978). According to these authors, pristane/phytane ratios of less than unity indicate deposition under anoxic conditions, whereas oxic conditions are indicated by ratios greater than 1. Both of these isoprenoid compounds are derived primarily from the phytanyl side chain of chlorophyll in phototrophic organisms, although other sources, such as the cell membranes of archaea (methanogens or halophiles) are known to contain pristane and phytane precursors (Chappe et al., 1982). Tocopherols have also been proposed as an additional source for pristane (Goossens et al., 1984). Volkman and Maxwell (1986) do not recommend use of the pristane/phytane ratio when assessing the palaeoenvironment for samples of low thermal maturity. For samples within the oil-generation window, high ratios (>3.0) indicate terrestrial organic matter deposited under oxic conditions and low values (<0.6) indicate anoxic, commonly hypersaline environments (Peters and Moldowan, 1993). As with many geochemical parameters, the pristane/phytane ratio is also influenced by thermal maturity. ten Haven et al. (1987) indicated an increase in this ratio with thermal maturity, whereas other authors found for different coals that the pristane/phytane ratio increased with increasing maturity to a maximum value corresponding to vitrinite

reflectance values between 0.7 and 1.0 percent beyond which the ratio decreased (Brooks et al., 1969; Radke et al., 1980; Connan, 1984).

The pristane/phytane ratios of the 8 crude oils and the two core samples from the Viking Graben vary from 0.7 to 2.9, with the lowest values being found in the oil leg (0.7) and tar mat (1.0) extracts. Most of the pristane/phytane ratio values are in the range 1.3 to 1.5 (Fig. 5.1.5). Variations in this ratio within the Viking Graben have been assigned to facies changes in the Kimmeridge Clay Formation (Cornford et al., 1983; Northam, 1985).

The pristane/phytane ratio of crude oils from the Viking Graben was suggested to be independent of maturity in many areas (Cornford et al., 1983), but facies dependent (Gormly et al., 1994). The authors discriminated between crude oils originating from (1) the Draupne Formation (marine shale) with pristane/phytane ratios of 1.0 to 1.5, (2) a mixed source (marine shale with a minor terrestrial component) with values between 1.5 and 2.15 and (3) the Heather Formation (marine shale with strong terrestrial contribution) with pristane/phytane

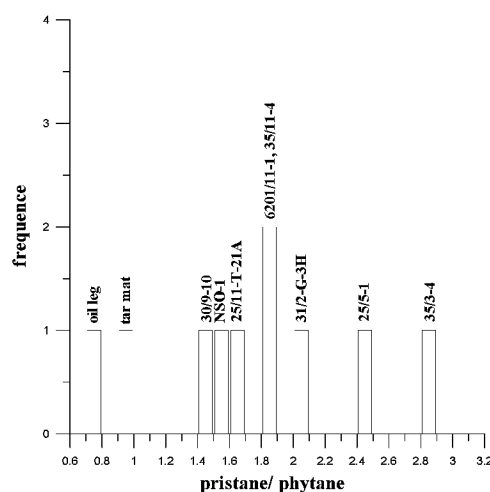


Fig. 5.1.5: Histogram of pristane/phytane ratios of oils and rocks from the Viking Graben

ratios in the range of 2.15 to 4.0. Chung et al. (1992) also concluded that the Heather Formation is a viable source of oils of a more terrestrial nature (pristane/phytane ratio between 2 and 3) in the northern Viking Graben. This would imply that all of the oils from the Oseberg Field and probably the Grane Field investigated in this study are sourced by the Draupne Formation, whereas the oil from Agat Field (well 35/3-4) originates from the Heather Formation, as suggested by Gormly et al. (1994). The relatively high value of pristane to phytane (2.4) in the oil from the Frøy Field (25/5-1) also indicates a strong terrestrial influence. However, Bhullar et al. (1998) proposed that this high ratio more reflects a higher maturity of the oil from this field. The pristane/phytane ratios in the oils from Troll West, 34/11-4 and 6201/11-1, suggest that they are mixed oils with different contributions from the two source rocks, which is in agreement with the results of the study of Gormly et al. (1994). The oil leg and tar mat samples from the Oseberg Field have low pristane/phytane ratios of 0.7 and 1.0,

respectively. These values are at the bottom end of the range of data (between 0.8 and 2.2) reported for Oseberg Field tar mat and oil leg extracts by Wilhelms and Larter (1994a).

Biomarkers

Biological markers or 'biomarkers' are complex organic compounds that can be considered molecular fossils, in that their structures can be especially related to formerly living organisms (Eglinton et al., 1964; Eglinton and Calvin, 1967). The original precursor structures may be subsequently modified during maturation and biodegradation (Seifert and Moldowan, 1986). In this study, the term 'biomarkers' is used only for the tetracyclic steranes and pentacyclic triterpanes. Many biomarkers may occur as different stereoisomers which are metastable with respect to geological time and temperature. Consequently, geological time and temperature can be monitored using ratios of biomarker compounds of different stability, which allows an estimation of source rock or petroleum maturity (Ensminger et al., 1977; Seifert and Moldowan, 1978). Many hopane and sterane derivatives can be used to characterise the oils with regard to maturity, facies and depositional environment. An account of the significance of the biomarker parameters used in the analysis of the samples from offshore Norway has been given in Chapter 4.7.

North Sea oils sourced from Upper Jurassic sediments are characterized by similar sterane distributions, sparse or absent gammacerane, abundant C₃₀ cholestanes (Bailey et al., 1990) and the almost ubiquitous occurrence, in varying abundance, of the diagnostic biomarker 28,30-*dinor*-17 α ,18 α ,21 β -hopane (Grantham et al., 1980). Distinguishable from oils from the Central Graben the oils and cores from the Viking Graben contain higher relative amounts of 28,30-*dinor*-17 α ,18 α ,21 β -hopane and have higher pristane/phytane ratios (Cornford et al., 1983; Northam, 1985). The crude oils and core extracts from the Oseberg Field, Troll West Field, Agat Field and from well 35/11-4 are attributed to mixed sources from the marine Draupne and Heather Formations, with a more terrestrial nature being suggested by the high pristane/phytane ratios (Chung et al., 1992; Gormly et al., 1994).

Horstad and Larter (1997) screened extracts of 796 reservoir core samples from the Troll area using the Iatroscan technique (TLC-FID). On the basis of this screening, 110 samples from the gas, oil and water zones were selected for detailed characterisation of

the extracted petroleum through GC-FID and GC-MS analysis of the saturated hydrocarbon fraction. Additionally, 39 samples from the Oseberg and Brage Fields and from block 35/11 were discussed in their study. Regarding the biological marker analysis they concluded that a broad classification into dominantly facies-controlled and maturity-influenced groups was possible. Statistical analysis of all conventional biological markers indicated that the best established facies-controlled biological marker parameters are the 28,30-*dinor*-17 α ,18 α ,21 β -hopane (DNH) to 30-*nor*-17 α ,21 β -hopane (30NH) ratio, the 25-*nor*-17 α ,21 β -hopane (25NH) to 30-*nor*-17 α ,21 β -hopane (30NH) ratio and the 25NH to DNH ratio.

The presence of the 25-*nor*-17 α ,21 β -hopane series is typical of many, but not all, heavily biodegraded oils (Reed, 1977b; Seifert and Moldowan, 1979; Rullkötter and Wendisch, 1982; Volkman et al., 1983; Nytoft et al., 2000). As described in Chapter 4.7 these compounds appear to result from the bacterial removal of the methyl group at C-10 from the regular hopanes. Other authors have suggested that 25-*nor*-17 α -hopanes are common in nondegraded oils and in source rock extracts (Blanc and Connan, 1992 and references therein). Horstad and Larter (1997) suggested that the relative concentration of 25-*nor*-17 α -hopanes in the Oseberg-Troll area represents an indicator of the depositional environment of the source rock rather than the extent of biological degradation of the oils. The authors showed that higher amounts of 25-*nor*-17 α -hopanes are accompanied by lower relative concentrations of 28,30-*dinor*-17 α ,18 α ,21 β -hopane. The detailed discussion about the occurrence of 25-*nor*-17 α -hopanes, presented in Chapter 4.7, leads to the conclusion that the relative amount of 25NH in an oil seems to be dependent on the extent of biodegradation for biodegraded oils whereas for non-biodegraded oils it is more related to facies.

Biomarkers – Facies Considerations

With the exception of the condensate from the Agat Field, biomarkers were quantified for all of the oil and core samples in the Viking Graben suite. In all samples, the hopane distribution pattern (m/z 191) was dominated by 17 α ,21 β -hopane. Horstad and Larter (1997) suggested that the 25-*nor*-17 α ,21 β -hopane to 28,30-*dinor*-17 α ,18 α ,21 β -hopane ratio and the 28,30-*dinor*-17 α ,18 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane ratio were related to changes in facies and the depositional

environment in this area but it was observed in the present study that 25-*nor*-17 α ,21 β -hopane normalised to 30-*nor*-17 α ,21 β -hopane is also a good indicator of facies variation (Fig. 5.1.6).

Compared to other oils from the Viking Graben the oil from the Frøy Field contains a slightly lower proportion of the C₂₈ cholestanes (25% compared with 28-32% for the other oils, see Appendix 3d); very low concentrations of 28,30-*dinor*-17 α ,18 α ,21 β -hopane and 25-*nor*-17 α ,21 β -hopane relative to 30-*nor*-17 α ,21 β -hopane (see Figure 5.1.6); and a high pristane/phytane ratio (2.45; Fig. 5.1.5) which points to a source other than the Kimmeridge Clay Formation which is commonly seen as the main source rock. The other oils and cores from the Viking Graben are relatively enriched in 25-*nor*-17 α ,21 β -hopane, with the highest amounts being found in the oils from the Grane Field and from well 6201/11-1 to the north of the Viking Graben [$25\text{NH}/(25\text{NH} + 30\text{NH}) = 0.44$ and 0.40 , respectively] (see Fig. 5.1.6). The high concentration of 25-*nor*-17 α ,21 β -hopane in the oil from the Grane Field could reflect biological degradation as described above, whereas for the oil from well 6201/11-1 the high concentration of 25-*nor*-17 α ,21 β -hopane accompanied by a low concentration of 28,30-*dinor*-17 α ,18 α ,21 β -hopane [$28,30\text{DNH}/30\text{NH} = 0.27$; see Figure 5.1.6] probably indicates a different facies, possibly dysoxic, low-salinity marine environments as described by Blanc and Connan (1992).

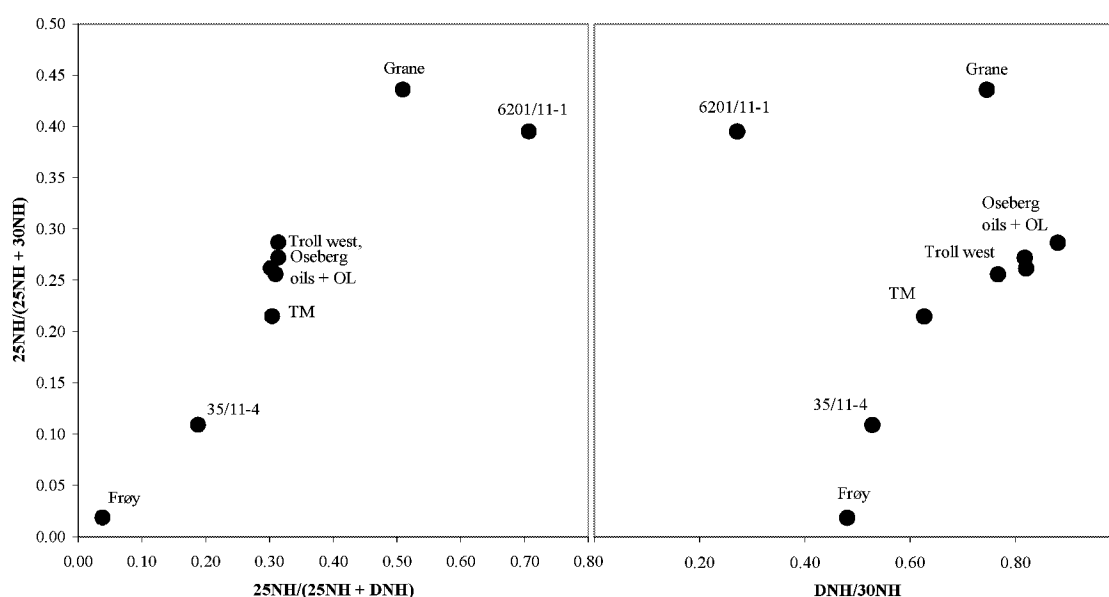


Fig. 5.1.6: Diagrams showing the variation in facies- and biodegradation-related biomarker parameters for the oils and cores from the Viking Graben (OL = oil leg; TM = tar mat – both Oseberg Field)

Biomarkers in the oils and cores from the Oseberg Field and the Troll West Field indicate a similar source facies for these samples. This is in accordance with the most likely migration routes for these oils defined by Field (1985), Thomas et al. (1985), and Horstad and Larter (1997). These authors concluded that a spillage from the Brage/Oseberg area to the Troll Field supplies one of two oil populations within the Troll Field. The tar mat sample (TM in Fig. 5.1.6) from the Oseberg Field has a slightly lower 25-*nor*-17 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane ratio than the Oseberg oils and oil leg (OL) sample; this is due to a higher concentration of 30-*nor*-17 α ,21 β -hopane.

The oil from well 35/11-4 is characterised by a much lower abundance of 25-*nor*-17 α ,21 β -hopane relative to 30-*nor*-17 α ,21 β -hopane (0.11) compared to the oils and core extracts from the Oseberg Field. This reflects the existence of a third oil population in this area with a different facies, as suggested in the study by Horstad and Larter (1997).

Biomarkers – Maturity Considerations

Using statistical methods, Horstad and Larter (1997) suggested that the best maturity-influenced biological marker parameters for the Oseberg-Troll area are 22,29,30-*trinorneo*-18 α -hopane (Ts) to 22,29,30-*trinor*-17 α -hopane (Tm); 30-*norneo*-18 α ,21 β -hopane (C₂₉Ts) to 30-*nor*-17 α ,21 β -hopane (30NH); 27-*nor*-15 α -methyl-17 α ,21 β -hopane (DH) to 30-*nor*-17 β ,21 α -moretane (30NM); and the 20S/(20S+20R) and 5 α ,14 β ,17 β /(5 α ,14 α ,17 α +5 α ,14 β ,17 β) ratios in the C₂₉ cholestanes (the significance of the ratios is discussed in Chapter 4.7).

The oil from the Frøy Field is characterised by high abundances of 27-*nor*-15 α -methyl-17 α ,21 β -hopane (DH) and 30-*norneo*-18 α ,21 β -hopane (C₂₉Ts) relative to 30-*nor*-17 α ,21 β -hopane (30NH) (0.47 and 0.90, respectively); a high ratio of diasteranes to regular steranes (2.51) and a Ts/(Ts+Tm) ratio of 0.63 (for data see Appendix 3b-c) which together indicate a high maturity, as described by Bhullar et al. (1998). The northernmost North Sea crude oil in this suite, from well 6201/11-1, has a high relative concentration of 27-*nor*-15 α -methyl-17 α ,21 β -hopane and a high diasterane to regular sterane ratio (2.76) which could indicate high maturity and/or a more oxic source rock depositional environment. The high Ts/(Ts+Tm) ratio of 0.73, the C₂₉ sterane

isomerisation ratio [$20S/(20S+20R) = 0.52$] and the high relative concentration of 30-*norneo*-18 α ,21 β -hopane indicate a high maturity for this oil. In contrast to these parameters, the high pristane/*n*-C₁₇ ratio and the API gravity of this oil indicate an immature condensate. Furthermore, the high 25-*nor*-17 α ,21 β -hopane concentration and the high pristane to *n*-heptadecane ratio could also indicate a biodegraded oil. A possible explanation for this inconsistent signature in the oil composition could be that the oil in well 6201/11-1 is a mature oil which was biodegraded and later mixed with a condensate (which typically contain low abundances of biomarkers) (cf. Rullkötter et al., 1984b).

The biomarker distributions of the oils and cores from the Oseberg Field are very similar to each other, as also reported by Wilhelms and Larter (1994a). They indicate a moderate maturity [$Ts/(Ts+Tm) = 0.60$ -0.63, $DH/30NH = 0.10$ -0.16], whereas the biomarker distribution of the oil from well 35/11-4 clearly shows a much higher maturity. This is expressed by the highest $Ts/(Ts+Tm)$ ratio (0.77, see Appendix 3b) in the data set and high relative amounts of 27-*nor*-15 α -methyl-17 α ,21 β -hopane and 30-*norneo*-18 α ,21 β -hopane normalised to 30-*nor*-17 α ,21 β -hopane (0.54 and 0.70, respectively, see Fig. 5.1.7). A higher maturity for oils from Block 35/11 in comparison to the oils and core extracts from the Oseberg-Troll area is in agreement with the study by Horstad and Larter (1997). These authors described the oils in the Troll West Field as a mixture of two oil populations, i.e. the moderately mature oil from the Oseberg Field and a more mature oil spilled from the northwestern area to the Troll Field. This

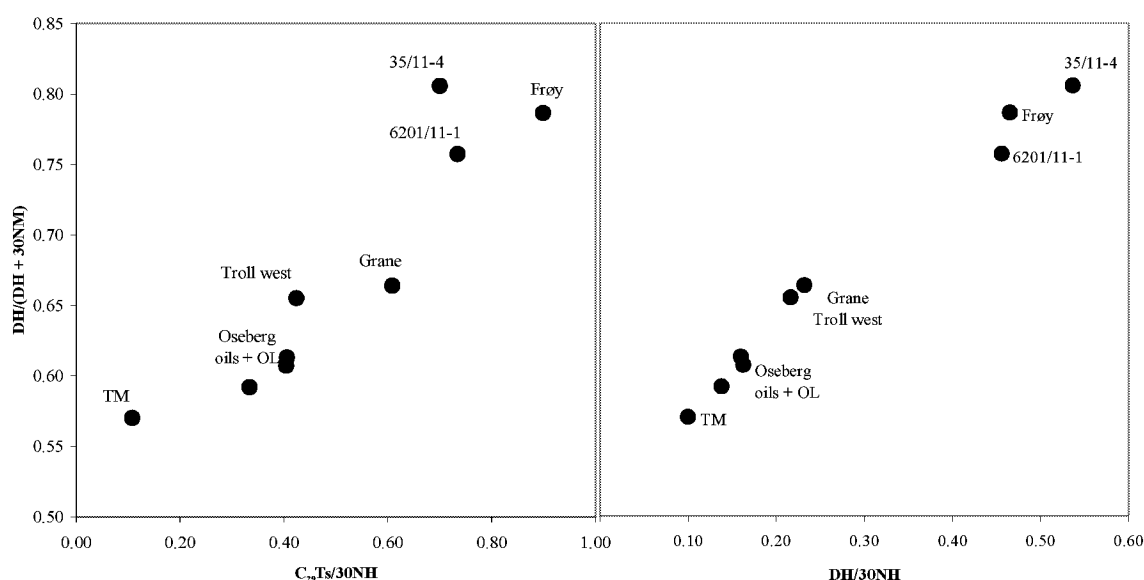


Fig. 5.1.7: Diagrams showing the variation in maturity-related biomarker parameters for the oils and cores from the Viking Graben

shift to a higher maturity is clearly illustrated in Figure 5.1.7.

The oil from the Grane Field has a maturity similar to that from the Troll West Field.

5.1.1.3 Conclusions

The Viking Graben isolated oils show a broad range of facies differences and maturity signatures consistent with those in the published literature. The condensate from the Agat Field is very mature, indicated by the very low pristane/*n*-heptadecane and phytane/*n*-octadecane ratios, the high API gravity and the high evaporative loss. The high pristane to phytane ratio of 2.87 indicates an origin from a more terrestrially influenced source, most probably the Heather Formation.

The northernmost North Sea oil analysed here, from well 6201/11-1, seems to be very mature based on the biomarker maturity signatures, and appears to represent a distinctly different facies expressed by low 28,30-*dinor*-17 α ,18 α ,21 β -hopane and high 25-*nor*-17 α ,21 β -hopane concentrations. The high 25-*nor*-17 α ,21 β -hopane concentration and the high pristane to *n*-heptadecane ratio suggest that it may be a mature oil which was biodegraded and subsequently mixed with a condensate containing low abundances of biomarkers.

The biomarker data for the oil from well 35/11-4 suggest a highly mature oil different from the oils in the Oseberg-Troll area. The pristane to phytane ratio and the more facies-controlled biomarker parameters indicate a mixed source from the Upper Jurassic Draupne and Heather Formations.

The oils and core extracts from the Oseberg Field have a very similar biomarker composition and have a moderate maturity. The Draupne Formation is suggested to be the only source of the Oseberg oils, whereas the oil from the Troll West Field is tentatively more mature and the pristane to phytane ratio of 2.08 indicates an additional terrestrial source. The Troll West oil is interpreted as a mixed oil composed of oil spilled from the southwest (via Oseberg-Brage-Troll) and oil from the northwest (more mature and terrestrially stamped source, probably the Heather Formation).

The oil from the Grane Field is biodegraded, mature and sourced from the Upper Jurassic Draupne Formation.

Despite the high pristane to phytane ratio, the oil from the Frøy Field is suggested to be very mature and sourced from the Draupne Formation.

5.1.2 Tampen Spur – Crude Oils

The Tampen Spur is an area with a complex reservoir filling history which has been controversially discussed in the past (Thomas et al., 1985; Karlsson, 1986; Horstad et al., 1995). New insights on the migration process gained from the present study will be given later in this thesis, in the heterocompound chapters. The following characterisation of the crude oils from the Tampen Spur using conventional, established hydrocarbon-based parameters allows differentiation of the various oil families within the petroleum system.

5.1.2.1 Bulk organic geochemical characteristics

Whole-oil characteristics

The whole-oil gas chromatograms for most of the oils from the Tampen Spur show similar distribution patterns dominated by short-chain *n*-alkanes and are typical of a mature, undegraded oil (see Appendix 2). Depletion of *n*-alkanes, indicating biodegradation, is noted in the biodegraded oil suite from the Gullfaks Field and to some extent in the oil from well 34/7-18. The oil from well 34/7-10 is noteworthy in that despite depletion of the *n*-alkanes, the whole-oil gas chromatogram shows no “hump” such as found for the oil from the Troll West Field (Appendix 2). The two oils from the Gullfaks Sør Field (34/10-30, 34/10-32R) are remarkable because the chromatograms show a strong predominance of long-chain *n*-alkanes with a distribution maximum at *n*-pentacosane. This could reflect a greater contribution of terrestrial organic matter to the source organic matter or the oils could be typical mature oils from which the light ends have been stripped.

Gross compound composition

The triangular plot in Figure 5.1.8 illustrates the relative abundance of saturated and aromatic hydrocarbons and NSO compounds. Apart from the biodegraded oils from the Gullfaks Field, in which the proportion of saturated hydrocarbons decreases with increasing degree of biodegradation, most of the oils from the Tampen Spur are very similar to each other with respect to their gross compound composition. The condensate

from the Gullfaks Gamma Field (34/10-35) contains the lowest percentage of NSO compounds, at 3.4%. Surprisingly, the proportion of saturated hydrocarbons in this sample is relatively low for a condensate; this is attributed to evaporation loss during sample handling. The two oils from the Gullfaks Sør Field (34/10-30, 34/10-32R) contain the highest proportion of saturated hydrocarbons, reflecting the predominance of the long-chain *n*-alkanes, whereas the highest relative abundance of NSO compounds (ca. 25%) are found in the oils from wells 34/7-4, 34/7-10 and 34/10-34.

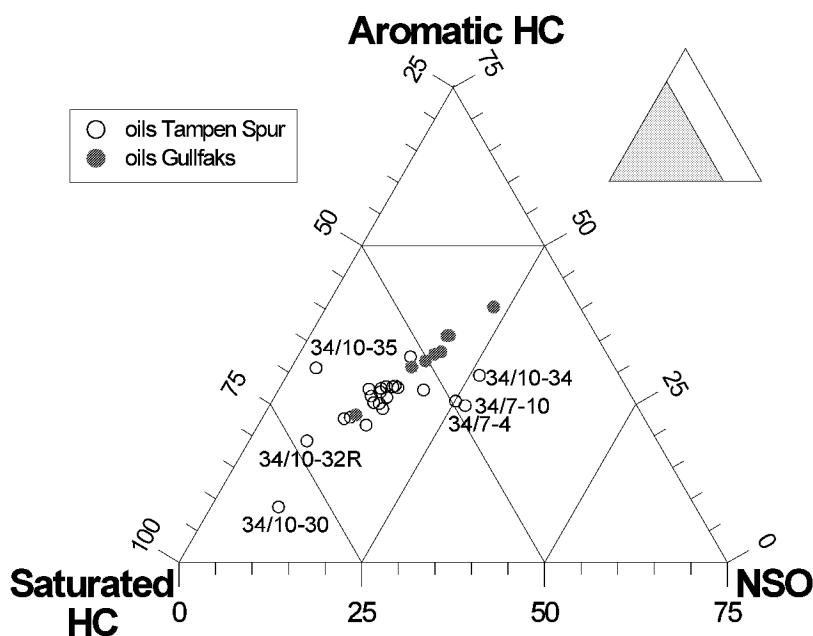


Fig. 5.1.8: Ternary diagram showing the gross composition (saturated and aromatic hydrocarbons, NSO compounds) of the crude oils from the Tampen Spur

API gravity

The API gravity of the oils from the Tampen Spur varies between 27° and 45°, as illustrated in Figure 5.1.9. As expected, the condensate from the Gullfaks Gamma Field (34/10-35) has the highest API gravity as well as the highest loss of volatile components. At the other end of the scale, the biodegraded oils from the Gullfaks Field and well 34/7-18, and the oils from the Gullfaks Sør Field, with high concentrations of long-chain *n*-alkanes, gave the lowest API gravity values and only minor loss of volatile components. It is assumed that this is the result of a facies difference or due to stripping of the light-end hydrocarbons in the subsurface rather than an indication of immaturity. Within the Snorre Field, an increase in API gravity from the south (34/7-10) to the north

(34/4-6) of the field is observed. This correlates with maturity trends described by Horstad et al. (1995).

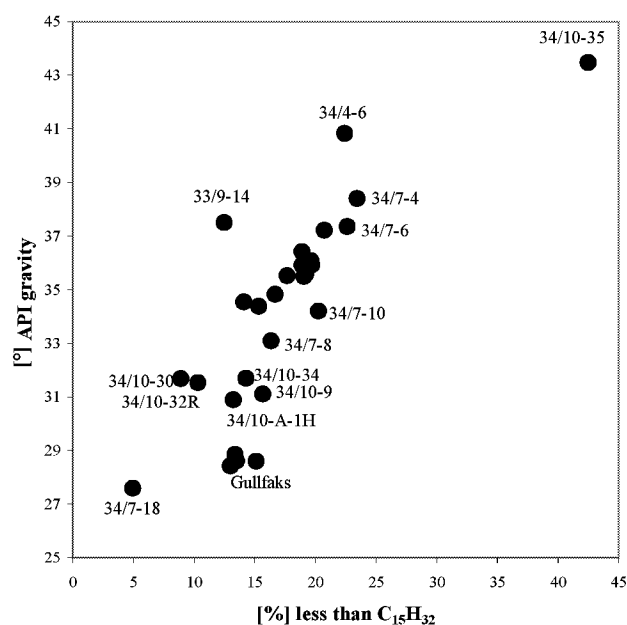


Fig. 5.1.9: Cross plot of API gravity (calculated from the density data) and evaporative loss for the Tampen Spur oils

5.1.2.2 Maturity and facies assessment using hydrocarbons

Alkanes

The *n*-alkane distribution patterns for most of the oils from the Tampen Spur area are very similar to each other, with a distribution maximum at *n*-tridecane or *n*-pentadecane (see Appendix 2). The CPI values (*n*-C₂₄₋₃₂) vary between 0.98 and 1.08 for all of the oils with the exception of the biodegraded sequence from the Gullfaks Field. A different *n*-alkane distribution pattern was observed for the oils from the Gullfaks Sør Field in which there is a shift of the distribution maximum to higher homologues, probably reflecting a higher terrestrial contribution to the source rock. Whereas the oils from the Gullfaks Field and the oil from well 34/7-18 are clearly affected by biodegradation, as evident from the lack of *n*-alkanes and the presence of a “hump” in the chromatograms, the predominance of isoprenoid compounds and the absence of a UCM for the oil from well 34/7-10 could indicate either biodegradation or a difference in the source facies.

Pristane/*n*-C₁₇ and phytane/*n*-C₁₈

Figure 5.1.10 shows the variation in the pristane to *n*-heptadecane ratio and the phytane to *n*-octadecane ratio for the oils from the Tampen Spur area. The entire data points plot tightly along the regression line, indicating that significant variation with respect to facies is unlikely. The oils from the Gullfaks Field are distributed over a broad range depending on the degree of biological degradation. A detailed discussion of these oils will be given in Chapter 5.1.3.

With the exception of the samples from wells 34/7-10 and 34/7-18, the oils from the Tampen Spur show ratios between 0.5 and 1.1 for pr/*n*-C₁₇ and between 0.2 and 0.9 for ph/*n*-C₁₈. The ratio values for the oils from wells 34/7-10 and 34/7-18 are significantly higher and lie within the ranges found for the biodegraded oils from the Gullfaks Field. Both samples show evidence of biodegradation, more so for the oil from 34/7-18. The inset in Figure 5.1.10 reveals that the lowest ratios are found in the oils from Gullfaks Gamma, Gullfaks Sør and the Rimfaks Field in the south of the Tampen Spur, and in the oils from the Visund Field and from well 34/4-6, which are from the eastern and northern margins of the area. This could indicate a higher maturity for these oils in

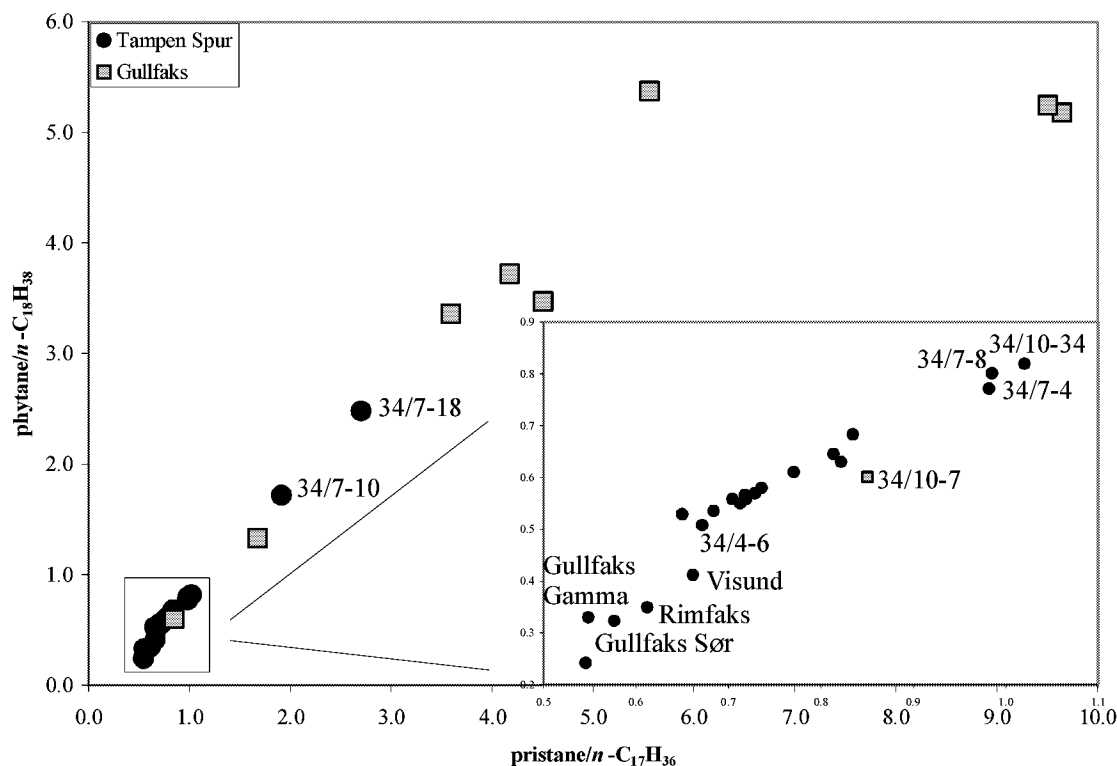


Fig. 5.1.10: Plot of phytane/*n*-C₁₈H₃₈ vs. pristane/*n*-C₁₇H₃₆ for oils from the Tampen Spur and the Gullfaks Field

comparison to the other oils. Conversely, the oils from wells 34/7-4, 34/7-8 and 34/10-34 appear to be more immature according to this criterion.

Pristane/phytane

The pristane/phytane ratio for crude oils from the Viking Graben has been reported to be independent of maturity (Cornford et al., 1983) and strongly facies dependent (Gormly et al., 1994). As described in the previous chapter, these authors differentiated between crude oils originating from (1) the Draupne Formation (marine shale) with pristane/phytane ratios of 1.0 to 1.5, (2) a mixed source (marine shale with minor terrestrial input) with values between 1.5 and 2.15 and (3) the Heather Formation (marine shale with strong terrestrial input) with pristane/phytane ratios in the range of 2.15 to 4.0. Chung et al. (1992) also concluded that the Heather Formation is a viable source of oils with a more terrestrial nature (pristane/phytane ratios between 2 and 3) in the northern Viking Graben.

Most of the oils from the Tampen Spur show very similar pristane to phytane ratios, in the range 1.30-1.53, as illustrated in Figure 5.1.11. According to Gormly et al. (1994), these oils originate from the Draupne Formation. The oils from the Gullfaks Gamma, Gullfaks Sør, Rimfaks and Visund Fields, and the oil from well 34/10-7, located in the easternmost part of the Gullfaks Field, are enriched in pristane indicating an additional source, most probably the Heather Formation.

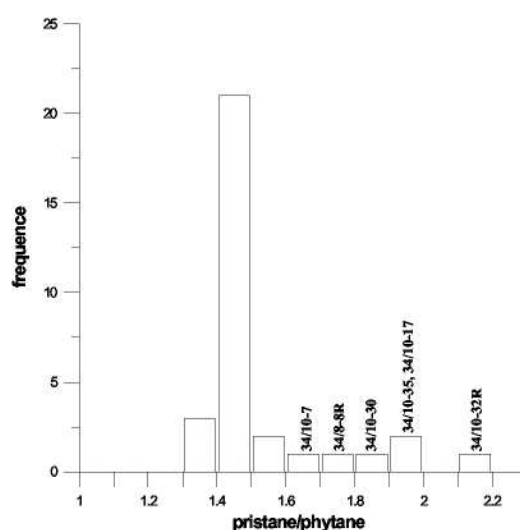


Fig. 5.1.11: Frequency histogram of pristane/phytane ratios for oils from the Tampen Spur

Biomarkers – Facies Considerations

As described by Horstad et al. (1995) the 25-nor-17 α ,21 β -hopanes occur only in trace amounts in oils from the Tampen Spur area [$25\text{NH}/(25\text{NH} + 30\text{NH}) \leq 0.10$, see Appendix 3b] and they cannot be used to discriminate between these oils.

The abundance of 28,30-*dinor*-17 α ,18 α ,21 β -hopane (DNH) normalised to 30-*nor*-17 α ,21 β -hopane (30NH) is one of the most useful parameters for differentiating oil populations in the North Sea. The relative amount of 28,30-*dinor*-17 α ,18 α ,21 β -hopane in an oil appears to depend more strongly upon the facies of the source rock from which the oil was expelled than upon its maturity at the time of expulsion (Horstad et al., 1995). However, when the maturity range of the analysed oils is large, the relative concentration of 28,30-*dinor*-17 α ,18 α ,21 β -hopane may include a significant maturity component.

The DNH/30NH ratios for the oils from the Tampen Spur area were in the range 0.29-1.01 (Fig. 5.1.12). The lowest values for the DNH/30NH ratio, between 0.29 and 0.40, were obtained for the oils from the Gullfaks Sør Field and the Rimfaks Field. These oils also have the highest pristane to phytane ratios, as shown in Figure 5.1.12, and an origin from the Heather Formation or a mixed origin is suggested.

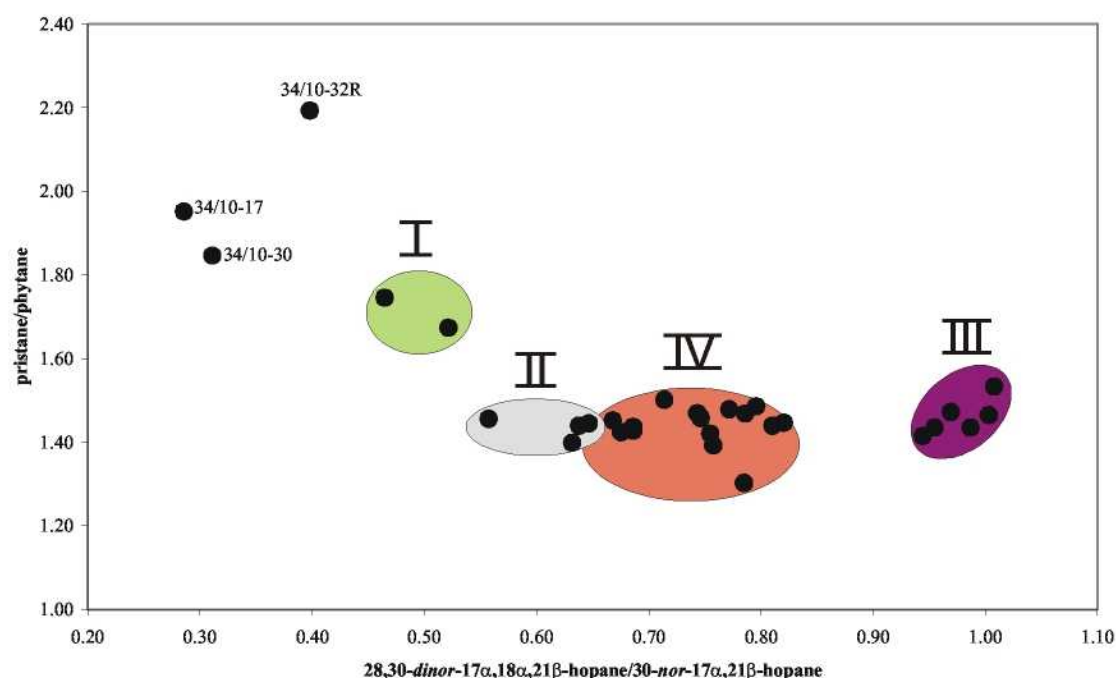


Fig. 5.1.12: The different oil populations within the Tampen Spur area, illustrated by pristane to phytane versus 28,30-*dinor*-17 α ,18 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane ratios (for locations see map in Figure 5.1.13 and the text in this facies section)

Oil population I (two oils analysed) is located in the Visund Field and in the eastern part of the Gullfaks Field (well 34/10-7) (see Figs. 5.1.12 and 5.1.13). The oils are characterised by a low relative abundance of 28,30-*dinor*-17 α ,18 α ,21 β -hopane

[28,30DNH/30NH = 0.46 and 0.52, respectively] and a higher pristane to phytane ratio compared to the oils in populations II-IV. These low concentrations reflect a different source facies for the type I oils in comparison with the type II-IV oils, and are probably attributable to part sourcing from the terrestrially influenced Heather Formation.

The oils from the other three populations are very similar to each other with regard to the pristane/phytane ratio, but can be differentiated by the 28,30-*dinor*-17 α ,18 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane ratio.

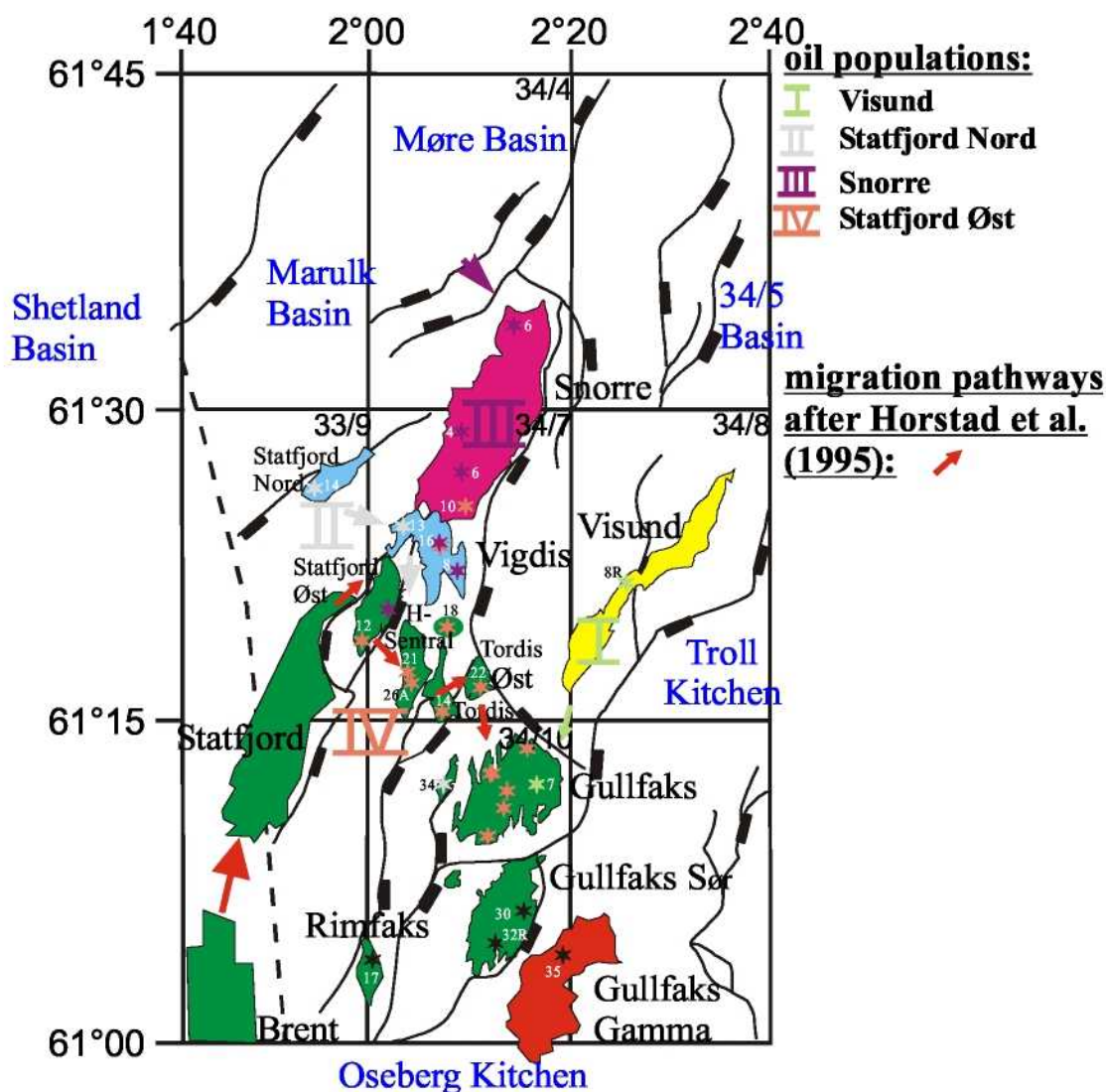


Fig. 5.1.13: Map of the Tampen Spur area showing the different oil populations and proposed migration pathways, after Horstad et al. (1995)

The Statfjord Nord oil population (II, four oils analysed) is reservoirised within the Upper Jurassic sandstones and the Brent Group in the Statfjord Nord Field and in the Brent Group in parts of the Vigdis Fields. The oils have a slightly higher 28,30DNH/30NH ratio compared to those in I, with values in the range 0.56 to 0.65.

Although the oil from well 34/10-34 can also be included in this group on the basis of the relative concentration of 28,30-*dinor*-17 α ,18 α ,21 β -hopane, it should be noted that it is part of a different drainage system in the region and is probably immature.

The oils comprising the third group, the Snorre Field population (**III**, six oils analysed), include petroleum reservoirs within the Statfjord Formation and the Lunde Formation and possibly within the Zeta structure to the north of the Snorre Field. The oils are clearly enriched in 28,30-*dinor*-17 α ,18 α ,21 β -hopane, with 28,30DNH/30NH ratios between 0.94 and 1.01. Additionally, two oils from the Vigdis Field (34/7-8, 34/7-16 DST.3) and the oil from well 34/7-23A located to the south of the Snorre Field, are also clearly enriched in 28,30-*dinor*-17 α ,18 α ,21 β -hopane and, according to this parameter, belong to this oil population.

The fourth and largest group is the Statfjord Øst oil population (**IV**, 15 oils analysed), which is comprised of the oils present in the Brent Group of the Statfjord Field, the Statfjord Øst structure, the Tordis Field and the Gullfaks Field. The oils in this population are characterized by 28,30DNH/30NH ratios of between 0.65 and 0.82. This group includes the oils from the Gullfaks (with the exception of the oil from well 34/10-7), Tordis, Tordis Øst, H-Sentral and Statfjord Øst Fields, and the oils from wells 34/7-16 (DST.2) and 34/7-10. Mixing of oils from the Statfjord Nord oil population with those from the Snorre Field oil population results in a composition similar to that in oils of the Statfjord Øst oil population. Because these three oil populations migrate towards the same apex in the central part of block 34/7, it is difficult to elucidate the migration pathways in this area.

Biomarkers – Maturity Considerations

Three maturity-related parameters were selected as the most useful ones to demonstrate maturity variations among the oils from the Tampen Spur. These are the Ts/(Ts+Tm) ratio, the percentage of 5 α ,14 β ,17 β -20(*R+S*) in the C₂₉ cholestanes and the DH/(DH + 30NM) ratio. Whereas most of the oils show only minor variations in the first two ratios, the DH/(DH + 30NM) ratio covers a broader range, as illustrated in Figure 5.1.14. This ratio was also described by Horstad et al. (1995) as the most useful parameter to demonstrate the maturity variations in oils from the Tampen Spur area.

Figure 5.1.14 shows that the Visund oil population **I** (34/8-8R and 34/10-7) is the most mature group within the Tampen Spur area, followed by the Statfjord Nord oil

population **II** (33/9-14 and 34/7-13). The immature signature of the oil from well 34/10-34 supports the suggestion that this oil is sourced more locally and is different from the Statfjord Nord oil population. The oils from the Gullfaks Sør Field and Rinfaks Field indicate a relatively high maturity.

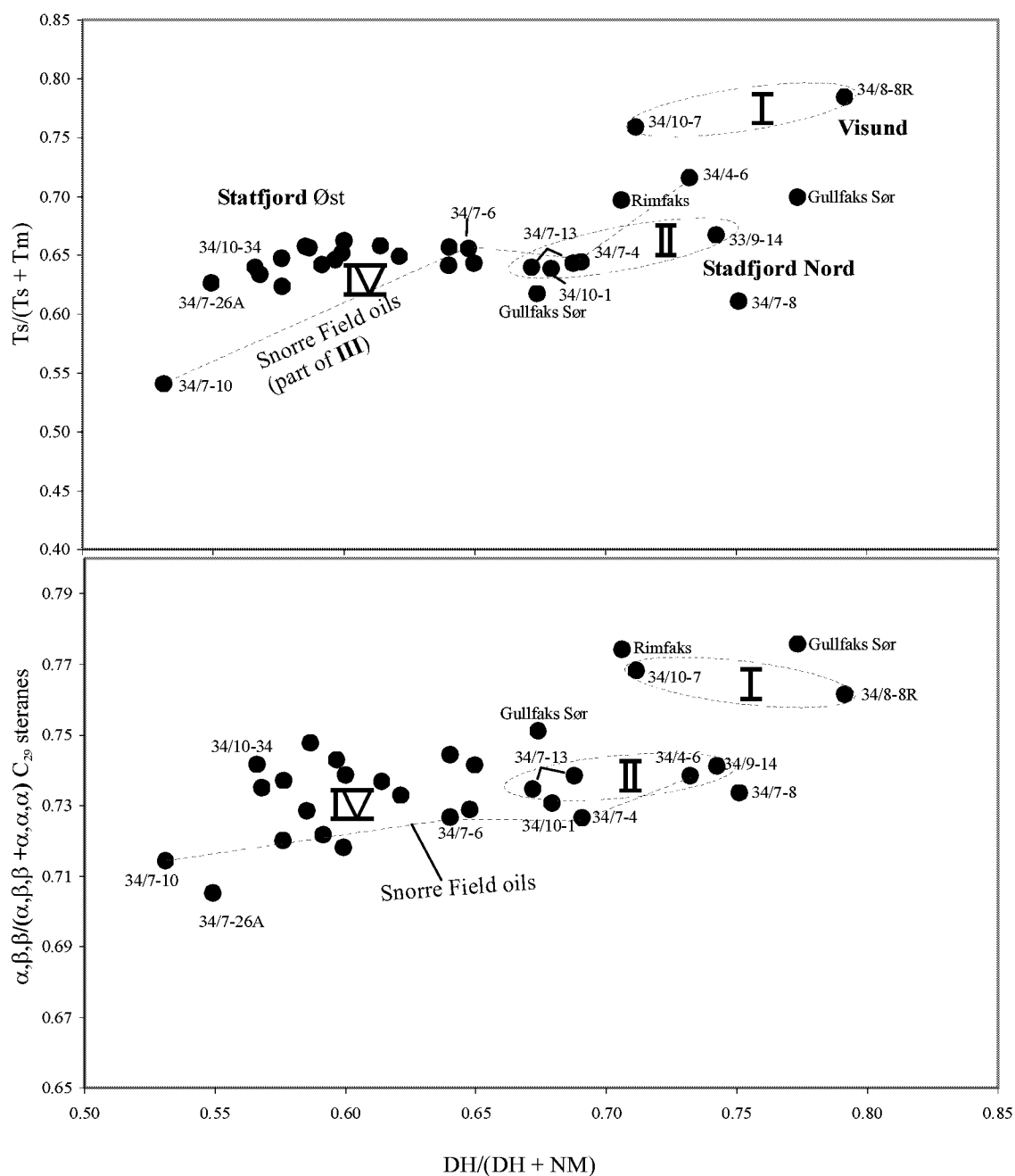


Fig. 5.1.14: Variation in $Ts/(Ts + Tm)$ and $\alpha,\beta,\beta/(\alpha,\beta,\beta + \alpha,\alpha,\alpha) C_{29}$ steranes versus $DH/(DH + NM)$, illustrating the maturity variation in the oils from the Tampen Spur (for key to compound labels see Chapter 4.7). Straight dotted line links the oils from the Snorre Field.

The maturity of the oils within the Snorre Field (part of the oil population **III**) increases from the south to the north (see straight dotted lines in the diagrams of Figure 5.1.14). This suggests that the Lunde Formation reservoir (34/4-6) in the northern part of the field drains a deeper and more mature part of the source rock kitchen than the Statfjord Formation reservoir in the southern part of the field, as described by Horstad et al. (1995). These authors concluded from their study of the Tampen Spur area that the Snorre Field was filled via at least two routes, one in the southwest charging the Statfjord Formation and one in the northwest charging the Lunde Formation.

The oils from the Statfjord Øst oil population **IV** have the lowest maturity.

5.1.2.3 Conclusions

Several of the oil fields in the Tampen Spur lie adjacent to multiple source kitchens and could have been filled from more than one direction. The GC-FID and GC-MS analyses reveal that the oils to the south of the Tampen Spur (Rimfaks, Gullfaks Sør and Gullfaks Gamma) are sourced from the Heather Formation or are at least mixtures containing oils from the Heather and the Draupne Formations. These oils are more mature than most of the other oils within the Tampen Spur.

Four oil populations were differentiated in the Tampen Spur. The Visund oil population comprises two mature oils from the Visund Field and the eastern part of the Gullfaks Field. This group is distinguishable from the other groups by the lowest relative 28,30-*dinor*-17 α ,18 α ,21 β -hopane concentrations and relatively high pristane/phytane ratios. These characteristics probably reflect a contribution of oils sourced from the terrestrially influenced Heather Formation.

The oils in the Statfjord Nord population, located in the reservoirs of the Statfjord Nord Field and Vigdis West Field, also have a higher maturity than those in the two groups described hereafter, this being manifest in the moderate DH/(DH + 30NM) ratios. The oil from well 34/10-34 has a similar relative 28,30-*dinor*-17 α ,18 α ,21 β -hopane concentration to the oils in the Statfjord Nord group but appears to be less mature. This oil is suggested to be sourced locally and thus genetically different from the Statfjord Nord population.

The Snorre Field oil population includes oils from the Vigdis East Field and from well 34/7-23A. These oils are characterised by the highest concentrations of 28,30-

dinor-17 α ,18 α ,21 β -hopane, with DNH/30NH ratios between 0.94 and 1.01. An increase in maturity was observed from the south to the north within the Snorre Field, the most mature oil being that from well 34/4-6 (Lunde Formation).

The Statfjord Øst oil population is comprised of oils from the Brent Group in the Statfjord, Tordis, Tordis Øst, H-Sentral and Statfjord Øst Fields, the oils from wells 34/7-16 (DST.2) and 34/7-10, and those from the Gullfaks Field (with the exception of the oil from well 34/10-7). This oil population is characterised by intermediate values for the 28,30DNH/30NH ratio, between 0.65 and 0.82. Mixing of oils from the Statfjord Nord oil population with oils from the Snorre Field oil population would result in a composition similar to those observed for oils of the Statfjord Øst oil population. As the oils in these three areas migrate towards the same apex in the central part of block 34/7, it is difficult to elucidate the migration paths in this area.

5.1.3 Gullfaks Field – Crude Oils

The Gullfaks Field, a part of the Tampen Spur, is a good example of lateral variability in the degree of petroleum biodegradation in a reservoir. The most severe biodegradation has taken place within the uneroded Brent Group sediments in the western part of the field. The oil sample suite from the Gullfaks Field was used to investigate the effect of biodegradation on heterocompound geochemistry.

5.1.3.1 Bulk organic geochemical characteristics

Whole-oil characteristics

The whole-oil gas chromatograms of the variably degraded oils from the Gullfaks Field demonstrate the classical systematic removal of *n*-alkanes with increasing degree of biodegradation (Appendix 2). A detailed discussion of the direction of increasing biodegradation and differences in the composition of the crude oils within the Gullfaks Field will be given in the following sections.

Gross compound composition

The triangular plot in Figure 5.1.15 shows the composition of the oils from the Gullfaks Field in terms of the relative abundance of saturated and aromatic hydrocarbons and NSO compounds. The variation in gross compound composition is consistent with the influence of biological degradation increasing on going from east (e.g., well 34/10-9) of the field to west (e.g., well 34/10-3). The oil sample from the easternmost part of the Gullfaks Field (well 34/10-7) clearly contains higher amounts of saturated hydrocarbons. As the composition of oils depends on maturity and facies as well as degree of biodegradation, it is suggested that the oil from the easternmost part of Gullfaks is sourced from the Visund Field, located to the northeast, via fill-spill, as discussed in Chapter 5.1.2.2 and shown in Figure 5.1.12 in relation to the pristane to phytane and 28,30-*dinor*-17 α ,18 α ,21 β -hopane to 30-*nor*-17 α -hopane ratios.

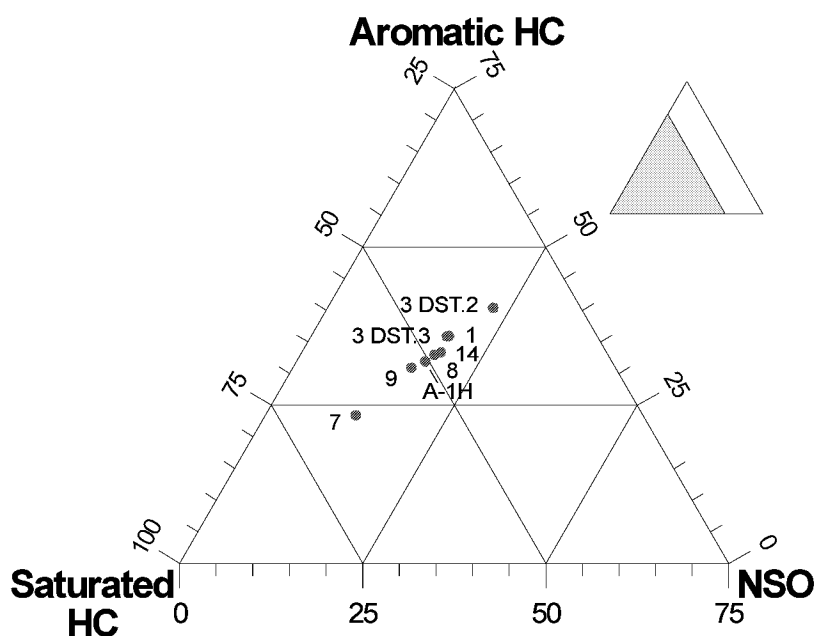


Fig. 5.1.15: Ternary diagram showing the gross composition (saturated and aromatic hydrocarbons, NSO compounds) of the crude oils from the Gullfaks Field (numbers denote the wells within the oil field)

Figure 5.1.16 shows the relative abundance of the different NSO compound class fractions versus the phytane to *n*-octadecane ratio. The phytane to *n*-octadecane and pristane to *n*-heptadecane ratios are good parameters to demonstrate biodegradation within the Gullfaks Field, as will be discussed in the following section. Both ratios decrease with increasing degree of biodegradation. The proportion of the high-polarity NSO fraction increases with increasing phytane/*n*-octadecane ratio up to a value of 4.5,

after which there is a decrease. It is difficult to explain the apparent removal of the high-polarity compounds in the highly degraded oils. The unusually low content of the medium- and high-polarity fraction, and the low content of the low-polarity fraction in the oil where phytane : *n*-octadecane = 4.5 suggests that there may have been a problem with analytical separation of this sample. An expected increase in the amounts of the acid fractions with increasing biodegradation was not observed. In addition, no trend is discernible for the relative abundances of the low- and medium-polarity fractions or of the base fraction.

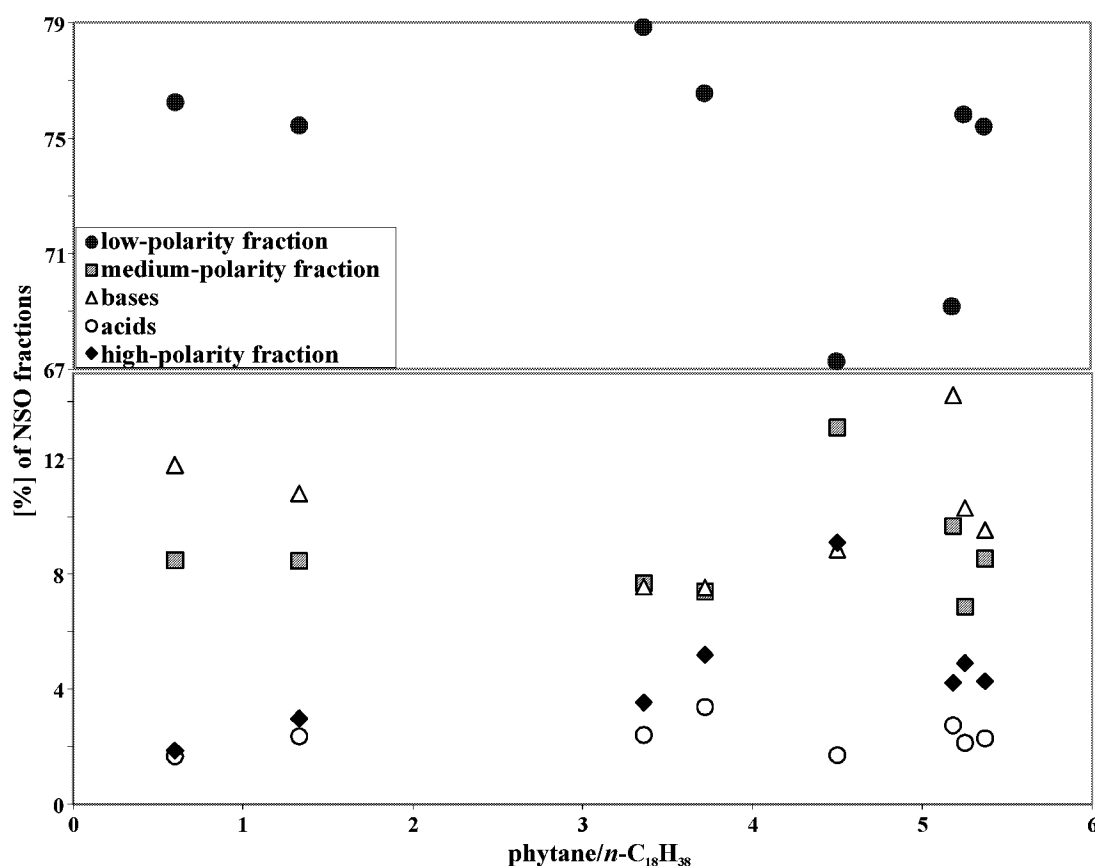


Fig. 5.1.16: Gravimetric composition of the heterocompound fractions of the biodegradation suite of oils from the Gullfaks Field. The ratio phytane to *n*-octadecane is used to indicate the degree of biodegradation.

API gravity

Biodegradation reduces the API gravity of an oil and increases the content of sulfur and other heteroatoms by selective removal of saturated and aromatic hydrocarbons compared to NSO compounds and asphaltenes. This effect is seen in Figure 5.1.17. The plots of the two affected biodegradation markers, phytane to *n*-octadecane ratio and the

sum of *n*-alkanes, against the API gravity show that the first ratio increases with decreasing API gravity whereas the second one decreases with decreasing API gravity. The API gravity of 37.2° for the oil from well 34/10-7 is significantly higher than those of the other oils. The large difference in API gravity between this oil and the only slightly biodegraded oil from well 34/10-9 could reflect mixing with oil from another oil family with higher maturity and different facies. As described in Chapter 5.1.2.2, the biomarker signature of this oil is similar to that of the oil from the Visund Field. Therefore, it is suggested that this oil reservoir is filled from the north-east. This is in accordance with fill-spill routes proposed by Horstad et al. (1995).

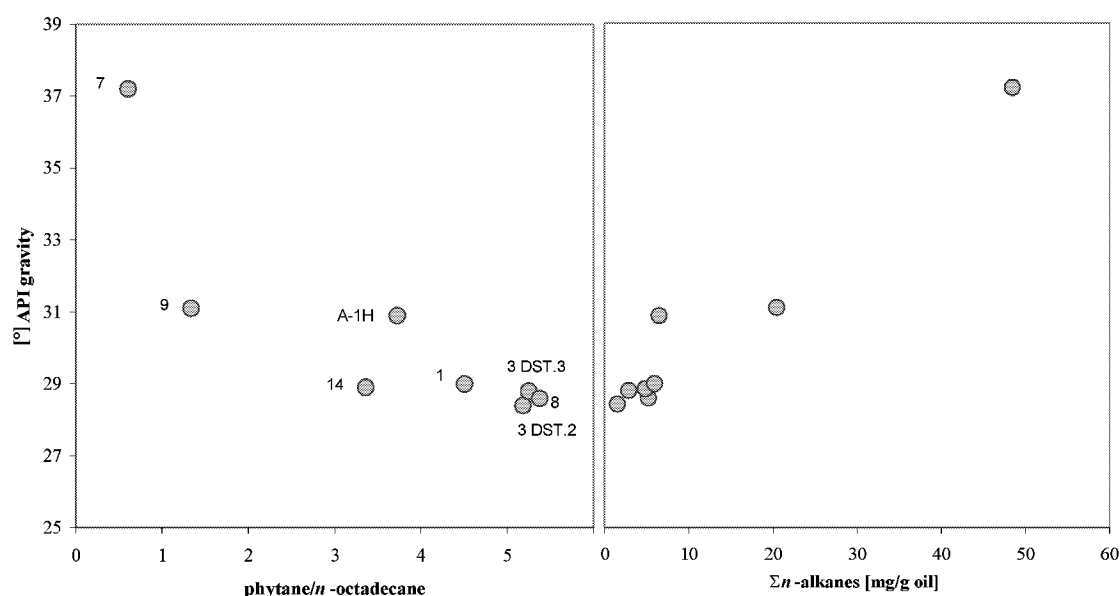


Fig. 5.1.17: Plots of API gravity versus two biodegradation parameters, the phytane to *n*-octadecane ratio and the sum of the *n*-alkanes.

5.1.3.2 Maturity and facies assessment

Alkanes

There is still some debate on the exact order in which different compounds are removed from crude oils during biological degradation but most studies seem to arrive at more or less the same degradation sequence, particularly for the hydrocarbons (e.g. Peters and Moldowan, 1993, p. 252ff.). Short-chain *n*-alkanes tend to be removed faster than longer-chain *n*-alkanes, which in turn are removed faster than branched and isoprenoid hydrocarbons. Biological markers are very resistant to biodegradation and will only be affected at severe stages of alteration. From comparison with several studies of biological degradation reported in the literature (e.g. Bailey et al., 1973a,b;

Jobson et al., 1979; Connan, 1984), it is concluded that the systematic decrease in the absolute amount of *n*-alkanes across the Gullfaks Field is due to their selective removal by biological degradation.

Horstad et al. (1990) analysed 226 reservoir core extracts and 23 drill stem test (DST) and repeat formation test (RFT) oil samples from the Gullfaks Field. They concluded that the best way to monitor the degree of biological degradation was by determination of the quantitative amounts of *n*-alkanes. They observed a systematic trend in the variation of the *n*-alkane concentration ($\Sigma n\text{-C}_9\text{-}n\text{-C}_{34}$) within the Brent Group, from 56.7 mg/g oil in the eastern part of the reservoir to 13.3 mg/g oil in the western part. The

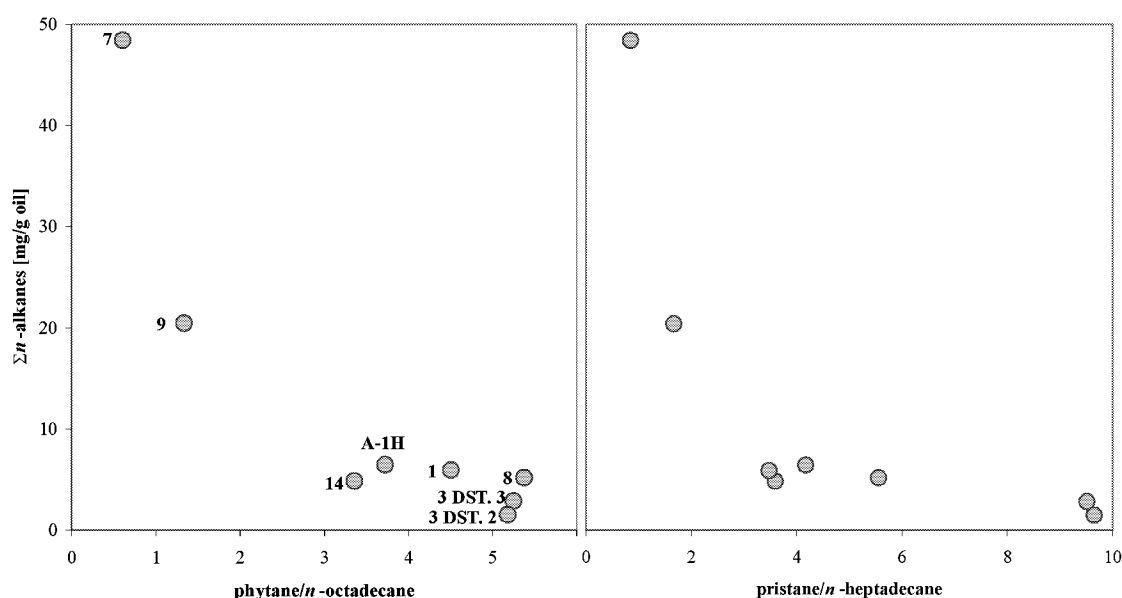


Fig. 5.1.18: Plots illustrating the effect of biodegradation by the absolute abundance of the *n*-alkanes.

absolute concentration of *n*-alkanes was found to be even higher in petroleum reservoirs within the Cook and Statfjord Formations further east (see Figure 3.6); this petroleum is described as belonging to another population, although of very similar composition. Horstad et al. (1990) concluded that after emplacement, the petroleum in the Brent Group, and to a lesser extent the petroleum in the Cook and Statfjord Formations, were degraded by aerobic bacteria. The oxygen and nutrient supply was from the west, resulting in a gradient in the extent of biological degradation decreasing from west to east.

The same trend was observed in the current study. The *n*-alkane concentrations ($\Sigma n\text{-C}_{10}\text{-}n\text{-C}_{38}$) decrease from 48.4 mg/g oil in the eastern part of the Gullfaks Field to only 1.5 mg/g oil in the western part, as illustrated in Figure 5.1.18. The three gas

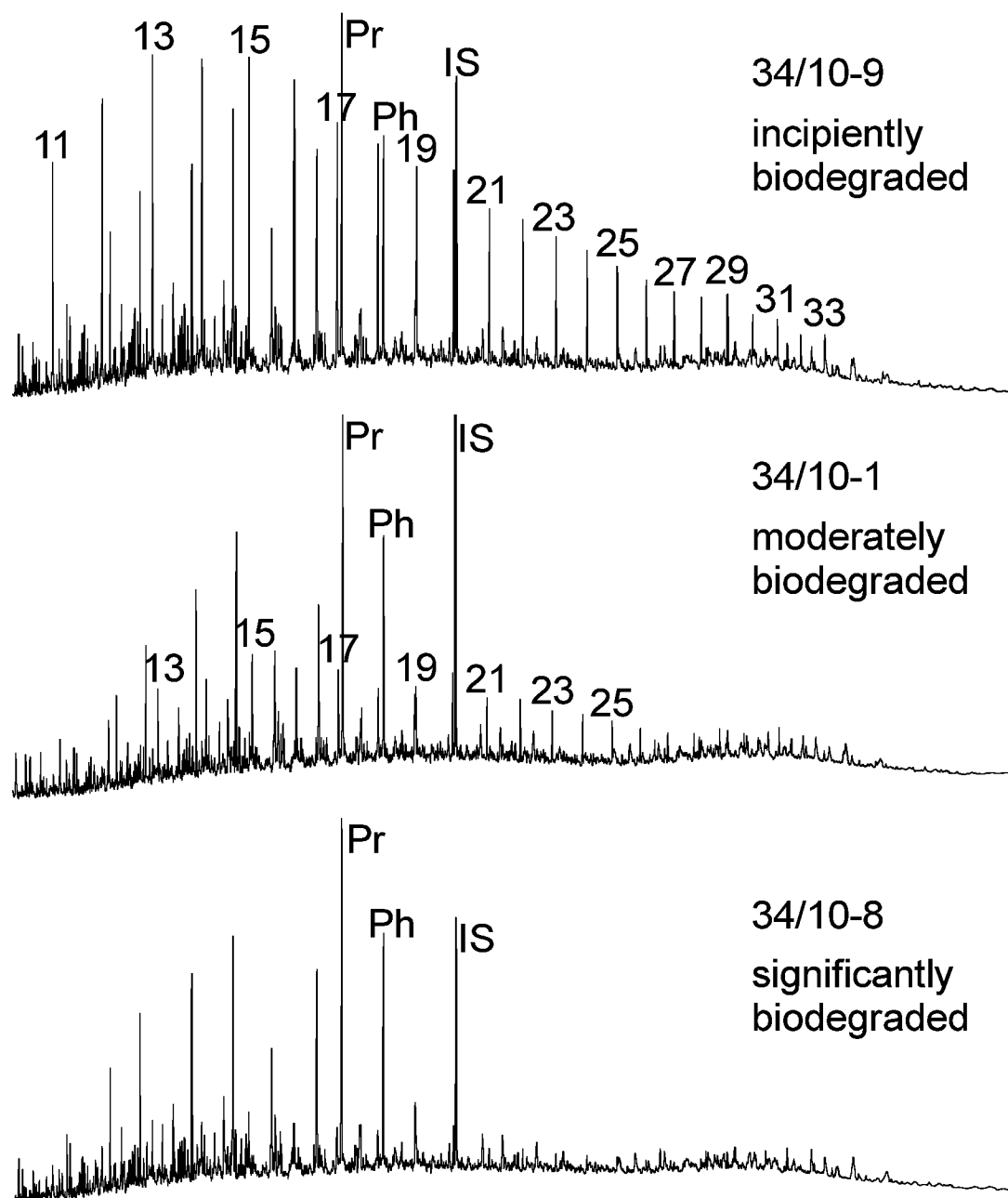


Fig. 5.1.19: Gas chromatograms of saturated hydrocarbon fractions of the oils from the Gullfaks Field showing the variation in the degree of biodegradation.

chromatograms shown in Figure 5.1.19 illustrate the sequence of biological degradation of the oils within the Gullfaks Field. Although the oils are clearly differently affected by biodegradation, the extent of biodegradation ranges only from “non-degraded” to level three on the Peters and Moldowan (1993) scale of degradation, as shown in Table 5.1.1.

Sample	34/10-1	34/10-3(2)	34/10-3(3)	34/10-7	34/10-8	34/10-9	34/10-14	34/10-A-1H
Degree of biodegradation	3	3	3	0	3	1	2	2

Tab. 5.1.1: Degree of biodegradation of the oils from the Gullfaks Field, after scale of Peters and Moldowan (1993).

Isoprenoids

The systematic removal of *n*-alkanes during biodegradation can also be expressed by the isoprenoid to *n*-alkane ratios (i.e. pristane/*n*-C₁₇ and phytane/*n*-C₁₈) for the oils within the Gullfaks Field (Horstad et al., 1990). As illustrated in Figure 5.1.20 the isoprenoid to *n*-alkane ratios increase with increasing biodegradation, up to values of 10 for pristane : *n*-heptadecane and values of 6 for phytane : *n*-octadecane. With the exception of the significantly biodegraded oil from well 34/10-8 which contains the highest concentrations of pristane and phytane, the oils also show a systematic removal

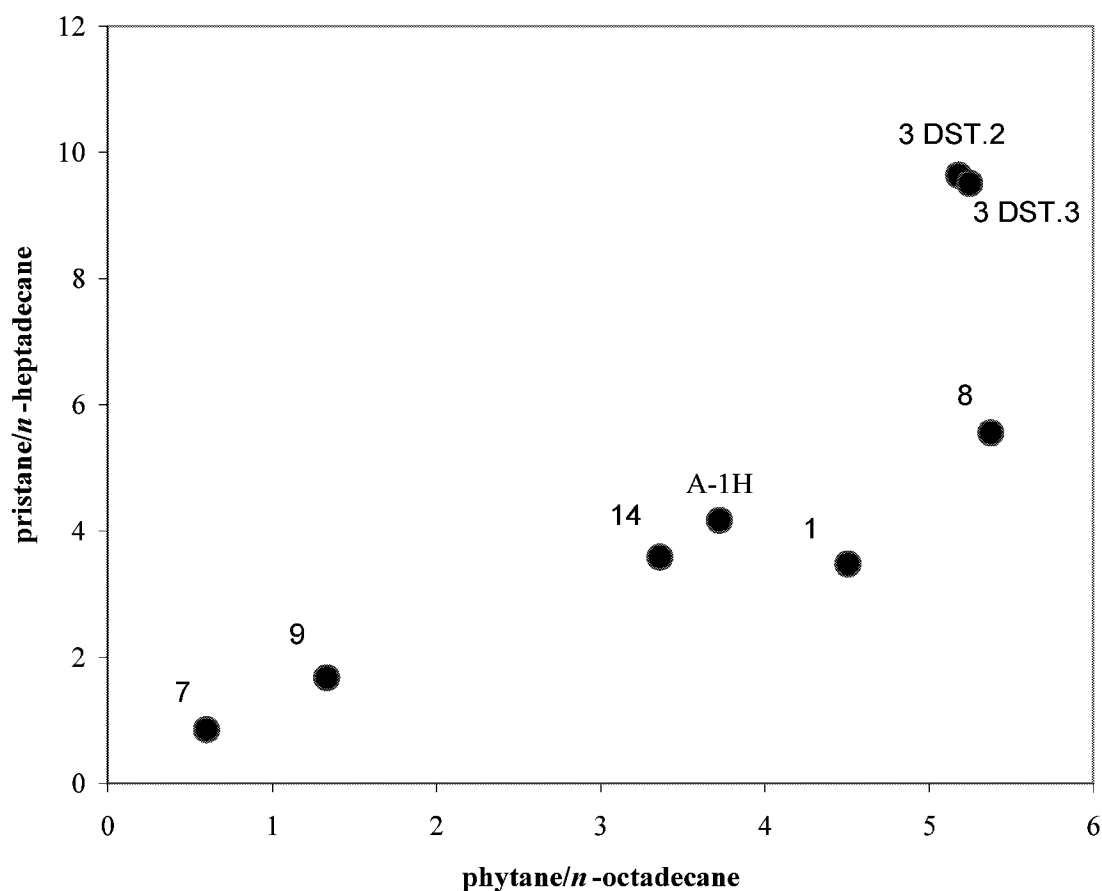


Fig. 5.1.20: The cross plot of pristane to *n*-heptadecane versus phytane to *n*-octadecane for oils from the Gullfaks Field, illustrating the variation in degree of biodegradation.

of pristane and phytane, although at a slower rate than that observed for the removal of *n*-alkanes.

The pristane to phytane ratio for most of the oils from Gullfaks were in the range 1.42 to 1.50, the exception being the easternmost oil from well 34/10-7 with a clearly higher ratio of 1.67. This demonstrates the similarity of the oils within the Brent Group, with a ratio typical for oils sourced from the Draupne Formation, and a different oil population in the easternmost part of the Gullfaks Field. The latter oil, from well 34/10-7, probably has mixed sources including the more terrestrial Heather Formation, as described above and by Horstad et al. (1995).

Biomarkers - Facies

Based on GC-MS analyses of the saturated hydrocarbon fractions, Horstad et al. (1990) distinguished two petroleum populations within their sample set from the Gullfaks Field: an early- to moderately-mature population present in the Brent Group in the western part of the oil field, and a slightly more mature population within the Cook, Statfjord and Lunde Formations in the eastern part of the oil field. The two populations show slight differences in the relative distribution of $5\alpha,14\beta,17\beta$ -cholestanes in the petroleum. Although there was considerable scatter in the data set, samples from the Brent Group reservoir generally contained less 24-methyl- $5\alpha,14\beta,17\beta$ -cholestanes (29-32% C_{28} steranes) than samples from the Cook, Statfjord and Lunde Formation (32-35% C_{28} steranes). The presence of two petroleum populations was also supported by the 28,30-*dinor*- $17\alpha,18\alpha,21\beta$ -hopane/30-*nor*- $17\alpha,21\beta$ -hopane (DNH/30NH) ratio. Within the Brent Group this ratio varied from 0.52 to 0.64, whereas within the Cook and Statfjord Formations further east the ratio ranged from 0.44 to 0.49.

The results of the current study are in accordance with the observations of Horstad et al. (1990). The DNH/30NH ratios for the majority of samples were in the range 0.65 to 0.81. Again, the exception was the oil from well 34/10-7, with a DNH/NH ratio of 0.52. This oil has a pristane to phytane ratio of 1.67, whereas all of the other oils have lower isoprenoid ratios, between 1.42 and 1.50.

Biomarkers - Maturity

Since the generation and expulsion of liquid petroleum from a source rock occurs over a certain depth and temperature range (typically 50°C at any location), a petroleum reservoir should receive more and more mature petroleum as it is filled from a continuously subsiding source rock basin, providing it remains in communication with the source rock (Horstad et al., 1990). Thus, if a reservoir is filled from one end in a sequential manner, as proposed by England et al. (1987), the most mature petroleum in the reservoir should be located nearest to the source rock basin or probable filling point (England et al., 1987; England and Mackenzie, 1989; Larter et al., 1990). However, given a certain relationship between the reservoir extension and elapsed time since filling, diffusion tends to homogenise the petroleum composition and destroy compositional gradients in the reservoir. This will occur on a time scale proportional to the square of the length of the petroleum column, as suggested by Horstad et al. (1990) and Karlsen and Larter (1991).

The relatively small maturity gradient across the Gullfaks Field observed by Horstad et al. (1990) is consistent with an earlier hypothesis in which the Gullfaks system was partially open during filling, the present gradient thus reflecting a relatively late-stage maturity window (the quantitatively most significant part) in the evolution of the source rock basin. However, it is also possible that the Late Cretaceous-Early Tertiary filling time of the reservoir allowed a significant amount of diffusion and lateral mixing of the petroleum column resulting in diminished gradients.

Star diagrams are multivariate plots in polar co-ordinates which can be used to depict the chemical compositions of oil and water samples from reservoirs. Whereas their use in organic geochemistry has been restricted to light hydrocarbons and branched and monocyclic alkanes (e.g. Slentz, 1981; Hwang et al., 1994; Halpern, 1995; Magnier and Huc, 1995; Wever, 2000), the star diagrams are applied here to differentiate between oil families of the Gullfaks Field using biomarkers. The star diagram in Figure 5.1.21 shows different facies- and maturity-related biomarker parameters for the biodegradation sequence of oils from the Gullfaks Field. This diagram reveals that the easternmost oil of the Gullfaks Field, from well 34/10-7, clearly contains a different biomarker distribution, reflected especially by the DNH/NH, Ts/(Ts+Tm) and DH/NH ratios. These parameters imply a different facies and higher maturity for this oil compared to the other oils from the Brent Group. The 28,30-*dinor*-17 α ,18 α ,21 β -hopane

to 30-*nor*-17 α ,21 β -hopane ratios for the Brent Group oils are in the range of 0.65 to 0.81, whereas the easternmost oil has a lower value (0.52) indicative of a different source facies. As the variation in the values within the Brent Group oils is not systematic (Horstad et al., 1990), any further interpretation is not possible.

The star diagram reveals the significantly higher maturity of the oil from well 34/10-7 compared to the other oils from the Gullfaks Field, especially by the Ts/(Ts+Tm) and the DH/30NH ratios. Most of the maturity-related parameters for the other Gullfaks oils were uniform and it was not possible to identify a tentative maturity gradient within the Brent Group using this limited sample set.

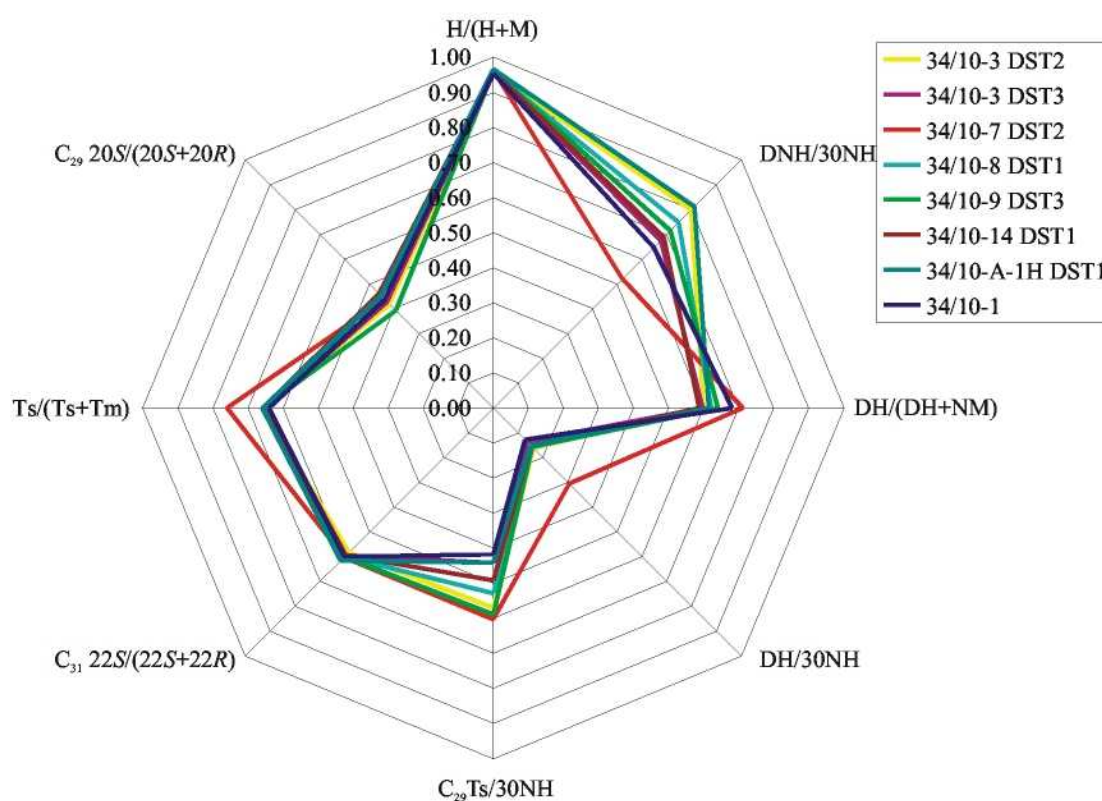


Fig. 5.1.21: Star diagram showing different biological marker parameters for the crude oils from the Gullfaks Field (for key to compound labels see Chapter 4.7).

5.1.3.3 Conclusions

The crude oils from the Gullfaks Field comprise a pronounced biodegradation sequence. This field has been investigated in detail in previous studies (e.g. Horstad et al., 1990) and the results of the present study are in good agreement with those reported earlier.

The different degrees of biodegradation of the Gullfaks oils are best illustrated by the removal of *n*-alkanes, seen in the reduction in absolute concentration of *n*-alkanes and in decreases in the pristane to *n*-heptadecane and phytane to *n*-octadecane ratios, and the API gravity. Within the Gullfaks Field the degree of biodegradation increases from the eastern to the western part of the field.

The expected variation in the amounts of the different heterocompound fractions with increasing biodegradation was not being observed.

The biological markers reveal that the oil from the easternmost part of the field (well 34/10-7) is of higher maturity (expressed by the highest Ts/(Ts+Tm) and 27-*nor*-15 α -methyl-17 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane ratios) and from a different facies (suggested by the low 28,30-*dinor*-17 α ,18 α ,21 β -hopane to 30-*nor*-17 α ,21 β -hopane and higher pristane to phytane ratios) in comparison to the other analysed oil samples from the Gullfaks Field. This suggests the presence of two different oil populations within the Gullfaks Field, with one filling direction from the west into the Brent Group and a second filling direction from the eastern side.

5.1.4 Central Graben – Crude Oils

Seven crude oils from the Central Graben, located in the southern part of the North Sea, were analysed in this section of the study. Some of the oils are unusual and of particular interest as regards for the occurrence and distribution of heterocompounds.

5.1.4.1 Bulk organic geochemical characteristics

Whole-oil characteristics

Two oils from the Fendris Field (15/12-5 and 15/12-6) and the oil from well 6/3-1 south of this field show similar whole-oil gas chromatograms, typical of undegraded, normally mature oils (Appendix 2). The oils from well 7/7-2, the Yme Field (9/2-1) and well 2/4-14 show a more mature hydrocarbon distribution pattern dominated by volatile components, whereas the GC-FID chromatogram of the oil from well 2/2-5 is clearly different being dominated by high concentrations of isoprenoids (*i*-C₁₄-*i*-C₂₀) but showing no signs of biodegradation (cf. oils from the Troll West Field and one oil from

the Snorre Field (34/7-10)). The oil from well 2/2-5 has been described as being sourced from a siltstone close to the Rotunda ammonite zone characterized by a high oil potential (TOC = 12%, S_2 = 80-100 mg HC/g rock) and which may have been deposited in a hypersaline environment related to salt piercement (Pancost et al., 2001; and personal information from Dr. Rolando di-Primio, Norsk Hydro).

Gross compound composition

The triangular plot in Figure 5.1.22 shows the relative abundance of saturated and aromatic hydrocarbons and NSO compounds and reveals the similarity between the oils from the northern part of the Central Graben (Fendris Field (15/12) and well 6/3-1). The atypical oil from well 2/2-5, despite the lack of *n*-alkanes, contains a high proportion of saturated hydrocarbons, reflecting its high content of isoprenoids. The relatively low abundance of NSO components (4.8%), a very high proportion of saturated hydrocarbons (84.1%) and a reservoir temperature of 165°C point to the oil from well 2/4-14 as being a highly mature fluid possibly resulting from in-reservoir oil cracking (Horsfield et al., 1992). Of the more ‘normal’ oils, that from the easternmost field, Yme (9/2-1), contains the lowest proportion of NSO compounds (12.2%) whereas the highest proportions of both NSO compounds (24.9%) and aromatic hydrocarbons (31.0%) were found in the oil from well 7/7-2 – the latter ostensibly reflecting a low maturity because evidence of biodegradation was not observed.

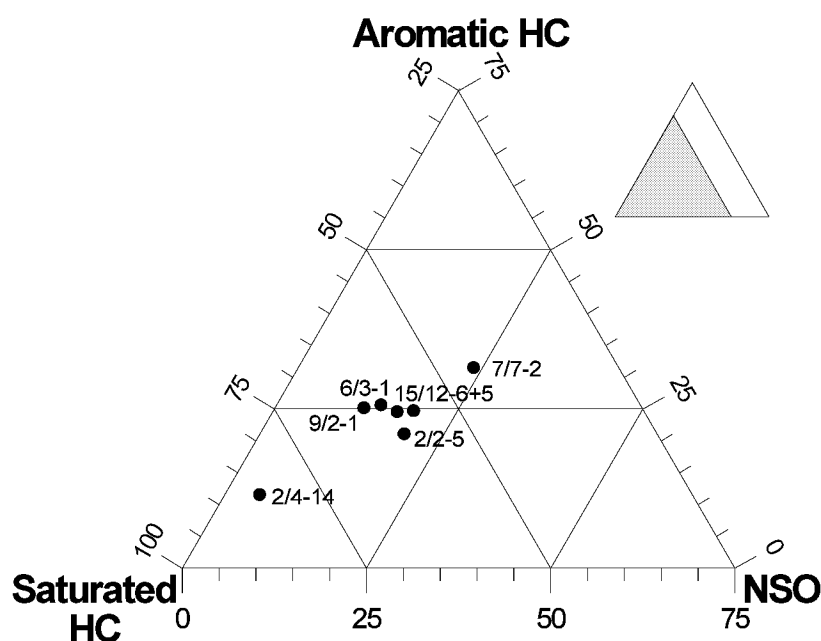


Fig. 5.1.22: Ternary diagram showing the gross composition (saturated and aromatic hydrocarbons, NSO compounds) of the crude oils from the Central Graben

Gross heterocompound composition

The heterocompound composition of the crude oils from the Central Graben depicted in Figure 5.1.23 shows that the highest abundances of low polar and medium polar compounds occur in the oils from wells 2/2-5 and 7/7-2. A slight increase in the abundance of acids is observed from the south to the north ($6/3-1 < 15/12-6 < 15/12-5$) within the northern part of the Central Graben whereas the two oils from the Fendris Field (also in the north) have the highest amounts of highly polar constituents. The low abundances of all polar fractions in the oil from well 2/4-14 indicate a high-maturity fluid.

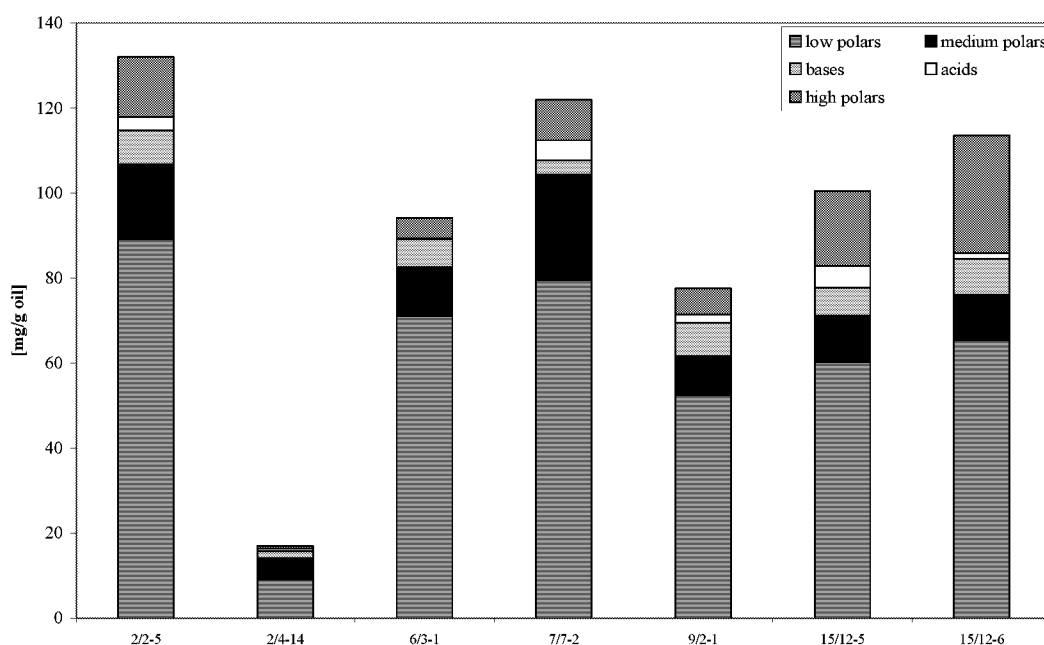


Fig. 5.1.23: Gravimetric composition of the heterocompound fractions of oils from the Central Graben

API gravity

It is well known that heavy oils are enriched in non-hydrocarbons, i.e. asphaltene and resin fractions, and that there is an inverse relationship between the stock tank API gravity and the non-hydrocarbon content of black oils (Tissot and Welte, 1984). The right-hand diagram in Figure 5.1.24 clearly illustrates this relationship between the proportion of NSO components in an oil and the API gravity. High abundances of NSO compounds result in low API gravity values; although this relationship often reflects

maturity variations, facies changes are also known to influence these parameters, as described, e.g., by Khavari-Khorasani et al. (1998).

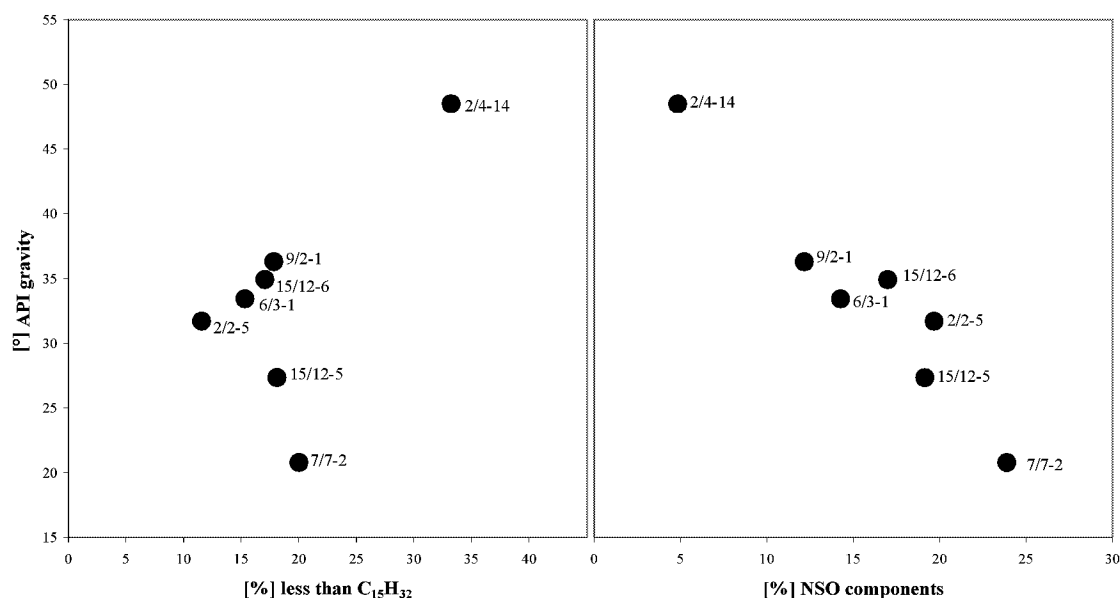


Fig. 5.1.24: Cross-plot of API gravity (calculated from density data) versus evaporative loss and the percentage of NSO components in the Central Graben oils

5.1.4.2 Maturity and facies assessment

Alkanes

With the exception of the oil from well 7/7-2 whose CPI value is 0.90, the crude oils from the Central Graben show no significant odd or even carbon number predominance of the long-chain *n*-alkanes (CPI = 1.02-1.08) (Fig. 5.1.25). The even carbon number predominance of the oil from well 7/7-2 may indicate a carbonate-influenced source rock (cf. Shimoyama and Johns, 1971; 1972), although such a rock type is rare on the Norwegian continental shelf.

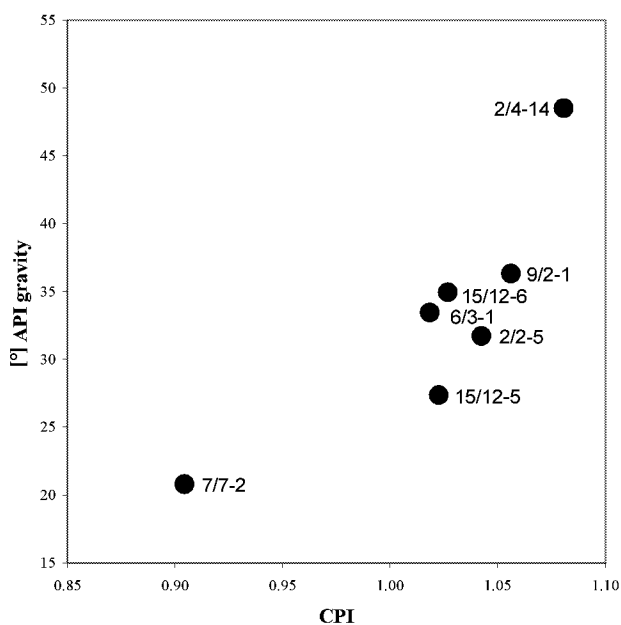


Fig. 5.1.25: Plot of API gravity versus CPI for the oils from the Central Graben

Isoprenoids

The logarithmic-scale cross-plot of pristane to *n*-heptadecane versus phytane to *n*-octadecane shows a fairly uniform composition for most of the oils from the Central Graben (Fig. 5.2.26). The high-maturity, *n*-alkane dominated fluid from well 2/4-14 exhibits the lowest isoprenoid/*n*-alkane ratios. The oil from well 2/2-5, enriched in isoprenoids as described above, gives ratios of 6.0 for pristane/*n*-heptadecane and 9.4 for phytane/*n*-octadecane.

The pristane to phytane ratios are between 1.32 and 1.54 for the oils from the northern and western part of the Central Graben and for the fluid from well 2/4-14 (see Appendix 3a). These values indicate a source in the Upper Jurassic Mandal and Farsund Formations which are the typical source rocks in this area (e.g. Fraser et al., 1993). Significantly different pristane to phytane ratios were found for the oils from wells 2/2-5 ($pr/ph = 0.72$) and 7/7-2 ($pr/ph = 0.98$). This indicates a different oil population sourced from a special zone within the Upper Jurassic,

especially for the oil from well 2/2-5, with the low pr/ph values (< 0.6) being typical of anoxic, commonly hypersaline environments (Peters and Moldowan, 1993, p. 150ff). In this regard, a general decrease in the pristane to phytane ratio in the Permian-age Kupferschiefer sequence, Germany, was interpreted by Schwark and Püttmann (1990) to indicate increasing paleosalinity. Taking this into account, together with personal information from Norsk Hydro Research indicating that photic zone anoxia and hypersalinity characterise the Rotunda ammonite zone, the oil from well 2/2-5 appears to have been generated by a hypersaline source rock. The other oil characterised by a low pristane to phytane ratio (well 7/7-2), is interpreted as being a mixed oil sourced from the Mandal/Farsund Formation and the hypersaline basin.

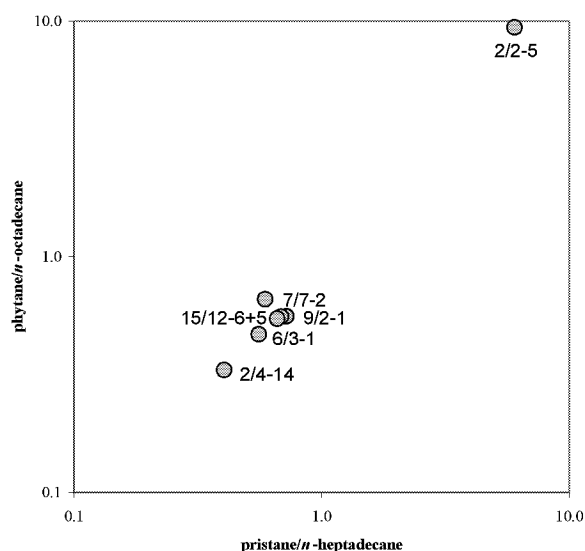


Fig. 5.1.26: Logarithmic scale cross-plot of pristane to *n*-heptadecane versus phytane to *n*-octadecane for the oils from the Central Graben

Biomarkers

Biomarkers were detected in all of the analysed oils from the Central Graben with the exception of the fluid from well 2/4-14. The oil from well 2/2-5 displays a high gammacerane index ($GI = \text{gammacerane}/17\alpha,21\beta\text{-hopane} \times 100$) of 25, a low diasterane/regular sterane ratio of 0.51, a low $Ts/(Ts+Tm)$ ratio of 0.44 and a low $DH/C_{29}Ts$ ratio of 0.46. All these parameter values support the idea (see above) that this oil was generated from a source rock deposited in a hypersaline anoxic environment, probably the siltstone close to the Rotunda ammonite zone in the Upper Jurassic. The MID mass chromatogram in Figure 5.1.27 shows the hopane distribution pattern for the oil from well 2/2-5, with unusually high amounts of gammacerane (G) compared with typical North Sea oils (see e.g. Figure 4.3).

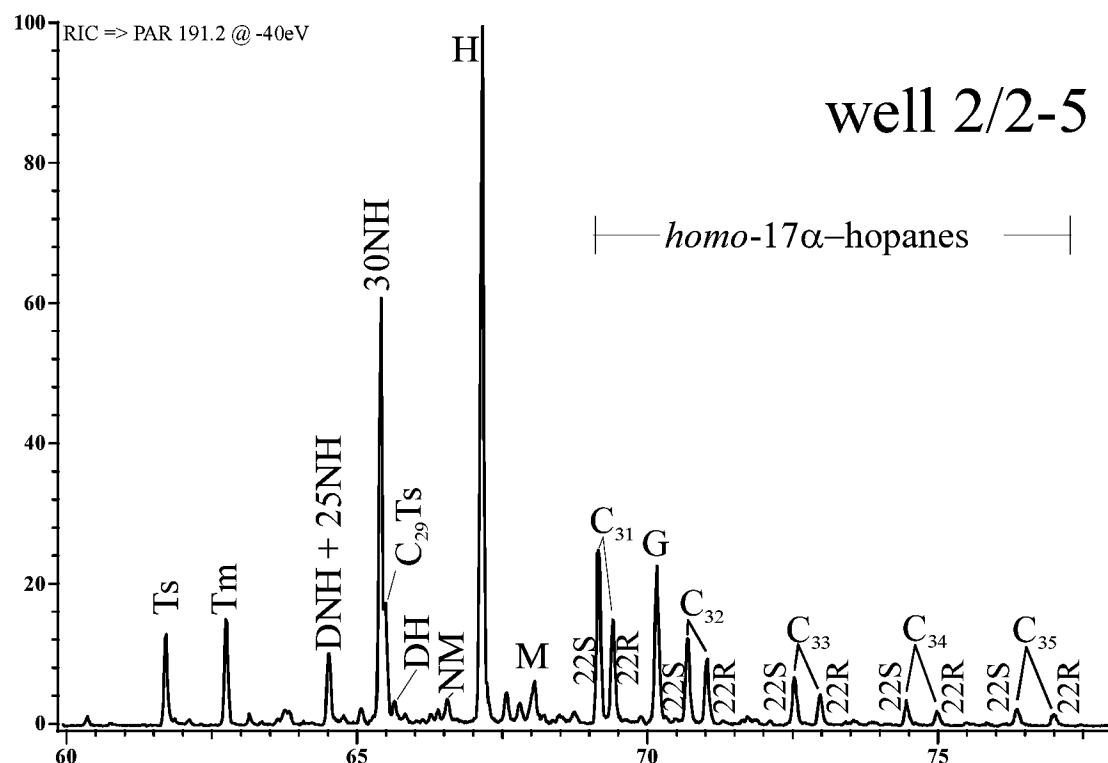


Fig.5.1.27: MID mass chromatogram (m/z 191) for hopanes in the saturated hydrocarbon fraction of the oil from well 2/2-5 (for key to labels see Chapter 4.7).

The second conspicuously atypical crude oil (well 7/7-2) of the sample set is also slightly enriched in gammacerane ($GI = 3.6$), has a low $Ts/(Ts+Tm)$ ratio of 0.55 and a C_{35} homohopane index of 13.4. Also taking into account the low CPI value and the pristane/phytane ratio observed for this sample (see above), a mixed oil co-sourced by the Upper Jurassic Mandal/Farsund Formation and the hypersaline siltstone is indicated.

However, the oil from 7/7-2 also has a high DNH/30NH ratio of 1.08 (cf. all other oils from the Central Graben, whose values are <0.22) and a slightly lower proportion of $5\alpha,14\beta,17\beta$ -24-ethylcholestane (*S+R*) (37%) compared to the other oils, suggesting a different, more strongly marine influence. Indeed, the relatively high abundance of $28,30$ -*dinor*- $17\alpha,18\alpha,21\beta$ -hopane suggests that a simple mixing model cannot fully explain the biomarker composition. The oil from the Yme Field (9/2-1) situated in the easternmost part of the Central Graben shows a similar biomarker distribution pattern to those for the oils from the Fendris Field (15/12) and from well 6/3-1. This reflects the similar maturity and facies characteristics of these oils which are generated from the Upper Jurassic Mandal/Farsund Formation.

5.1.4.3 Conclusions

Seven crude oils from the Central Graben have been investigated. The oil from well 2/4-14 is characterised as being very mature. The oils from the Fendris Field and from wells 6/3-1 and 9/2-1 were generated from similar facies of the Upper Jurassic Mandal/Farsund Formation and have reached similar maturity levels. The oil from well 2/2-5 shows a clearly different composition from the rest of the oils. High abundances of isoprenoids as well as high amounts of gammacerane ($GI = 25$) and a low pristane to phytane ratio of 0.72 point to a hypersaline anoxic depositional environment for the source rock which is considered to be the siltstone close to the Rotunda ammonite zone in the Upper Jurassic. Biomarker data reveal that the oil from well 2/2-5 has a lower maturity than the other oils in the Central Graben.

Many biological marker parameters of the oil from well 7/7-2 indicate a mixed oil derived from the two different source rocks described above. This is supported by a low pristane to phytane ratio and a slightly higher gammacerane index compared to most of the oils. However, a high DNH/NH ratio and a slightly lower proportion of $5\alpha,14\beta,17\beta$ -24-ethylcholestane (*S+R*) as compared to all other oils is remarkable and indicates an overall more marine influence.

5.1.5 Haltenbanken and Barents Sea - Crude Oils

Twenty-three crude oils from Haltenbanken and three crude oils from the Barents Sea area were analysed in this part of the study. Thirteen of the (partly biodegraded) Haltenbanken oils are from wells in the Heidrun Field and three are from wells in the Midgard Field. The seven remaining oil samples are from different locations within the Haltenbanken area.

5.1.5.1 Bulk organic geochemical characteristics

The whole-oil gas chromatograms in Appendix 2 show a wide variety of 'fingerprints'. Biodegradation has probably severely affected three Heidrun Field oils from well 6508/8-4, two oils from well 65507/7-2 and the oil from well 6507/7-6 (DST.1), this being based on the depletion of *n*-alkanes and the presence of a 'hump' in the chromatograms. Other oils from the Heidrun Field seem to be moderately biodegraded (oils from wells 6507/7-3 and 6507/7-6 (DST.2)). Moderate biodegradation evident from a low 'hump' was also observed for the oils from wells 6507/7-2 (DST.4A), 6507/7-5 (DST.1) and 6507/7-8 (DST.1), whereas the two oils from wells 6507/7-5 (DST.2) and 6507/7-8 (DST.2) show no 'hump' and are therefore considered undegraded. Whitley (1992) suggested that the petroleum column in the central well (6507/7-2) of the Heidrun Field (Fig. 3.7) was biodegraded when the reservoir was c. 1000 m shallower than today, and that this biodegraded fluid was then mixed with oil arriving later. The extensively biodegraded oils from well 6507/7-2 and the significant 'hump' in the chromatograms of the oils from the Heidrun flank wells (e.g. 6507/7-5, 6507/7-3 and 6507/7-8) may reflect the fact that the reservoir compartment penetrated by well 6507/7-2 did not receive large volumes of fresh non-biodegraded oil from the potential source basin to the southwest (Karlsen et al., 1995). Non-biodegraded oil was probably more effectively mixed with biodegraded oil down-flank. The occurrence of variably biodegraded oils within the Heidrun Field probably also reflects the lack of intra-reservoir communication between different compartments, e.g. the central part of the structures penetrated by well 6507/7-2 may have been shielded or represent a dead end with respect to later arriving oil.

The whole-oil gas chromatograms of the oils from the Midgard Field (6507/11-3), Njord Field (6407/7-4), Trestakk (6406/3-2), Smørbukk (6506/11-2), Smørbukk Sør

(6506/12-3) and Alve Fields (6507/3-1), and one oil from the Barents Sea (well 7124/3-1) show distribution patterns dominated by short-chain *n*-alkanes typical of mature oils. An even carbon number predominance in the *n*-C₁₉ to *n*-C₂₆ range was observed for the oils from Smørbukk and Smørbukk Sør and may reflect a different facies from that of the other oils. This is in accordance with the observations made by Karlsen et al. (1995). This even carbon number predominance of the *n*-alkanes is known to occur in oils sourced from carbonate-influenced facies (Shimoyama and Johns, 1972).

Markedly different GC-FID distribution patterns were obtained for the oils from well 6406/11-1S and from the Snøhvit Field (well 7121/5-1), these being dominated by long-chain *n*-alkanes with a maximum at *n*-pentacosane. The chromatograms for these oils seem to be similar to those for the two oils from the Gullfaks Sør Field discussed in Chapter 5.1.2. The distribution pattern may reflect a greater contribution of terrestrial organic matter or, alternatively, they may indicate conventional oils from which the light ends have been stripped. The GC-FID chromatogram of the oil from the Draugen Field (6407/9-1) is typical of that obtained for a mature oil from which the short-chain *n*-alkanes have been stripped. The alkane distribution pattern for the oil from well 7120/1-2 is similar to that for the oil from well 6201/11-1, described in Chapter 5.1.1, with high abundances of pristane and phytane relative to the *n*-alkanes which could reflect an immature condensate.

Gross compound composition

The triangular plot of the relative abundance of the saturated and aromatic hydrocarbons and NSO compounds, shown in Figure 5.1.28 (for data see Appendix 1), reveals the wide variation in the composition of the oils from Haltenbanken and the Barents Sea.

The trend observed for many of the oils from the Heidrun Field reflects varying degrees of biological degradation, with the proportion of saturated hydrocarbons decreasing with increasing degradation. An exception is observed for the oil from Heidrun well 6507/8-4 (DST.4) in which NSO compounds were essentially absent. The whole oil chromatogram for this oil reveals that only light-end components (up to C₁₁, see Appendix 2) are present, suggesting that this oil may have undergone fractionation within the complicated reservoir system of the Heidrun Field. The oils and condensates from the Midgard Field and the Alve Field contain relatively low concentrations of

NSO compounds. Oils with high relative abundances of long-chain *n*-alkanes (Smørbukk, Smørbukk Sør, well 6406/11-1S, Njord, Alve, Midgard and Snøhvit) are typically most enriched in saturated hydrocarbons.

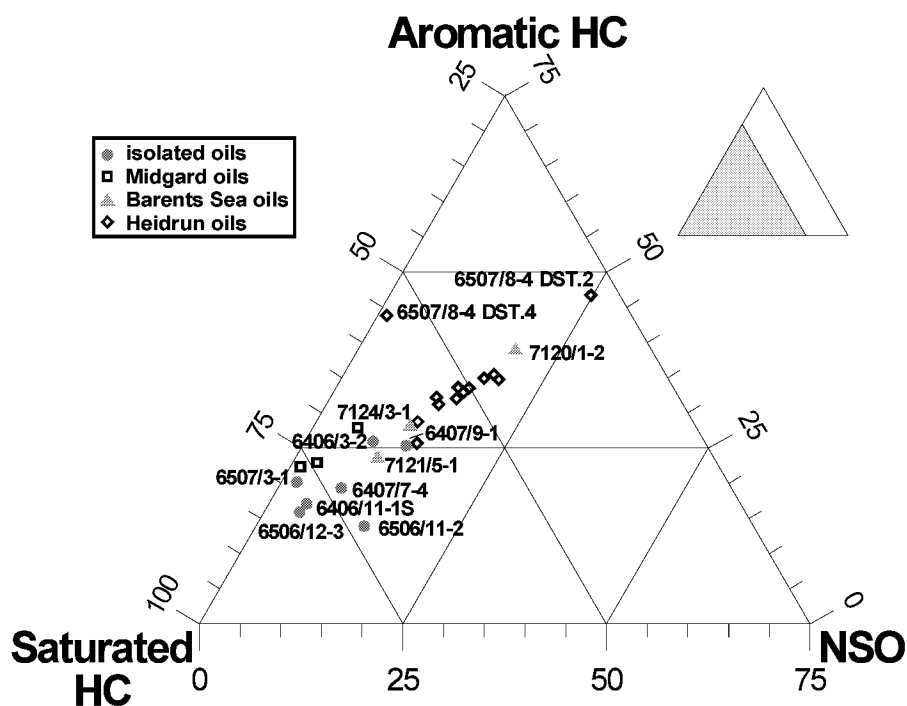


Fig. 5.1.28: Ternary diagram showing the gross composition (saturated and aromatic hydrocarbons, NSO compounds) of the crude oils from Haltenbanken and the Barents Sea

Gross heterocompound composition

The abundances of the different heterocompound fractions in the oils are shown graphically in Figure 5.1.29 (Heidrun oils) and 5.1.30 (Haltenbanken/Barents Sea oils). The oils from the Heidrun Field contained higher concentrations of acids than the other oils from offshore Norway. The most severely biodegraded oils from the Heidrun Field (wells 6507/8-4, 6507/7-2 (DST.2 and DST.3) and 6507/7-6 (DST.1)) contain the highest amounts of NSO components and are especially enriched in the low polar fraction. The oil from well 6507/8-4 (DST.4) contains exceptionally low amounts of NSO compounds, probably resulting from fractionation within the reservoir system.

In well 6507/11-3 in the Midgard Field, the amount of NSO compounds is lower in the deepest fluid (DST.1) than in the shallower oil (DST.3) due to a decrease in the amount of the low polar fraction. This observation also applies to most of the oils from the Heidrun Field and probably reflects fractionation in the field system.

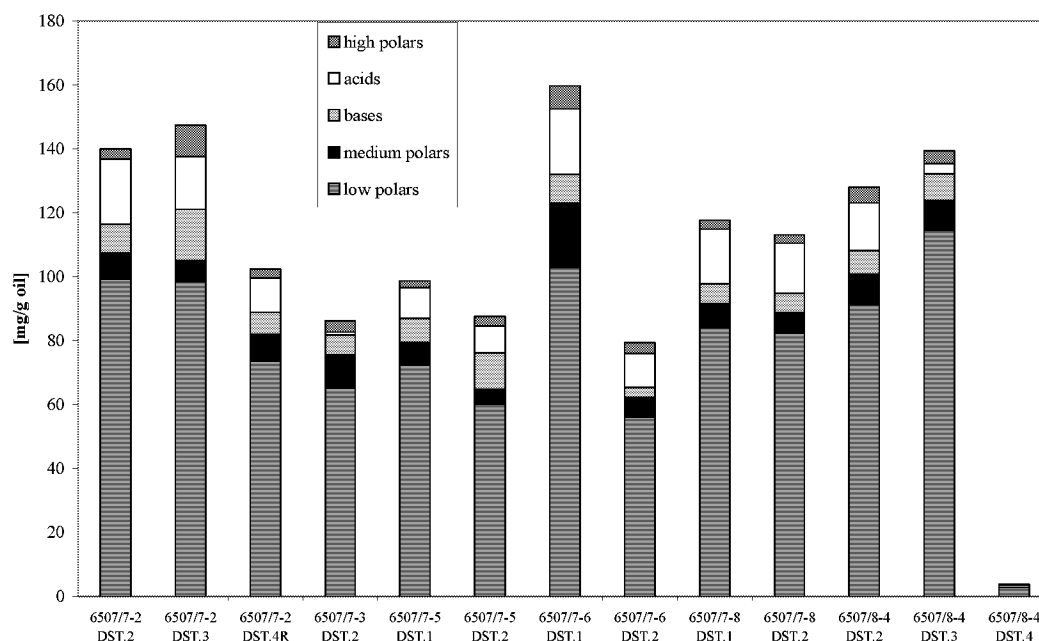


Fig. 5.1.29: Gravimetric composition of the heterocompound fraction of oils from the Heidrun field

Figure 5.1.30 shows that the mature condensates and oils from the Alve, Smørbukk Sør and Midgard Fields, and the probably immature condensate from well 6406/11-1S contain the lowest amounts of NSO compounds, as might be expected. Interestingly, the

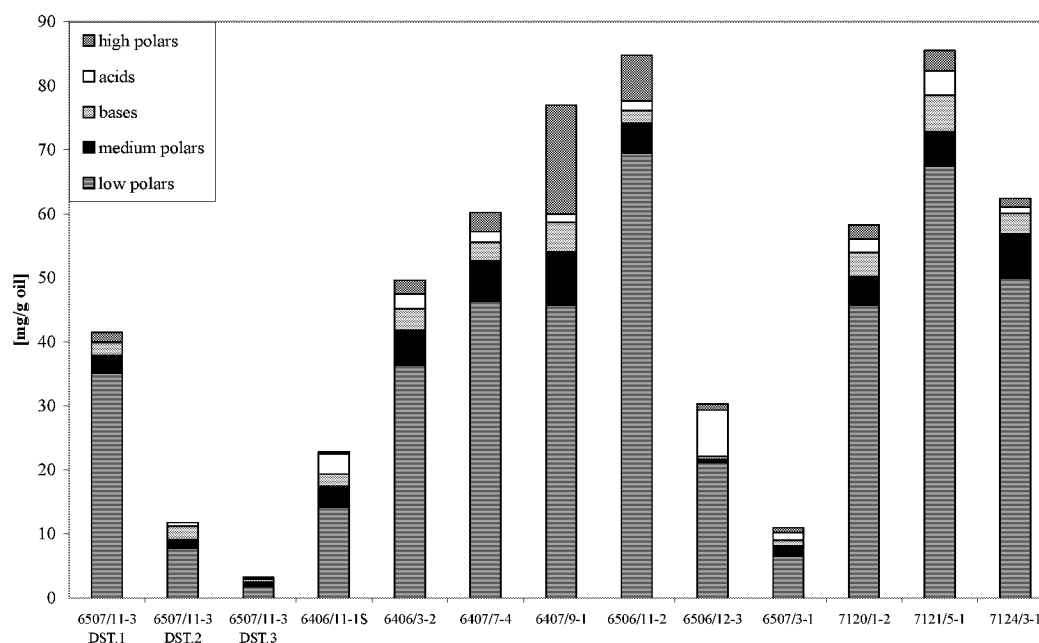


Fig. 5.1.30: Gravimetric composition of the heterocompound fractions of oils from Haltenbanken and the Barents Sea

condensates from the Smørbukk Sør Field and well 6406/11-1S are enriched in acids despite there being no indication of biological degradation. The highest concentrations of the low polar fraction were found in the oil from the Smørbukk Field and in the Snøhvit oil from the Barents Sea.

API gravity

The measurement of API gravity using specific gravity data was only possible for some of the oils from the Haltenbanken area due to limited sample availability. A classification of the fluids was made from the plot of API gravity versus evaporation loss (Figure 5.1.31). The high API gravity ($>35^\circ$) of the fluids from the Alve, Smørbukk and Smørbukk Sør reveal their condensate character and high maturity. The biodegraded oil

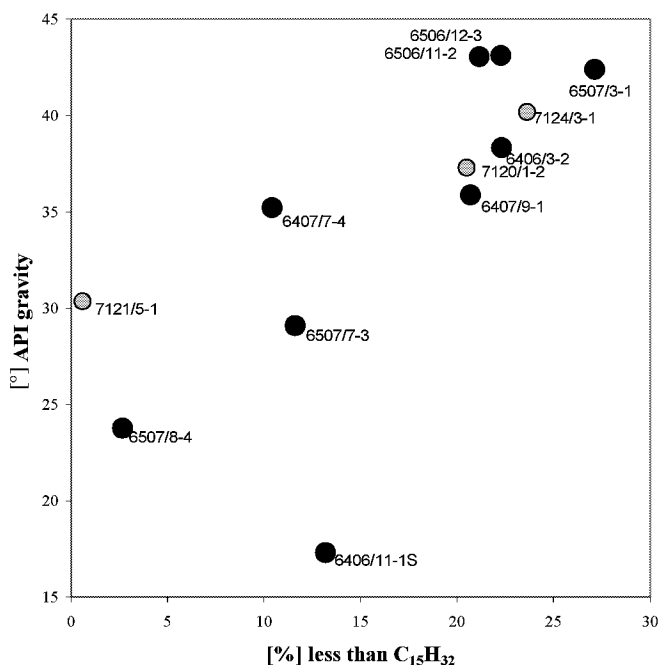


Fig. 5.1.31: API gravity versus evaporative loss for the Haltenbanken oils (black dots) and Barents Sea oils (grey dots)

from the Heidrun Field (6507/8-4), with an API gravity of 24° , is classed as a heavy oil. It is interesting that the oil from well 6406/11-1S has the lowest API gravity, only 17° . As the composition of this oil shows no evidence for biodegradation, it is assumed that such a low API gravity could reflect low maturity and/or a different source rock facies. The oil from the Snøhvit Field (7121/5-1) is classed as a medium gravity oil whereas the other two oils from the Barents Sea (7120/1-2 and 7124/3-1), with high API gravity, are classed as light oils.

5.1.5.2 Maturity and facies assessment

Alkanes

The CPI data (based on the *n*-alkanes from *n*-C₂₄ to *n*-C₃₂) for the oils from Haltenbanken and the Barents Sea are shown in Figure 5.1.32. The CPI values range from 0.98 to 1.12. The oils and condensates from the easternmost part of the Haltenbanken area (Alve, Midgard), from well 6406/11-1S and from the Snøhvit Field exhibit the highest odd carbon number predominance, possibly reflecting a different source and/or a lower maturity. The oils from the western part of the Haltenbanken area (Trestakk, Smørbukk) and also one oil from the Heidrun Field (well 6507/7-3) have the lowest CPI values which could reflect a slightly higher maturity than the other oils in the sample suite. Since the CPI range for these oils is very narrow, this parameter has only limited use in classification.

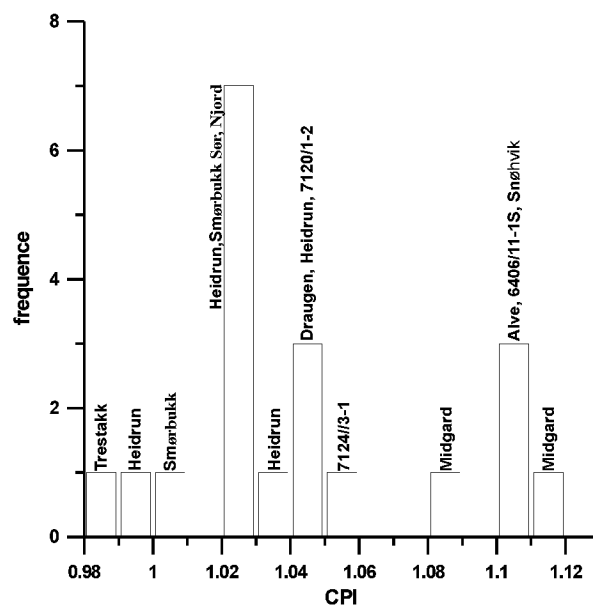


Fig. 5.1.32: Histogram illustrating the CPI values of oils from Haltenbanken and the Barents Sea

Pristane/*n*-C₁₇ and phytane/*n*-C₁₈

Figure 5.1.33 illustrates the variation in the pristane to *n*-heptadecane ratio versus the phytane to *n*-octadecane ratio for the oils from Haltenbanken and the Barents Sea. These ratios were determined for all of the studied oils with the exception of some oils from the Heidrun Field (6507/7-6 (DST.1), 6507/8-4 (DST.2, 3, 4)) which were totally depleted in *n*-alkanes because of biodegradation. High isoprenoid to *n*-alkane ratios were found for two oils from the Heidrun Field (well 7-2 (DST.2, 3)) and reflect biological degradation, but the highest ratios were observed for the oil from well 7120/1-2. This oil is apparently not biodegraded but it may be immature. The oils from the Alve, Midgard, Njord and Draugen Fields, in the eastern part of the Haltenbanken area, show a trend of a decrease in both ratios from the south to the north and again this

could reflect increasing maturity because none of the typical molecular indications of biodegradation are observed. These oils have higher pristane to *n*-heptadecane ratios than the oils from the western part of Haltenbanken (Trestakk, Smørbukk and Smørbukk Sør), indicating a more terrestrially-derived nature of the source rock organic matter. These two groups of oils are indicated by the trend lines in Figure 5.1.33. Karlsen et al. (1995) suggested that the former oil group (in the east) is related to a source rock deposited in a dysaerobic to anoxic proximal depositional environment whereas the second group, from the western part of the area, may be sourced by a more marine anoxic distal organic facies. The difference between the condensate and oil leg samples from the Midgard Field and fluids from the other fields has been suggested by Mo et al. (1989) to indicate that the petroleum in the Midgard Field is sourced mainly from the coal-bearing Åre Formation. Any contribution from the Spekk Formation was described to be of minor importance. The equivocal nature of the source of these two groups of oils is discussed later in relation to the biomarker and heterocompound distributions.

Most of the oils from the Heidrun Field have isoprenoid to *n*-alkane ratios

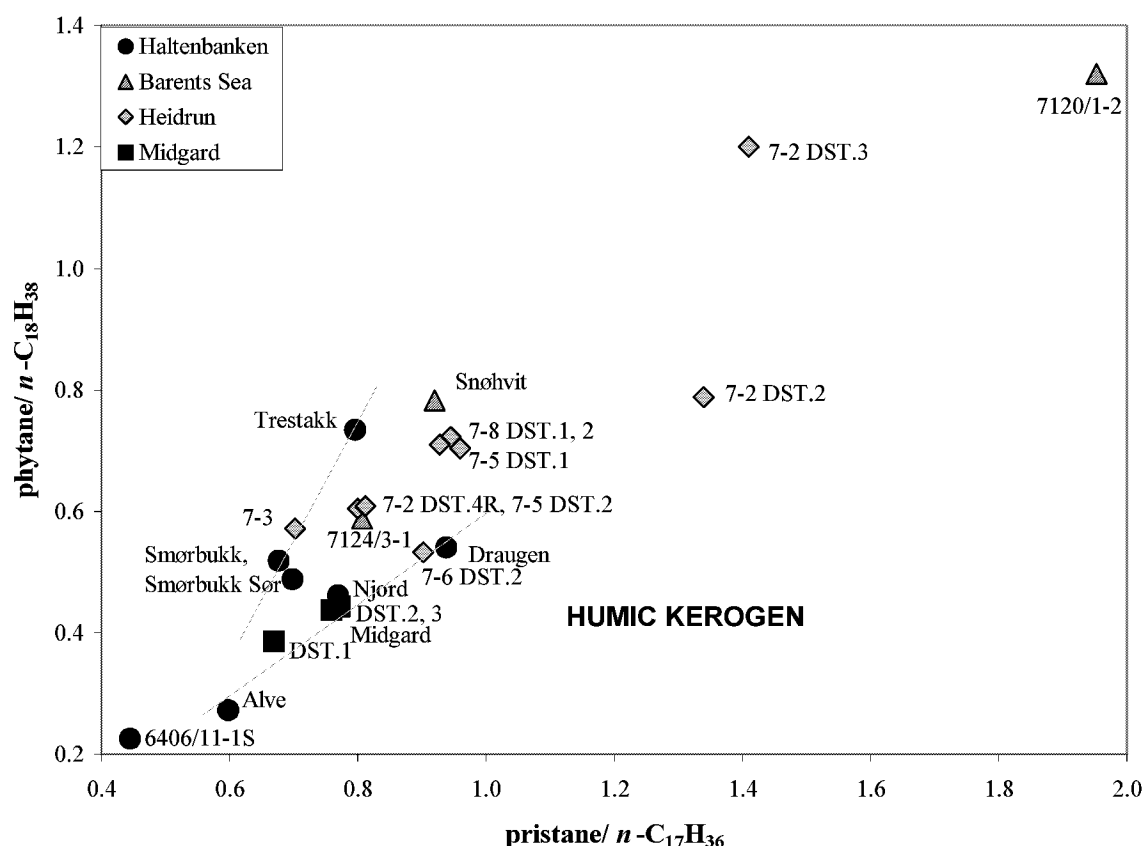


Fig. 5.1.33: Plot of pristane/*n*-C₁₇H₃₆ vs. phytane/*n*-C₁₈H₃₈ for oils from Haltenbanken and the Barents Sea

intermediate between these two trends (Fig. 5.1.33). The lowest isoprenoid to *n*-alkane ratios were observed for the oil from well 6406/11-1S. Since this oil is not thought to be very mature, these low ratios and the low API gravity indicate a different source.

Pristane/phytane

The pristane/phytane ratio of crude oils and source rocks from the Haltenbanken area has been described to be facies dependent. Cohen and Dunn (1987) concluded the facies dependence of this ratio by the fact that an east to west increase in maturity concurred with an increase in the pristane/phytane ratio from west to east. The pristane/phytane ratio of the Upper Jurassic Spekk Formation varies between 0.86 and 1.6 whereas in the Lower Jurassic Åre Formation values in the range of 1.6 - 6.6 have been reported (Cohen and Dunn, 1987).

The pristane to phytane ratio was determined for all of the oils from the Haltenbanken area and the Barents Sea with the exception of three highly biodegraded oils from the Heidrun Field (6507/8-4 (DST.2, 3 and 4)). The crude oils in the present study show pristane/phytane ratios in the range 1.2 to 2.4 (Fig. 5.1.34). An increase in the ratio is observed from the western part (Trestakk, Smørbukk) of the Haltenbanken area to the eastern part (Alve, Midgard), as described by Cohen and Dunn (1987).

Two of the oils from the Midgard

Field and the condensate from the Alve Field, which have pristane/phytane ratios between 2.2 and 2.4, are said to have originated from the Lower Jurassic Åre Formation (Cohen and Dunn, 1987). Karlsen et al. (1995) suggested that the Spekk Formation is the only source of the oils from Haltenbanken and that the variability in pristane/phytane ratio (1.2-2.4) reflects the great variability within the Upper Jurassic Spekk Formation. Elvsborg et al. (1985) interpreted the abundance of pristane and

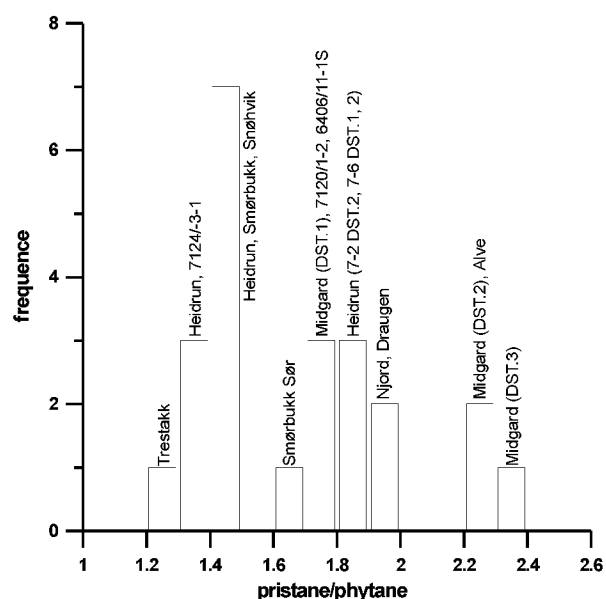


Fig. 5.1.34: Histogram of pristane/phytane ratios of oils from Haltenbanken and the Barents Sea

phytane, and the high pristane to phytane ratio, in the gas condensate of the Midgard Field as being related to an origin from a partly or mainly terrestrial source rock. Therefore, they favoured the Lower Jurassic Åre Formation as the main source rock. This is in agreement with a correlation study of source rocks and reservoired light gas/condensates from the Midgard Field by Hagevang and Rønnevik (1986). They concluded that the Coal Unit (Åre Fm.) is the main source rock. Cohen and Dunn (1987), Hvoslef et al. (1987), Odden et al. (1998) and Odden (1999) also described the importance of the Åre Formation in the easternmost part of Haltenbanken, whereas Khorasani (1989) and Forbes et al. (1991) additionally proposed that thermal cracking of the Åre Formation coals in the southwestern and western Halten Terrace (e.g. Smørbukk Sør Field) is the major source of gas and condensates in this area.

The three oil samples from the Barents Sea have intermediate pristane/phytane ratios, in the range 1.3 to 1.8, with a slightly higher value for the oil from well 7120/1-2.

Biomarkers

Most of the biomarker signatures for the oils from Haltenbanken are generally relatively uniform, but the parameters do not correlate well with each other. Karlsen et al. (1995) explained this lack of correlation by complications in mixed systems. They suggested that most of the petroleum in the Haltenbanken area represent the integration of less mature black oil with relatively high biomarker concentrations, with condensates with low biomarker contents. The authors also consider that some of the biomarker parameters are not sensitive measures of expulsion maturities for source rocks at relatively low maturity and that they are significantly influenced by organic facies. The conclusion of their study was that there was no evidence from their data to suggest that any of the petroleum samples were sourced from predominantly coaly source rocks. Thus, either the Åre Formation did not contribute to the reservoir fluids or it did not contribute to the biomarker distributions in the present petroleum. The latter interpretation was favoured by Karlsen et al. (1995) because the Åre Formation, over a large area, is significantly higher in maturity than the Spekk Formation. Accordingly, the present reservoir petroleum will have biomarker distributions which are influenced more by the relatively high biomarker concentrations in the moderately mature Spekk Formation than by the lower concentrations of biomarkers in the more mature petroleum fraction derived, at an earlier stage, from the Åre Formation. Such a

petroleum could eventually have dismigrated from the traps or become diluted by petroleum arriving later from the Spekk Formation.

With the exception of one oil from the Heidrun Field (6507/8-4 (DST.4), which was depleted in heavy-end compounds, and two condensates from the Midgard Field, the biomarkers were quantified for all of the oils from Haltenbanken and the Barents Sea.

Biomarkers – Facies Considerations

In addition to the facies relationship of the pristane/phytane ratio in the Haltenbanken oils, Karlsen et al. (1995) noted the occurrence of 28,30-*dinor*-17 α ,18 α ,21 β -hopane. The sterane distributions showed that the oils are sourced principally from rocks of the same organic facies. They took this as strong evidence that the Spekk Formation is the source of the bulk of the oils, this being reinforced by the observation that the Åre Formation coals have a totally different sterane distribution dominated by C₂₉ steranes.

In the present study, a rather uniform sterane distribution pattern for most of the oils was also observed. Figure 5.1.35 reveals that the oils from the Heidrun Field have a very uniform 5 α ,14 β ,17 β -sterane distribution pattern, and that these oils are slightly

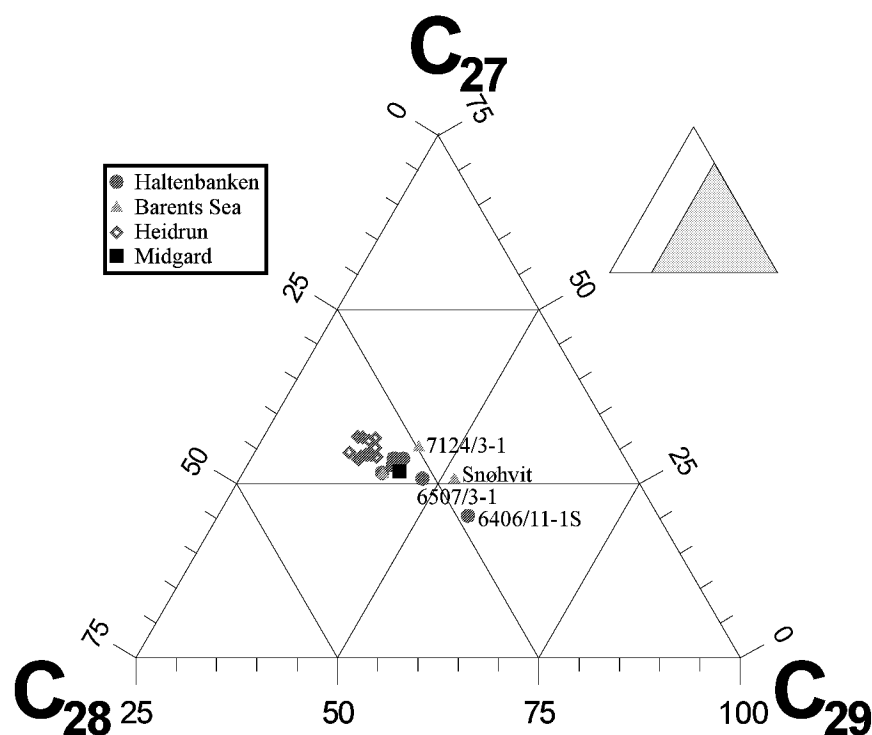


Fig. 5.1.35 Triangular plot illustrating the 5 α ,14 β ,17 β (S+R) sterane distribution pattern for the oils from Haltenbanken and the Barents Sea

depleted in C₂₉ steranes relative to the other oils analysed. Whereas the sterane distributions for most of the Haltenbanken isolated oils are very similar to each other, the oil from the Alve Field (6507/3-1) and (especially) the oil from well 6406/11-1S are relatively enriched in C₂₉ steranes, indicating a higher proportion of terrestrial organic matter in the source rock. In addition, one oil from the Barents Sea (Snøhvit Field) also indicates an enhanced contribution of terrestrial organic matter.

The abundance of 28,30-*dinor*-17 α ,18 α ,21 β -hopane (DNH) relative to 17 α ,21 β -hopane plus 28,30-*dinor*-17 α ,18 α ,21 β -hopane is very similar for all of the oils from the Haltenbanken area, with values between 0.13 and 0.24 (see Appendix 3b). The corresponding values for the oils from the Barents Sea were in the range 0.07 to 0.09. Thus, it can be concluded that the high variability observed for the ratio 25NH/(25NH + DNH), with values between 0.06 and 0.78, is primarily controlled by changes in the

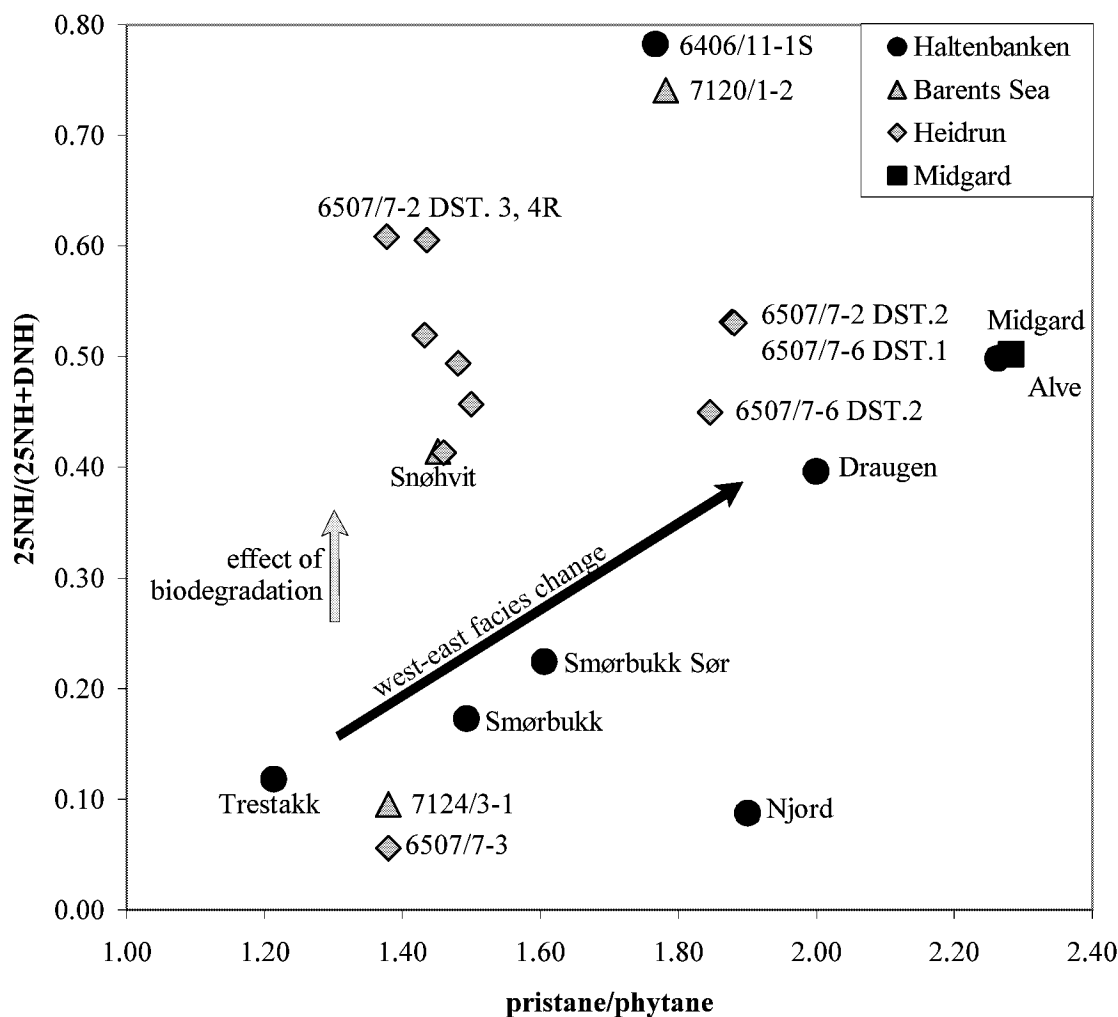


Fig. 5.1.36: Cross plot of two facies-related biomarker parameters for the oils from Haltenbanken and the Barents Sea

concentration of 25-*nor*-17 α ,21 β -hopane (25NH). Figure 5.1.36 shows that the 25NH/(25NH + DNH) ratio increases with an increase in the pristane/phytane for the Haltenbanken isolated oils. This trend reflects an increase in the abundance of 25-*nor*-17 α ,21 β -hopane in the oils on going from the west (Trestakk, Smørbukk, Smørbukk Sør) to the east of Haltenbanken (Alve, Midgard, Draugen) and indicates a stronger terrestrial influence for the latter fields.

The increase in relative abundance of 25-*nor*-17 α ,21 β -hopane in the Heidrun Field oils could also reflect, apart from a facies dependence, biological degradation. The slightly higher pristane to phytane ratios of the biodegraded oils from Heidrun wells 6507/7-6 and 6507/7-2 (DST.2) indicate that these oils belong to one oil family. The other two oils from Heidrun well 6507/7-2 are remarkable in having the highest relative abundances of 25-*nor*-17 α ,21 β -hopane even though (especially) the shallowest accumulated oil (DST.4R) shows no evidence of biodegradation. This could reflect facies changes but it could also provide evidence of mixed oils. As discussed earlier, Whitley (1992) suggested that the oils in the central part of the Heidrun Field were biodegraded when the oil field was c. 1000 m shallower than today and that these oils were subsequently mixed with later-arriving oil. The oil from well 6507/7-3 is notable because of its extremely low relative abundance of 25-*nor*-17 α ,21 β -hopane in comparison to all of the other oil samples from the Heidrun Field. Thus, this oil seems to be essentially unaffected by biological degradation and may have originated from a different source rock, whereas the other oils from the Heidrun Field are enriched in 25-*nor*-17 α ,21 β -hopane because of biodegradation. Whereas 25-*nor*-17 α ,21 β -hopane is enriched in the oils from wells 6406/11-1S and 7120/1-2, it is relatively depleted in the oil from the Njord Field in comparison to concentrations in most of the other oils from the Haltenbanken area which lie on the west-east trend (see Fig. 5.1.36). The facies and source-rock environmental history of these three oils seems to be different from that of most of the oils from this area. Although the other two oils from the Barents Sea (Snøhvit Field and well 7124/3-1) are very similar with regard to the pristane to phytane ratio, they are very different in terms of the relative abundance of 25-*nor*-17 α ,21 β -hopane. The whole-oil gas chromatogram of the oil from the Snøhvit Field shows a 'hump', indicative of biological degradation, and this may reflect a mixed (biodegraded/undegraded) oil as described for the oils from the Heidrun Field, accounting for the higher relative concentration of 25-*nor*-17 α ,21 β -hopane. However,

the oil from well 7124/3-1 is clearly not affected by biodegradation yet 25-nor-17 α ,21 β -hopane is present. As the abundances of 25-nor-17 α ,21 β -hopane appear to be dependent upon both biodegradation and facies, this parameter has been used with caution.

Biomarkers – Maturity Considerations

Many maturity-related biomarker parameters do not correlate well with each other due to the occurrence of mixed oils in many fields in the Haltenbanken area. Karlsen et al. (1995) suggested that the best parameter to estimate the maturity of these oils was the DH/(DH + NM) ratio.

Figure 5.1.37 shows this parameter plotted against Ts/(Ts+Tm). This plot reveals the higher maturity of the oils located in the western part of the Haltenbanken area (Trestakk, Smørbukk and Smørbukk Sør) and in the Midgard and Njord Fields. The biomarker data also indicate a high maturity for the oil from well 7120/1-2 from the Barents Sea. This seems to be in conflict with observations made previously (high isoprenoid/*n*-alkane ratio) and could indicate a mixed oil scenario in which an originally emplaced mature oil was biodegraded and later mixed with a condensate containing minor amounts of biomarkers. This would result in high abundances of 25-nor-17 α ,21 β -hopane, high isoprenoid to *n*-alkane ratios and biomarker signatures indicative of high maturity.

Whereas the biomarkers in most of the oils from the Heidrun Field show high maturity, those in the oil from well 6507/7-3 indicate a lower maturity. The significant difference in the 22,29,30-trinor-hopane ratio (Ts/(Ts + Tm)) of the oil from well 6507/7-3 is probably also attributable to a difference in facies, as discussed in the previous section.

The two oils from the Barents Sea (Snøhvit Field and well 7124/3-1) and the oil from well 6406/11-1S are the least mature oils in the suite whereas the oils from the Draugen Field and the Alve Field are more moderately mature. This gross maturity estimation is in accordance with the observations made in the study by Karlsen et al. (1995).

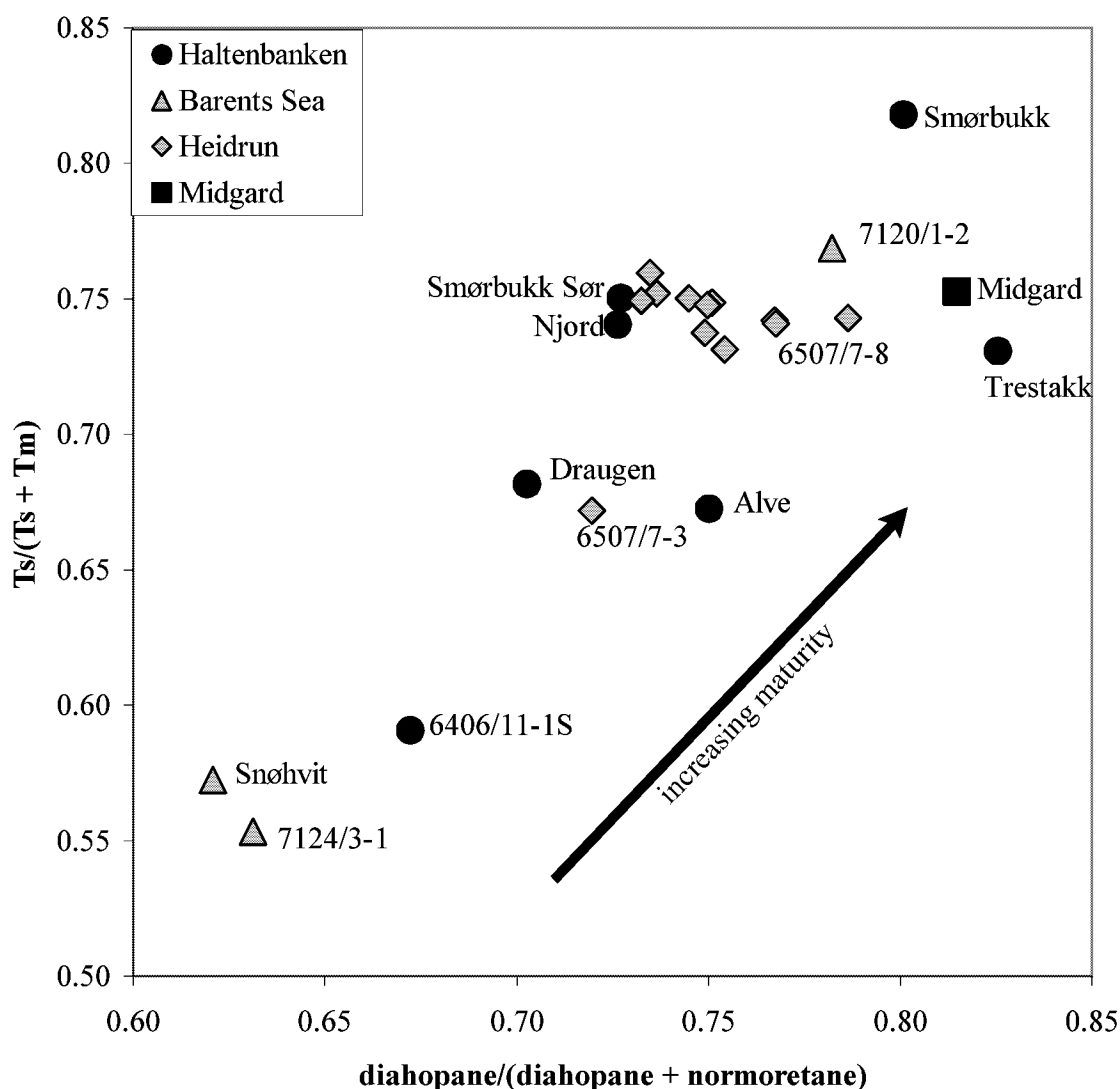


Fig. 5.1.37: Plot illustrating the maturity variation in the oils from Haltenbanken and the Barents Sea

5.1.5.3 Conclusions

Twenty-three crude oils from Haltenbanken and three crude oils from the Barents Sea were analysed in this part of the study. Many of the oils seem to be mixed oils sourced at different times. Within the Haltenbanken area, a facies change from the western part (more marine) to the eastern part (more terrigenous) could be observed. This is revealed by pristane to phytane ratios, isoprenoid to *n*-alkane ratios and the percentage of 25-*nor*-17 α ,21 β -hopane to the sum of 25-*nor*-17 α ,21 β -hopane and 28,30-*dinor*-17 α ,18 α ,21 β -hopane – the last being a new facies-related parameter. The heavy oil (17° API) from well 6406/11-1S, located in the southernmost part of the

Haltenbanken area, is remarkable due to the high abundances of long-chain *n*-alkanes dominated by *n*-pentacosane; the highest percental proportion of 5 α ,14 β ,17 β -20(S+R) C₂₉ steranes; the highest relative abundance of 25-*nor*-17 α ,21 β -hopane; and a pristane to phytane ratio of 1.77. The parameters indicate a more terrigenous source for this oil. The oil from well 6406/11-1S also has the lowest maturity of all the investigated oils from Haltenbanken, whereas the oils and condensates from Smørbukk, Smørbukk Sør, Trestakk, Midgard and Njord are clearly of higher maturity.

Most of the oils from the Heidrun Field are mixed oils and biodegraded. The degree of degradation is indicated by the presence of a significant ‘hump’ in the whole-oil gas chromatograms, in the isoprenoid to *n*-alkane ratios, the higher amounts of acids and an increased relative abundance of 25-*nor*-17 α ,21 β -hopane in comparison to most of the other oils from the Haltenbanken area. An exception is seen in the oil from Heidrun well 6507/7-3 which has the lowest abundance of 25-*nor*-17 α ,21 β -hopane and the lowest amount of acids in comparison to the other oils from the Heidrun Field. A triangular plot of the relative abundance of the C₂₇, C₂₈ and C₂₉ 5 α ,14 β ,17 β -20(S+R) steranes revealed that the Heidrun Field oils are all depleted in C₂₉ steranes compared to other oils from Haltenbanken. Higher pristane to phytane ratios (1.85-1.88) for the oils from wells 6507/7-6 (DST.1, 2) and 6507/7-2 (DST.2) in comparison to all of the other oils from the Heidrun Field (1.38-1.50) indicate that they belong to one oil family and differ slightly from the other oils. Most of the Heidrun oils are of moderate maturity and are very similar in composition, the exception being the oil from well 6507/7-3 which is of lower maturity and represents an isolated oil within the Heidrun Field.

The whole-oil gas chromatograms of the three oils from the Barents Sea are very different from each other. The oil from well 7120/1-2 is very similar to the oil from well 6201/11-1 and, as discussed in Chapter 5.1.1, is remarkable due to a very high isoprenoid to *n*-alkane ratio, the highest abundance of 25-*nor*-17 α ,21 β -hopane and biomarker compositions indicating high maturity. These characteristics are interpreted as being indicative of a mixed oil comprised of a mature oil which was biodegraded in the reservoir and subsequently mixed with a later charge of an immature condensate containing minor amounts of biomarkers. The oils from the Snøhvit Field and well 7124/3-1 are of lower maturity, and pristane to phytane ratios of 1.45 and 1.38, respectively, indicate a typical marine source. The presence of a moderate ‘hump’ in the whole-oil chromatogram, higher isoprenoid to *n*-alkane ratios and higher abundance of

25-*nor*-17 α ,21 β -hopane indicate biological degradation of the oil from the Snøhvit Field whereas no indication of biodegradation was observed for the oil from well 7124/3-1.

5.1.6 Haltenbanken - Source Rocks

Two main possible source rocks exist in the Haltenbanken area: the Upper Jurassic Spekk Formation and the Lower Jurassic Åre Formation. The Spekk Formation is generally accepted as the main source rock in this area. This formation attains as much as 400 m of accumulated thickness and is generally rated immature in the eastern platform areas (the Trøndelag Platform) and overmature to the west, i.e. towards the Vøring Basin. Peak oil generation maturity is believed to have been reached during the Late Tertiary on the Halten Terrace (Champbell and Ormaasen, 1987). Leadholm et al. (1985) estimated the peak oil generation to have occurred over large parts of the Haltenbanken area at c. 3400 m burial depth, whereas Cohen and Dunn (1987) rated the initial oil expulsion to have occurred at 120°C, equivalent in their dataset to 3100 m burial depth, and initial oil to gas cracking at 150°C (3900 m burial depth). In contrast, Heum et al. (1986) determined the threshold for primary migration at 0.7% vitrinite reflectance equivalence (VRE) which corresponds to a burial depth of c. 3900 m.

The second potentially oil-prone source rock of Haltenbanken is the deeper Åre Formation, consisting of coals and shales. These coals and shales are considered by some investigators to have expelled about 135 kg of petroleum/tonne rock during burial to c. 4% vitrinite reflectance (Heum et al., 1986) and are likely to be mature in some of the eastern proximal basinal regions where burial of the Spekk Formation is too shallow for significant oil generation (Whitley, 1992). Over much of the Haltenbanken area the maturity of the Åre Formation is about 0.2-0.5% R_c higher than that of the overlying Spekk Formation (Leadholm et al., 1985; Heum et al., 1986; Whitley, 1992). Thus, the oil potential of the Åre Formation is considered by some workers to be at least locally important (Thompson et al., 1985; Heum et al., 1986)). Mo et al. (1989) estimated the Åre Formation to be quantitatively more important than the Spekk Formation in terms of the oil generated in the drainage area of the Midgard Field (generating about 6.5 times as much as the Spekk Formation). Forbes et al. (1991) ascribed most of the oil

generation in the drainage area of the Smørbukk Sør accumulation to the Åre Formation (about six times as important volumetrically with respect to the expelled C₁₅₊ hydrocarbons compared to the Spekk plus the Melke Formation). They further suggested that expulsion from the Spekk Formation in this region became significant as late as 5 Ma BP, whereas in the Åre Formation significant expulsion (quantitatively similar to the Spekk Formation) probably occurred as early as 40 to 50 Ma BP. Petroleum expulsion is initiated at a vitrinite reflectance between 0.5 and 0.85% R_c for coals, and between 0.7 and 0.85% R_c for shales (Heum et al., 1986).

5.1.6.1 Bulk organic geochemical characteristics

Nine source rocks from the Haltenbanken area were analysed; five from the Upper Jurassic Spekk Formation and four from the Lower Jurassic Åre Formation. Two of the Spekk samples are from the broader environs of well 6406/11-1S and three samples are from the vicinity of the Draugen Field. Two very deeply buried samples of the Åre Formation are from the western part of Haltenbanken, in the vicinity of the Trestakk Field and two shallow buried equivalents are from the north-east, close to the Alve Field (see Fig. 3.7).

Screening Data

Elemental and Rock-Eval data for the Haltenbanken source rock samples are presented in Table 5.1.2. The TOC contents of the Spekk Formation range from 2.6 to 6.5%. The immature source rock samples of the Åre Formation have TOC values of 37.1 and 42.7%, and the mature equivalents have TOC contents of 60.5 and 66.8%.

E-number	48161	48162	48163	48157	48158	48159	48160	48155	48156
well	6407/9-3	6407/9-3	6407/9-3	6406/12-2	6406/12-3	6507/3-2	6507/3-3	6406/2-1R	6406/2-1R
depth [m]	1623.3	1627.5	1675	3744	3749	1406.4	1406.5	5647.15	5647.6
Formation	Spekk	Spekk	Spekk	Spekk	Spekk	Åre	Åre	Åre	Åre
TOC [%]	6.5	3.7	4.9	3.8	2.6	42.7	37.1	66.8	60.5
TC [%]	6.6	3.9	4.8	4.2	3.0	41.7	37.0	58.8	59.1
TS [%]	4.2	5.7	2.5	3.3	2.2	1.1	1.1	8.1	1.7
S1 [mg HC/g rock]	2.7	1.1	1.6	3.6	3.9	5.5	1.5	1.0	1.4
S2 [mg HC/g rock]	21.8	7.3	10.7	11.4	7.7	80.7	36.2	20.6	15.8
S3 [mg CO ₂ /g rock]	0.60	0.60	0.60	0.60	0.59	2.72	2.85	5.18	5.05
Tmax [°C]	398.5	406	410.5	433.5	434.5	410	413	497	509
PI (S1/(S1+S2))	0.11	0.13	0.13	0.24	0.34	0.06	0.04	0.05	0.08
HI [mg HC/g TOC]	334.8	194.5	219.7	302.7	300.8	189.1	97.6	30.9	26.2
OI [mg CO ₂ /g TOC]	9.2	16.2	12.4	15.8	23.2	6.4	7.7	7.8	8.4

Tab. 5.1.2: Elemental and Rock-Eval data for the source rocks from Haltenbanken

The pseudo-van Krevelen diagram shown in Figure 5.1.38 reveals a difference between these two formations. The oxygen indices of all of the source rock samples are low, between 6 and 23 mg CO₂/g TOC. The higher hydrogen index values of the Spekk Formation samples compared to those of the Åre Formation point to the higher oil potential of the Spekk Formation and indicate a kerogen type II. The data for the coaly samples from the more deeply buried Åre Formation indicate a kerogen type II/III or III.

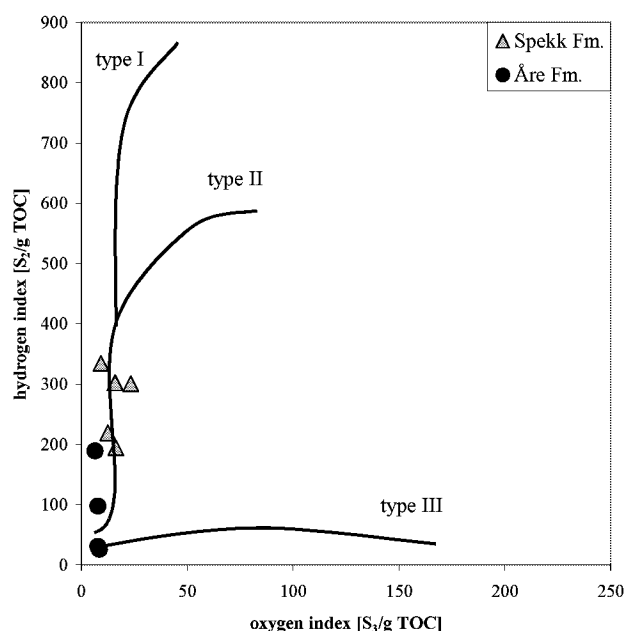


Fig. 5.1.38: Hydrogen index versus oxygen index values used for kerogen typing

A decrease in HI with increasing maturity (Espitalié et al., 1985) is observed for both source rocks, the decrease being from over 300 to approximately 200 mg HC/g TOC for the Spekk Formation, and down to 30 mg HC/g TOC for the very mature source rocks from the Åre Formation.

Barker (1974), Claypool and Reed (1976) and Espitalié et al. (1977) showed that the production index ($PI = (S_1/(S_1+S_2))$) and the temperature of maximum pyrolysis yield (T_{max}) are maturity dependent. In accordance with data for other humic coals (cf. Durand and Paratte, 1983) low PI values were recorded for both the immature and very mature source rocks of the Åre Formation. The Spekk samples are from both the beginning of the oil window stage ($PI = 0.11-0.13$) and the end of this zone ($PI = 0.24$ and 0.34) according to the classification of Tissot and Welte (1984, p. 521). The right-hand diagram in Figure 5.1.39 demonstrates the increase in T_{max} with increasing depth, attributable to increasing maturity. T_{max} increases with increasing maturity for both formations, from 398 to 435°C for the source rocks from the Spekk Formation and from 410 to 509°C for the coaly sample set. The temperature at which the generation of hydrocarbons reaches its maximum during Rock Eval pyrolysis depends not only on maturity, but also on the type of organic matter. Whereas the sensitivity of T_{max} values of the hydrogen-rich type I kerogen is low, T_{max} values of oxygen-rich type III organic matter strongly depend on the thermal maturity of the samples (Espitalié et al., 1985). The cross-plot of HI versus T_{max} in Figure 5.1.39 is useful for kerogen typing. Whereas the data for the coaly samples from the Åre Formation point to kerogen type III and II/III, the data for the mature samples from the Spekk Formation indicate kerogen type II. Two of the immature samples of the Spekk Formation also suggest kerogen type II/III.

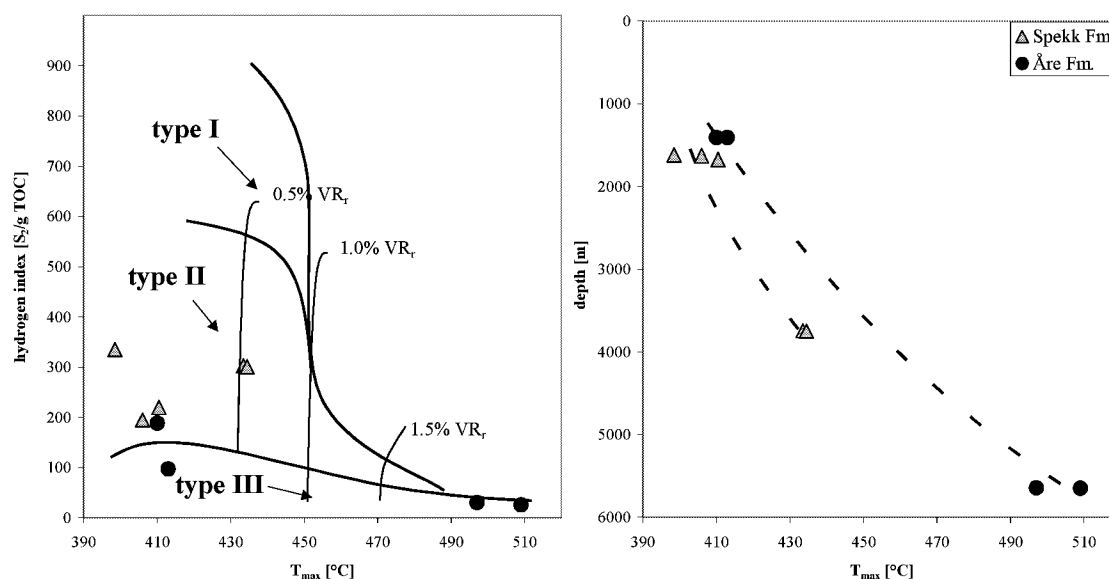


Fig. 5.1.39: Cross-plots showing the variation in the T_{max} of the Rock-Eval S_2 peak with HI and depth of the source rock samples from Haltenbanken.

Gross compound composition

The triangular plot of the relative abundance of saturated hydrocarbons, aromatic hydrocarbons and NSO compounds (Figure 5.1.40) shows that NSO compounds dominate the source rock extracts, and that the extracts from the Spekk Formation contain a higher relative abundance of saturated hydrocarbons than those from the Åre Formation. A decrease in the relative abundance of NSO compounds and, an increase in the proportion of aromatic hydrocarbons with increasing maturity is observed for both formations (cf. (Tissot and Welte, 1984), p. 189).

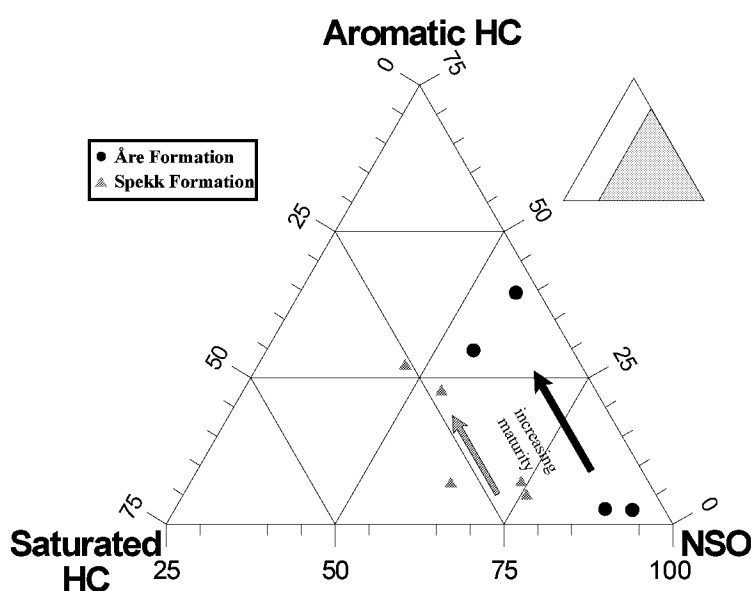


Fig. 5.1.40: Triangular plot showing the gross compound composition (saturated and aromatic hydrocarbons and NSO compounds) of the source rocks from Haltenbanken

Gross heterocompound composition

Figure 5.1.41 shows the percentages of the five component groups which make up the NSO fraction of the Haltenbanken source rock extracts. The most obvious differences between the immature and mature source rocks is the higher content of acids in the immature samples from both formations and the higher amount of the highly polar fraction in the immature coaly extracts from the Åre Formation. The percentage of the low polar fraction increases with increasing maturity. A comparison of the data for the two different source rocks reveals that the relative amounts of the medium polars and bases in the extracts of the Åre Formation are higher than or equal to those of the Upper Jurassic Spekk Formation. However, most of the variation in the composition of the heterocompound fraction is controlled by maturity.

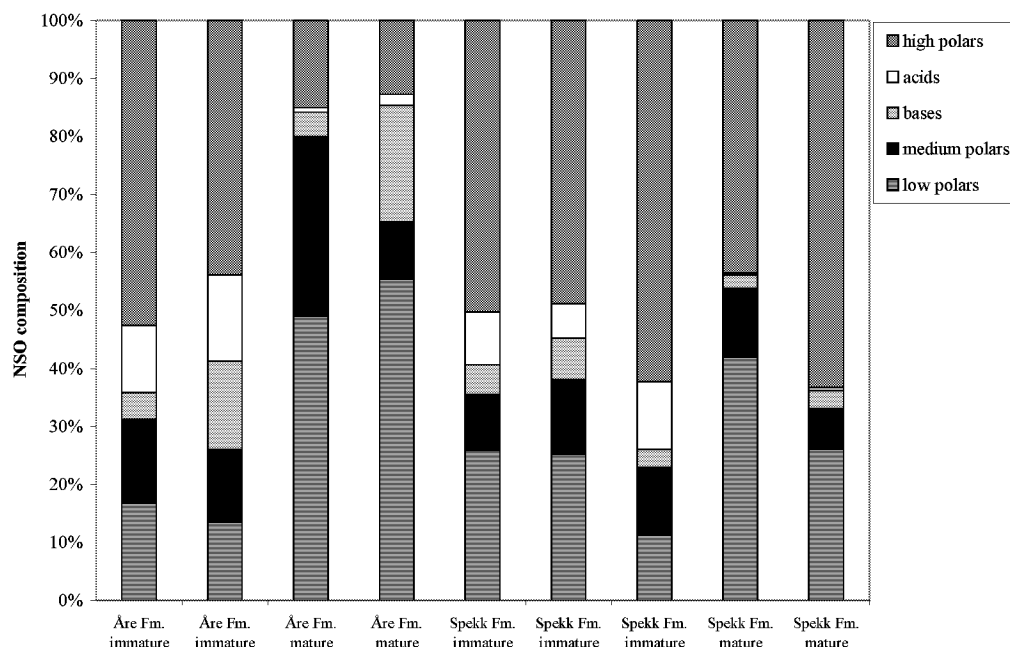


Fig. 5.1.41: Percentage of the five NSO fractions within the heterocompound fraction of the source rocks from Haltenbanken

5.1.6.2 Maturity and facies assessment

Alkanes

Gas chromatographic analysis of the saturated hydrocarbon fraction of the source rock extracts reveals a wide variation in *n*-alkane distribution pattern. A selection of chromatograms is shown in Figure 5.1.42. The chromatograms from the immature coaly samples from the Åre Formation show a bimodal distribution of *n*-alkanes with maxima around *n*-C₁₅₋₁₆ and *n*-C₂₅. The longer-chain *n*-alkanes are dominant in the chromatogram and show an odd carbon number preference. This is indicative of the terrestrial nature of the coaly samples. In contrast, the chromatograms from the immature samples from the Upper Jurassic Spekk Formation are strongly dominated by short-chain *n*-alkanes with a distribution maximum at *n*-heptadecane, which points to the marine character of the organic matter in this formation. These features disappear with increasing maturity in both formations due to *n*-alkane formation from kerogen.

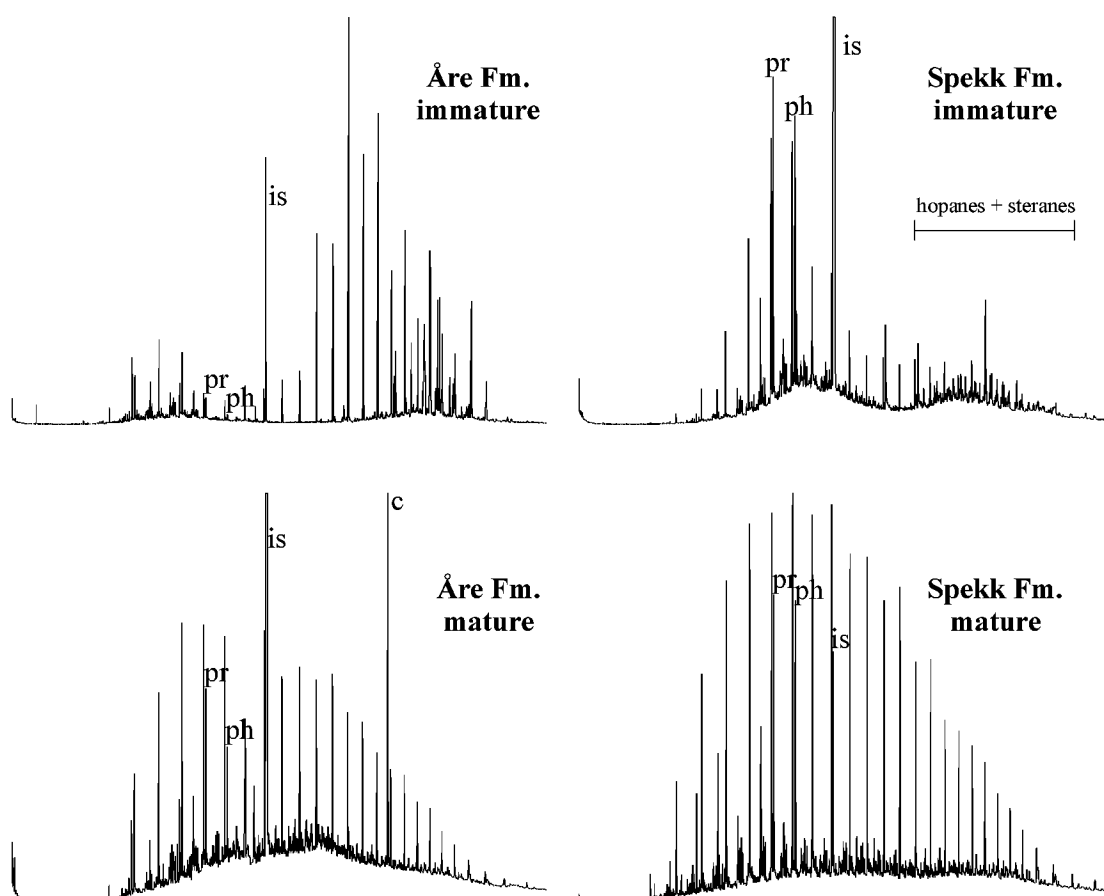


Fig. 5.1.42: Gas chromatograms of saturated hydrocarbon fractions from immature and mature source rocks from the Åre and Spekk Formations (is=internal standard; pr=pristane; ph=phytane; c=diethyl sebacate, contamination, plasticizer)

The relative abundance of odd and even carbon-numbered *n*-paraffins can be used to provide a crude estimate of the thermal maturity of rock extracts and petroleum. These parameters include the carbon preference index (CPI; Bray and Evans, 1961) and the odd : even preference (OEP; Scalan and Smith, 1970). In the present study the CPI is based on the *n*-alkanes in the range *n*-C₂₄-*n*-C₃₂, whereas the OEP1 is based on the *n*-alkanes in the range *n*-C₂₁-*n*-C₂₅. The odd-to-even predominance of the *n*-alkanes in the Haltenbanken source rocks decreases with increasing maturity from about 2 to 1 for both parameters, as demonstrated in Figure 5.1.43. Since the abundances of long-chain *n*-alkanes are very low for the immature Spekk samples, the OEP1 parameter is considered more reliable for maturity assessment.

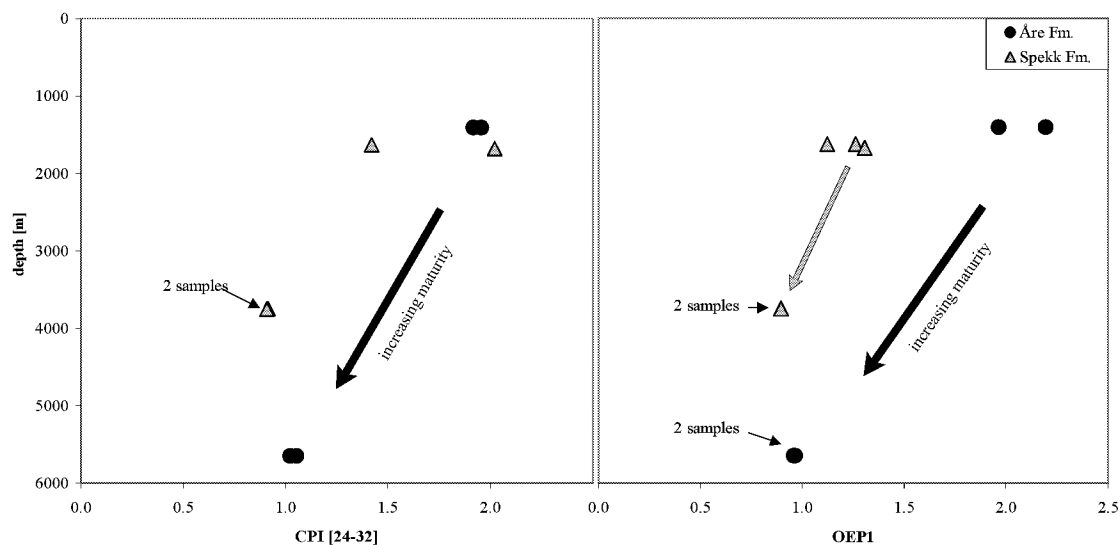


Fig. 5.1.43: Plots of CPI [24-32] and OEP1 [21-25] versus depth, indicating the variation in the *n*-alkane distribution pattern with increasing maturity

Isoprenoids

Figure 5.1.44 illustrates the variation in the pristane to *n*-heptadecane ratio with the phytane to *n*-octadecane ratio and $T_{\max}$ for the two potential source rocks from the Haltenbanken area. The isoprenoids to *n*-alkanes ratios show that in the C_{17} - C_{20} carbon number range the source rock extracts from the Spekk Formation are dominated by *n*-alkanes whereas most of the coaly source rocks are enriched in isoprenoids. For the

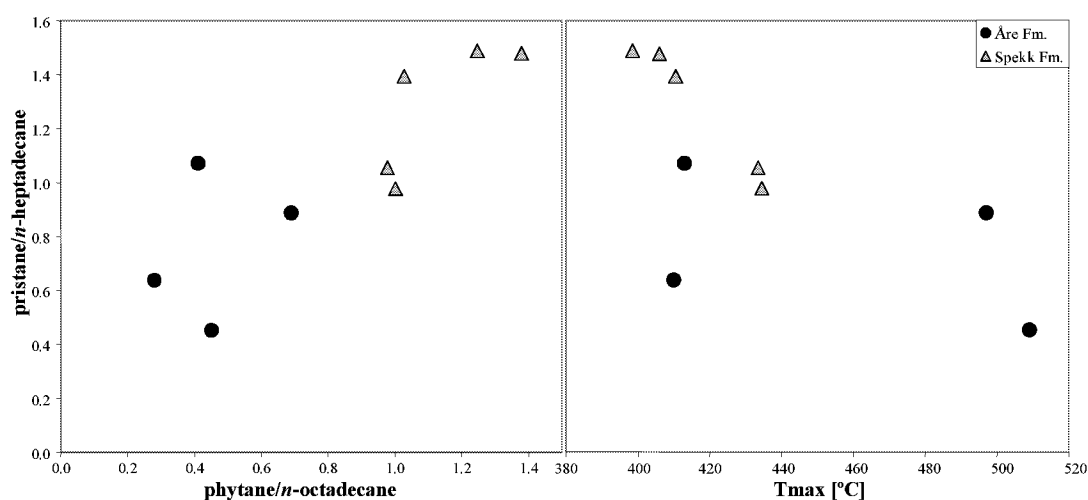


Fig. 5.1.44: Plots of pristane/*n*-heptadecane versus phytane/*n*-octadecane and $T_{\max}$ for the source rocks from Haltenbanken

Spekk source rock extracts, the pristane/*n*-heptadecane ratio decreases with increasing $T_{\max}$ (Fig. 5.1.44). This trend is not observed for the extracts from the Åre Formation and it is suggested that the variation in isoprenoid : *n*-alkane ratios for the coaly Åre Formation samples probably reflects facies variation.

The pristane to phytane ratio for the source rock extracts varies over a wide range, between 0.8 and 3.3, as illustrated in Figure 5.1.45. For both source rock formations, the lowest pristane : phytane ratios are associated with the most mature (deepest) samples. However, this ratio is not useful to discriminate between the two different potential source rocks from each other.

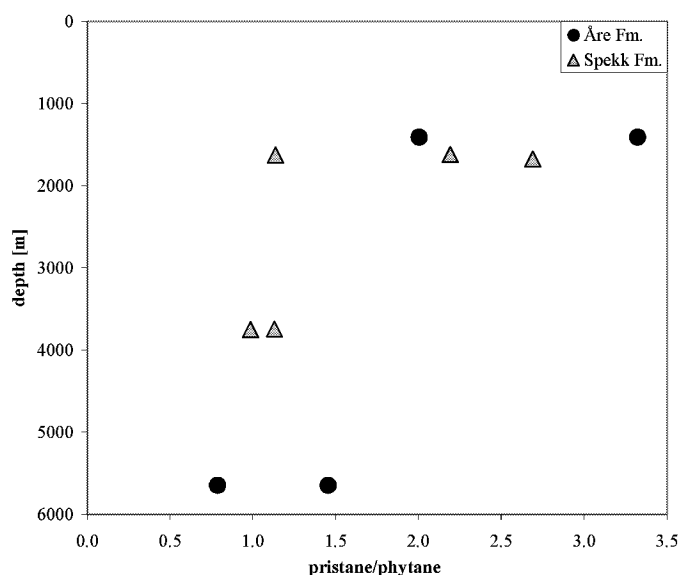


Fig. 5.1.45: Plot of the pristane to phytane ratio versus the depth for source rock extracts from Haltenbanken

Aromatic hydrocarbons

The methyl dibenzothiophene ratio ($MDR' = 4\text{-MDBT}/(1\text{-MDBT} + 4\text{-MDBT})$) could be determined for all of the samples except the immature extracts from the Åre Formation. This ratio, described by Radke and Willsch (1994), correlates well with $T_{\max}$ and increases systematically from 0.49 for the immature Spekk samples to 0.96 for the mature

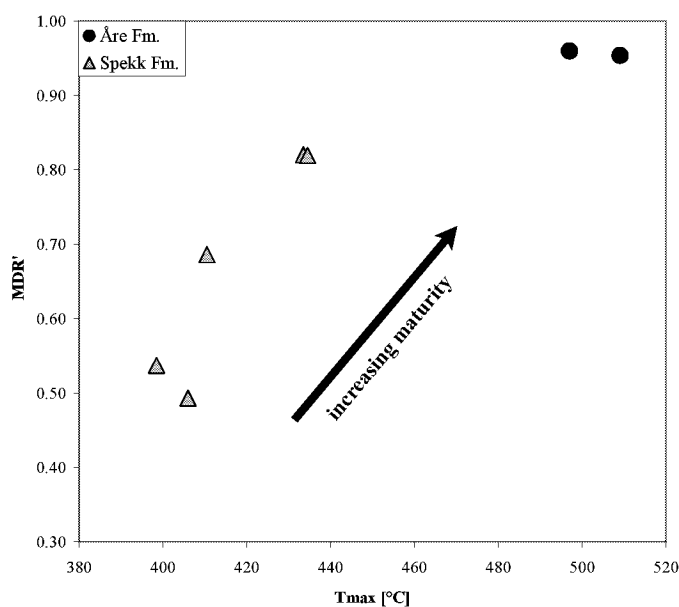


Fig. 5.1.46: Plot of MDR' versus $T_{\max}$ of the source rock extracts from Haltenbanken

coaly samples as illustrated in Figure 5.1.46. According to Radke and Willsch (1994) this variation corresponds to a range in vitrinite reflectance (R_{cs}) of 0.58 to 2.25%.

Biomarkers

The biomarker distribution patterns for the selected source rocks from Haltenbanken indicate a broad range of maturity. Whereas the very mature samples from the Åre Formation contain no quantifiable biomarkers, the biomarker distributions for the immature samples of this formation support their very immature character. This is substantiated by the dominance of $17\beta,21\beta$ -hopanes and unsaturated hopenes and sterenes. The analysis of the saturated hydrocarbon biomarkers of the mature Spekk Formation samples reveals high values for the 17α -hopane to moretane ratio [$H/(H + M) = 0.88$], the isomerisation ratio of *dihomo*- 17α -hopanes [$22S/(22S + 22R) = 0.6$] and the isomerisation ratio of 24-ethylcholestanes [$\alpha,\beta,\beta/(\alpha,\beta,\beta + \alpha,\alpha,\alpha) = 0.78$]. The biomarkers from the immature samples of the Spekk Formation indicate a maturity between the mature samples of this formation and the immature coaly source rocks from the Åre Formation. This is illustrated by the m/z 191 mass chromatograms in Figure 5.1.47 which show the hopane distribution pattern for three different maturity levels. In addition to hopanes and steranes, ferenes -which probably originate from ferns (Vliex et al., 1994; Kvenvolden et al., 1995; Paull et al., 1998)- were detected in the coaly samples. However, this compound class was once reported to occur also in a bacterium (Howard et al., 1984). Other terrestrially derived compounds such as oleanane could not be identified in the samples, probably due to age limitations. Oleanane, a diagenetic product of β -amyrin, which is an abundant constituent of angiosperms only, became widespread during Late Cretaceous – Early Tertiary times, whereas the coaly samples are from Early Jurassic.

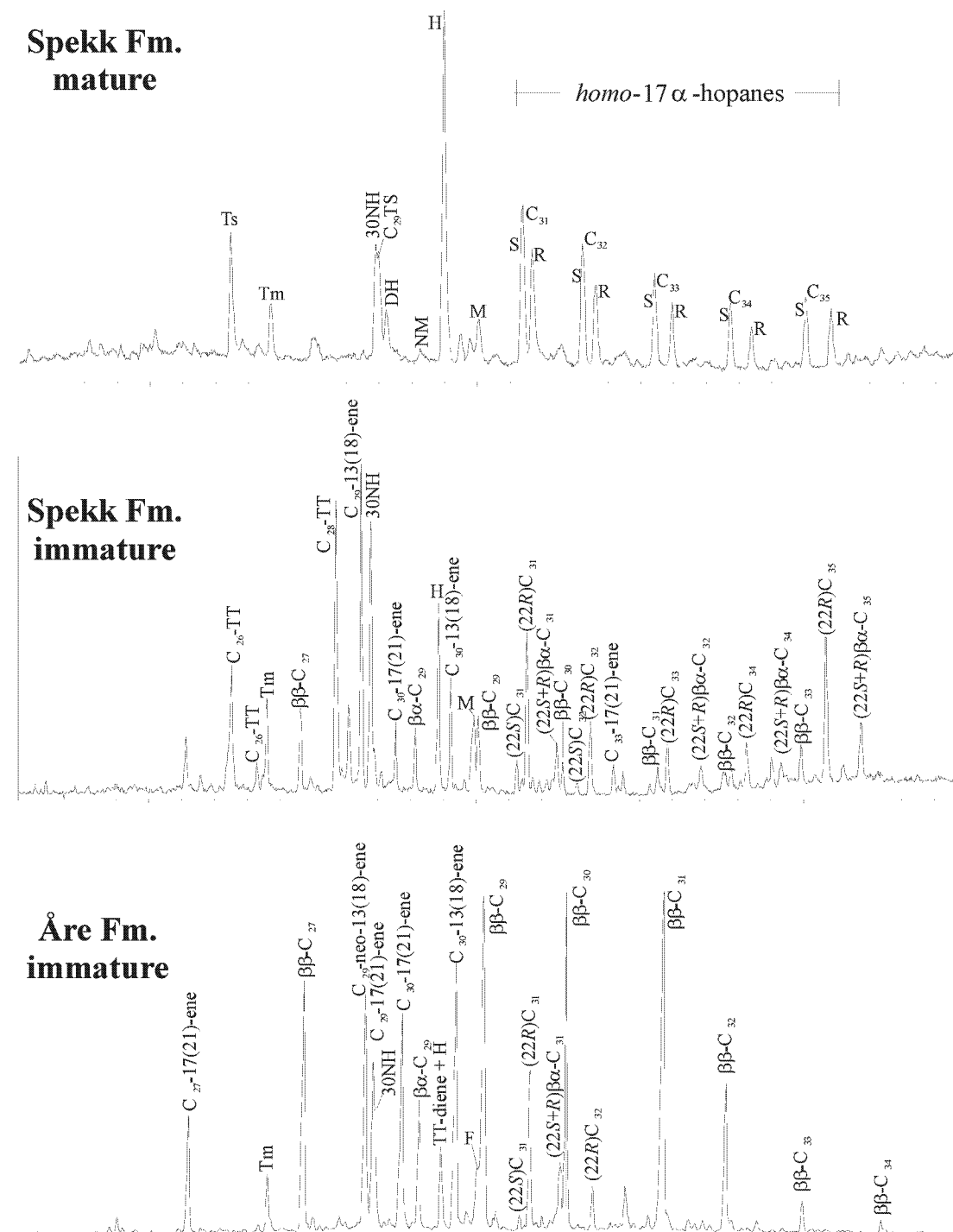


Fig. 5.1.47: Partial mass chromatograms (m/z 191) of saturated hydrocarbon fractions from source rocks of Haltenbanken, indicating the influence of maturity on the distribution of biomarkers. For key to labels see Table 4.1.

5.1.6.3 Conclusions

Nine oil-prone source rock samples, five from the Upper Jurassic Spekk Formation and four from the Lower Jurassic Åre Formation, were analysed in this study. The data from Rock Eval pyrolysis indicate a broad range of maturity and differences in the oil potential. Whereas the Spekk Formation samples contain kerogen type II, the coaly source rocks from the Åre Formation contain kerogen types III and II/III. This is supported by the odd carbon number predominance of the longer-chain *n*-alkanes as well as by the isoprenoid to *n*-alkane ratios. The presence of ferenes in the source rocks of the Åre Formation points to an input of fern-derived lipids and supports a terrestrial plant source.

The two deeply buried samples from the Åre Formation are highly mature whereas the other two samples of this formation are very immature. This is supported by the biomarker distribution patterns. The immature samples are dominated by 17 β ,21 β -hopanes and unsaturated hydrocarbons such as hopenes and sterenes. The high maturity of two source rocks from the Spekk Formation is substantiated by high values for the 17 α -hopane to moretane ratio [$H/(H + M) = 0.88$], the isomerisation ratio of *dihomo*-17 α -hopanes [$22S/(22S + 22R) = 0.6$] and the isomerisation ratio of 24-ethylcholestanes [$\alpha,\beta,\beta/(\alpha,\beta,\beta + \alpha,\alpha,\alpha) = 0.78$]. The biomarkers of the shallower samples from the Spekk Formation indicate a maturity between the mature samples of this formation and the immature coaly source rocks from the Åre Formation.

5.1.7 Hydrous pyrolysis experiments

The sample used in this study is a limestone from the Ghareb Formation (Upper Cretaceous) at El Lajjun, Jordan. The TOC content is 19.6 wt.%. Elemental composition of the isolated kerogen indicates that the rock contains immature Type II-S organic matter ($R_0 = 0.39\%$) with an atomic H/C ratio of 1.38, an atomic O/C ratio of 0.07, and an atomic S_{org}/C ratio of 0.07 (Koopmans et al., 1998).

The effect of progressive diagenesis and early catagenesis on the amounts and distributions of hydrocarbons, organic sulfur compounds and S-rich geomacromolecules using these experiments was documented by Koopmans et al. (1998). They observed

that with increasing thermal maturation, large amounts of alkanes and alkylthiophenes with predominantly linear carbon skeletons are generated from the kerogen whereas the alkylthiophene isomer distributions do not change significantly with increasing maturity. Further, for a given carbon skeleton, the saturated hydrocarbons, alkylthiophenes and alkylbenzo[*b*]thiophenes are stable forms at relatively high temperatures, whereas the alkylsulfides are not stable.

Six expelled oils and their corresponding recovered rocks were available from a series of hydrous pyrolysis experiments. Artificial maturation was accomplished by heating the rock chips isothermally for 72 h at 310, 330, 345, 355, 360 and 365°C which represents a maturity range of 0.8 to 1.3% R_r according to Lewan (1985), Clegg et al. (1998) and Koopmans et al. (1998).

5.1.7.1 Bulk organic geochemical characteristics of expelled oils and recovered rocks from hydrous pyrolysis of an immature source rock from the Ghareb Formation

A detailed description of the conventional organic geochemistry of the hydrous pyrolysis of this immature source rock from the Ghareb Formation was reported by Koopmans et al. (1998). Therefore, in the present study the investigations were focussed on the heterocompound fractions, especially on the low-polarity fractions.

The polar fractions comprise between 40 to 62% of the residual bitumens whereas their amounts in the corresponding expelled oils are significantly smaller, between 12% and 22%. As illustrated in the top diagram of Figure 5.1.48, the low-polarity fractions dominate the polar fractions of all of the oils whereas in the bitumens the medium- and high-polarity fractions are also abundant components. This results in a higher relative contribution of the low-polarity fraction to the total polar fraction in the oils as compared to the bitumens. The amount of the low-polarity fractions decreases with increasing (artificial) maturity in both the expelled oils and the recovered rock extracts. In addition, for both the oils and bitumens the relative abundance of the low-polarity fraction decreases with increasing maturity in comparison with that of the medium-polarity fraction (bottom diagram of Fig. 5.1.48).

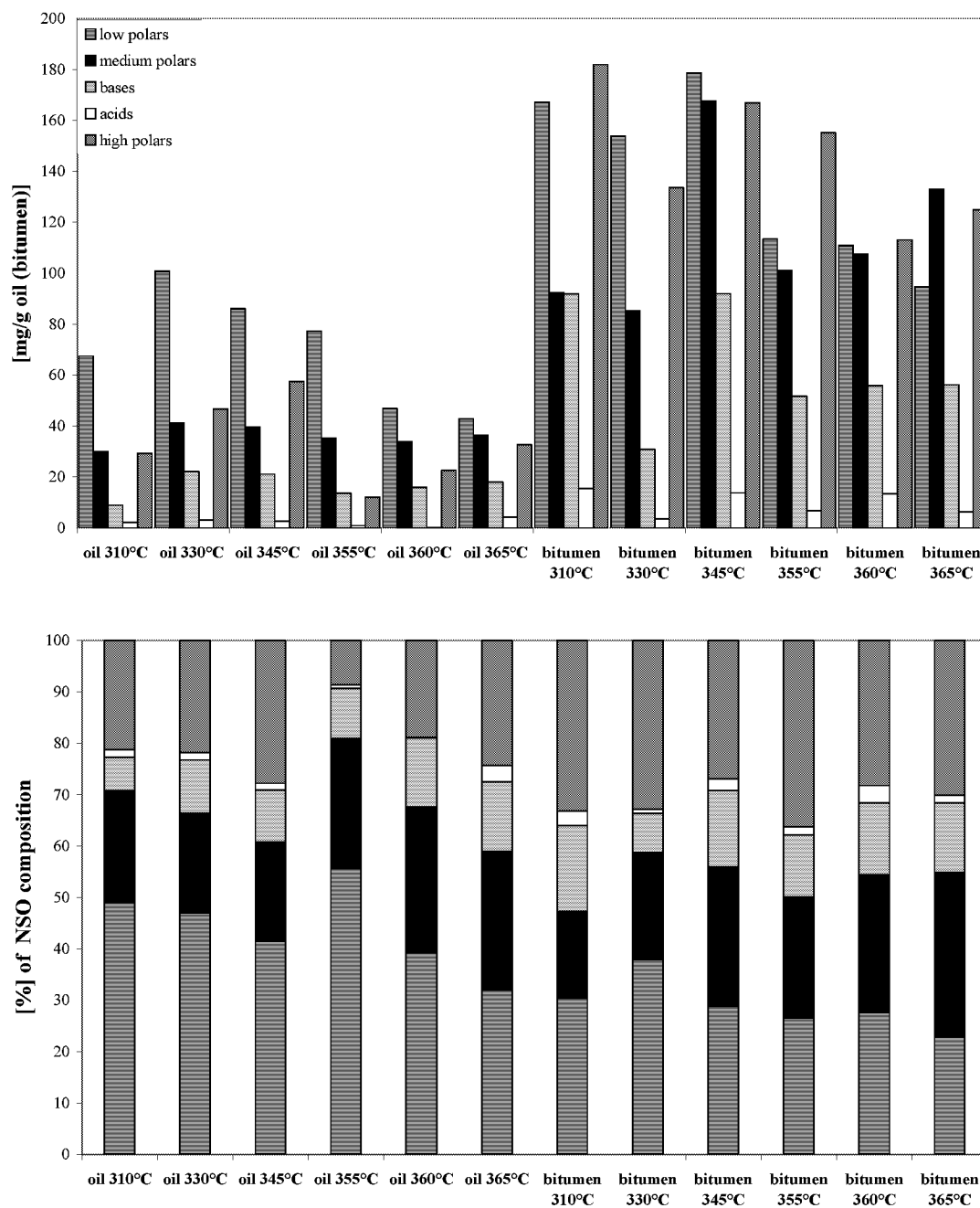
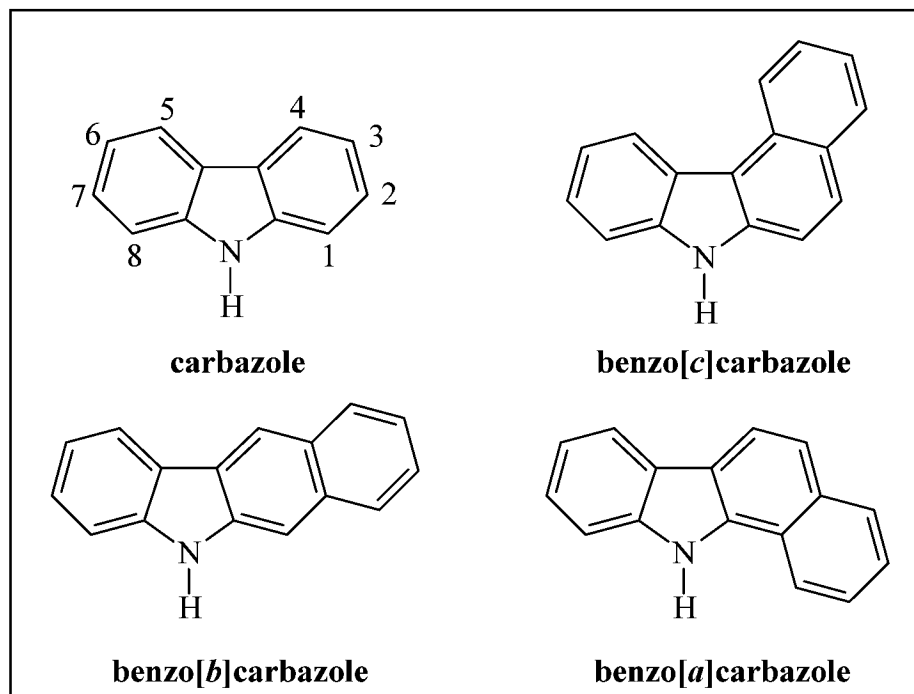


Fig. 5.1.48: Diagrams illustrating the distribution of the polar fractions in the expelled oils and recovered rock extracts from hydrous pyrolysis of the Ghareb Formation source rock

5.2 Carbazoles and Benzocarbazoles



5.2.1 Introduction

The nitrogen content of crude oils is usually much less than 1% by weight (Tissot and Welte, 1984, p. 401). More than two thirds of the nitrogen content is in the form of the non-basic pyrrolic ring compounds such as carbazole and its derivatives (Helm et al., 1960; Seifert, 1969). Carbazoles and benzocarbazoles are common constituents of petroleum systems, and their occurrence has been documented by numerous workers (e.g. Helm et al., 1960; Snyder et al., 1968; Dorbon et al., 1984; Frolov et al., 1989; Bakel and Philp, 1990).

The origin of non-porphyrinic nitrogen compounds in the geosphere is unclear. The chemical structure of these compounds may be either directly inherited from biological precursors or represent diagenetic artefacts through intensive reworking of nitrogen-containing sedimentary organic matter or incorporation of inorganic nitrogen species into organic carbon skeletons (Li et al., 1995). Snyder (1965) proposed that many of the alkylcarbazoles and alkylbenzocarbazoles in petroleum may be derived from alkaloids with an indole nucleus, which are commonly found in higher land plants (Kapil, 1971; Hesse, 1974) and cyanobacteria (Cardellina et al., 1979). More recently, however, it has been stated that alkaloids are unlikely to be the precursors of carbazoles and

benzocarbazoles. Li et al. (1995) pointed out that if the alkaloids were the origin of carbazoles then the linearly annelated benzo[*b*]carbazole structure should be absent, and there should be a predominance of alkyl substituents on only one of the aromatic rings of the carbazole and benzocarbazole backbones. Neither is true, as shown by Dorbon et al. (1984) and Li et al. (1995) and in this thesis. Other sources of nitrogen must therefore be considered, e.g. condensation reactions involving proteins and pigments.

Recently, the relative abundances of certain carbazole derivatives have been proposed as useful indicators of primary and secondary migration processes (Li et al., 1994, 1995; Larter et al., 1995). These authors described an enrichment of alkylcarbazoles relative to alkyl-benzocarbazoles, an enrichment of so-called nitrogen-shielded isomers to nitrogen-exposed isomers and an enrichment of higher to lower molecular weight homologues with increasing migration distance. Larter et al. (1996a) proposed the relative abundance of benzo[*a*]carbazole/(benzo[*a*]carbazole + benzo[*c*]carbazole) as a maturity-independent tool for the study of the relative secondary migration range of source-related petroleum. This was supported by molecular dynamics calculations (van Duin and Larter, 1998) and by an experimental investigation of geochromatography during secondary migration (Larter et al., 2000). Although some case studies have described successful application of benzocarbazoles as migration tracers in foreland basin settings (Li et al., 1997, 1998; Terken and Frewin, 2000) there is clear evidence that maturation and facies also control both this parameter and the distribution of other carbazole derivatives in many source rock extracts and crude oils. For example, the benzocarbazole [$a/(a+c)$] ratios of Tithonian source rocks and their expelled crude oils from the Sonda de Campeche (Mexico) and the Posidonia Shale of Germany first increase and then decrease with increasing maturity (Horsfield et al., 1998). Artificial maturation (hydrous pyrolysis) of an organic-sulphur-rich source rock (Ghareb Formation, Jordan) showed the same maturity dependence of the carbazole and benzocarbazole isomers as described above (Clegg et al., 1998a). The influence of different facies reflecting deposition of carbonates under transgressive and regressive conditions in the Keg River Formation (Western Canada) on the distribution of carbazoles was described by Clegg et al. (1997). More recently, Bakr and Wilkes (2002) showed that the benzocarbazole and alkyl carbazole ratios in oils from the Gulf of Suez depend on facies and depositional environment. The aforementioned studies suggest that factors such as source facies, maturity, and partitioning can all play a

significant role in determining the distribution of carbazoles in oils and source rock extracts.

The aim of the present study was to investigate the influence of these factors and, additionally, those of water washing and biodegradation on the isomeric distribution of carbazoles in crude oils and source rocks from offshore Norway.

5.2.2 Occurrence of carbazoles

The samples analysed in this study comprised 72 oils, 2 core samples and 9 source rock samples from offshore Norway as well as expelled oils and recovered rock extracts resulting from the hydrous pyrolysis of an immature source rock from the Ghareb Formation (see Chapters 3, 5.1 and Appendix 1). The carbazoles and benzocarbazoles are contained in the low-polarity NSO fraction together with fluorenones and xanthenes and were quantified as described in Chapter 4.

Source rocks

The concentrations of the C₀-C₂ alkylcarbazole homologue groups and of the benzocarbazoles in the source rock extracts from the Åre and Spekk Formations in the Haltenbanken area range from <2 µg/g extract for the immature source rock to 900 µg/g extract for the very mature source rock from the Åre Formation (Fig. 5.2.1). It is clear from the figure that there is a correlation between carbazole concentrations and depth/maturity of the source rocks. This will be discussed in more detail in Section 5.2.4.

In the source rocks from the Spekk Formation, the concentrations of the four selected compound groups increase in the order carbazole < benzocarbazoles < methylcarbazoles < C₂-carbazoles irrespective of maturity. In contrast, the distributions of these compound groups in the extracts from the coaly Åre Formation are dominated by the benzocarbazoles, and there is also a significant depletion of the C₂-alkylcarbazoles in the more mature samples. It is not possible to compare the data with those obtained in previous studies (Clegg et al., 1998b; Horsfield et al., 1998) because only the mature Spekk samples fall into the same maturity range.

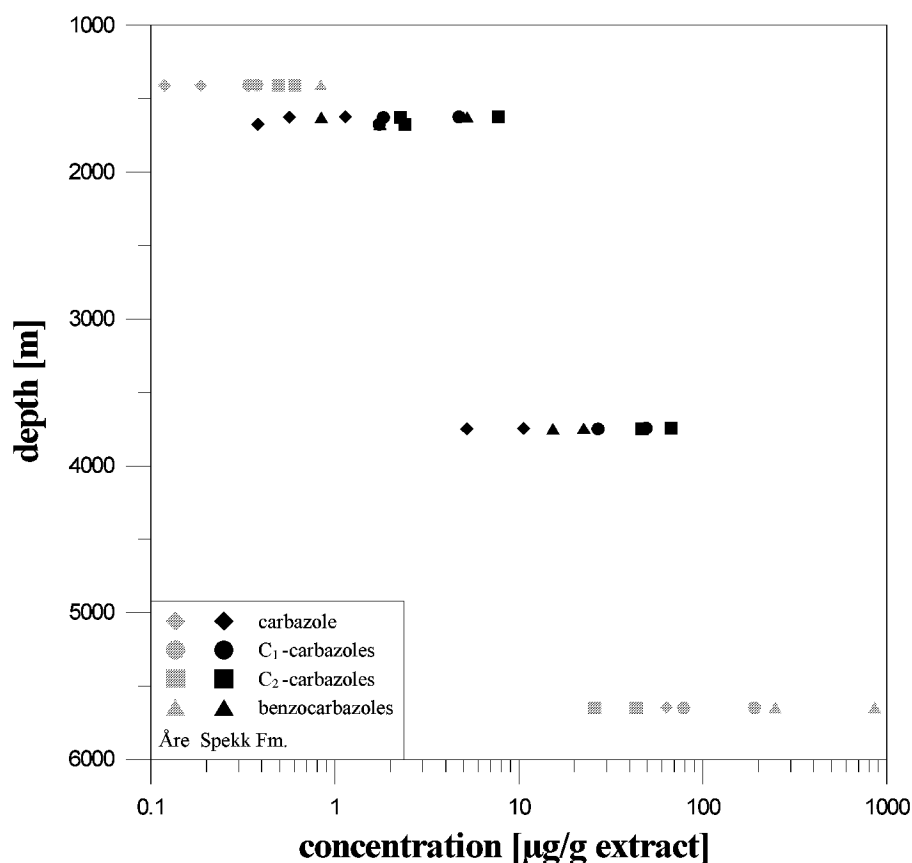


Fig. 5.2.1: Concentrations of carbazoles in source rock extracts from Haltenbanken (note the logarithmic scale on the x-axis).

Crude oils

As illustrated in Figure 5.2.2, 75% of the oils analysed had carbazole concentrations of less than 2 $\mu\text{g/g}$ oil and 90% of the oils had benzocarbazole concentrations of less than 2 $\mu\text{g/g}$ oil. This is in accordance with other investigations of crude oils from this study area (Larter et al., 1996b; Bennett et al., 2002). The concentrations of the carbazole groups in the mature source rock from the Spekk Fm. (within the oil-window) are significantly higher than in the crude oils, which indicates fractionation effects during expulsion and secondary migration. This is most clearly seen in the benzocarbazoles, reflecting the influence of molecular shape and size as well as the higher dipole moment. In this regard, a greater depletion of benzocarbazoles relative to alkylcarbazoles in crude oils compared with extracts from clastic source rocks has also been observed by Li et al. (1995, 1997) and was attributed to fractionation during primary and secondary migration. In contrast, a study of the Tithonian carbonate source

rock and related crude oils of the Sonda de Campeche showed no primary migration fractionation effect (Clegg et al., 1998b). These different observations possibly indicate the influence of the mineral matrix of the source rock on the distribution of carbazoles.

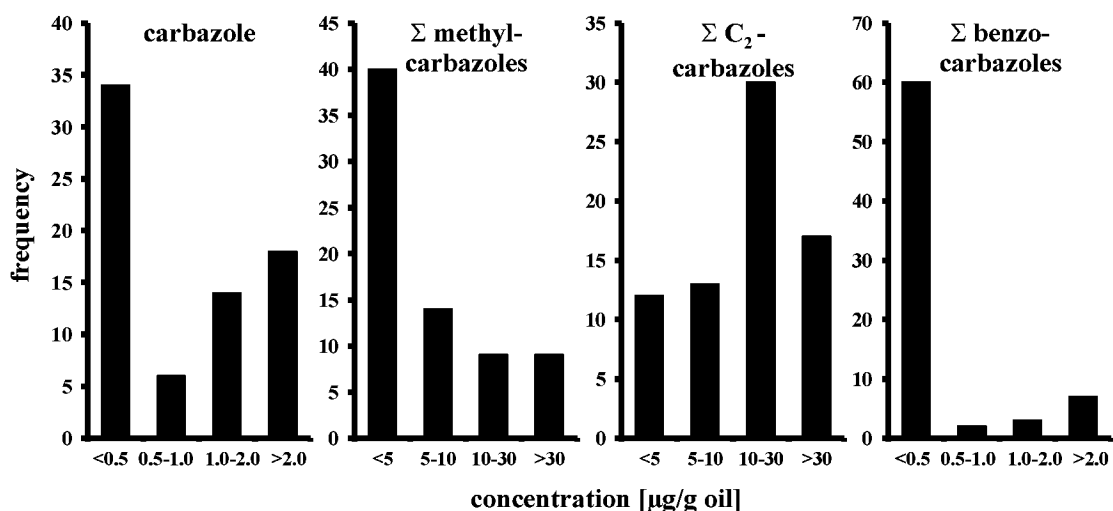


Fig. 5.2.2 Histograms showing the concentrations of carbazoles in crude oils from offshore Norway.

Although most (75%) of the oils had summed C₁- and C₂-alkylcarbazole concentrations of 30 µg/g oil or less, some oils were clearly enriched in these compounds. Table A4 in the appendix shows that many of these enriched oils are from the Heidrun Field (Haltenbanken) and are mostly biodegraded oils depleted in hydrocarbons. This depletion results in a relative increase in NSO content and consequently an enrichment of the carbazoles.

Hydrous pyrolysis experiments

The concentrations of carbazoles in expelled oils and recovered rock extracts resulting from the hydrous pyrolysis of an immature source rock from the Ghareb Formation vary over a broad range. As illustrated in Figure 5.2.3 the amounts of the different isomer groups range from 3 to 224 µg/g oil for the oils and from 6 to 788 µg/g extract for the recovered rock extracts. Clegg et al. (1998a) performed a similar hydrous pyrolysis study using the same immature source rock and reported similar concentrations of carbazole and benzocarbazoles but lower levels of the C₁- and C₂-alkylcarbazoles. The relative abundance of the different isomer groups for the oils and

the extracts was in the order benzocarbazoles < carbazole < C₁-carbazoles < C₂-carbazoles, and was similar to that described by Clegg et al. (1998a). The influence of maturity on the concentrations of carbazoles will be discussed in Section 5.2.4.

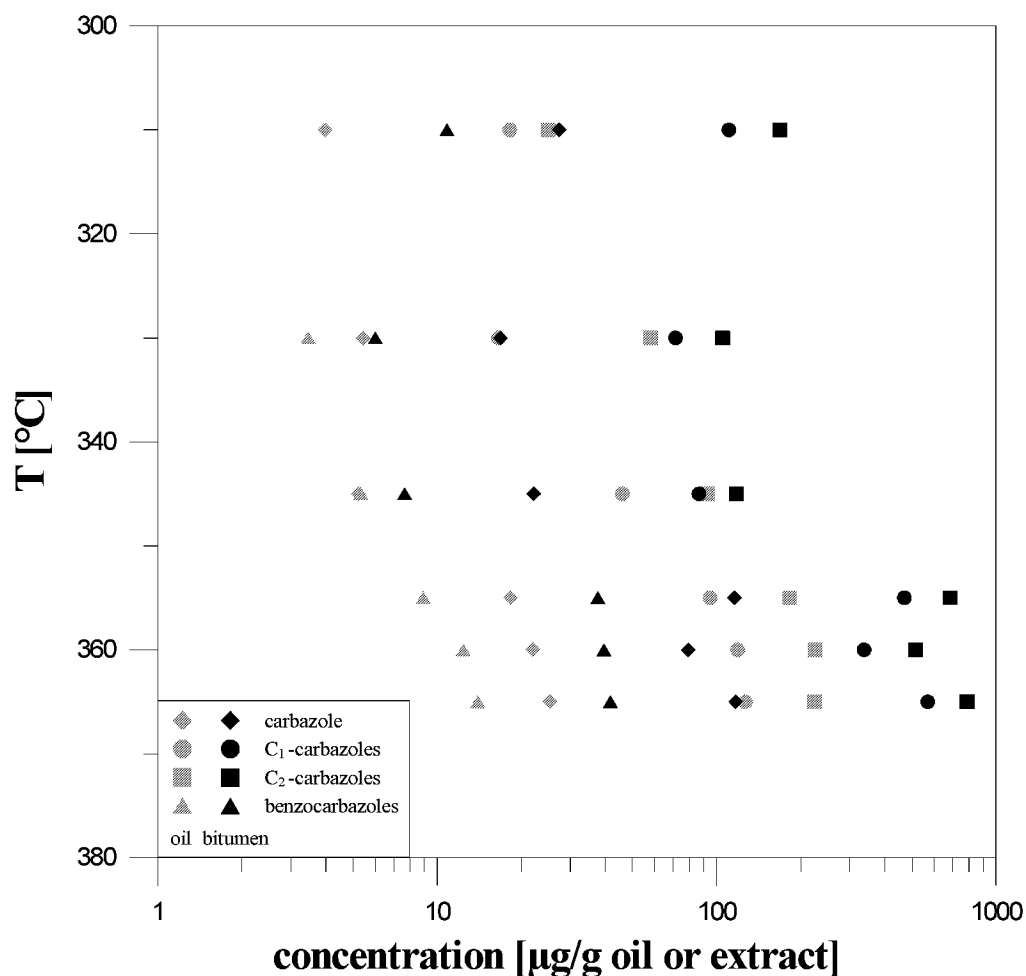


Fig. 5.2.3 Concentrations of carbazoles in oils and extracted bitumens resulting from the hydrous pyrolysis of an immature source rock from the Ghareb Formation, Jordan (note the logarithmic scale on the x-axis).

5.2.3 Influence of facies on the distribution of carbazoles

- HALTENBANKEN -

Source rocks

There are significant differences in the carbazole distributions in the two potential source rocks (Åre and Spekk Fm.) from Haltenbanken as illustrated by the representative mass chromatograms in Figure 5.2.4. The extracts from the Åre Fm. are dominated by benzocarbazoles and carbazole, whereas C₁- and C₂-carbazoles dominate the carbazole distribution of the extracts from the Spekk Fm. In addition, benzo[*b*]carbazole is clearly enriched in the coaly Åre Fm. in comparison to the Spekk Fm. which has only minor proportions of benzo[*b*]carbazole.

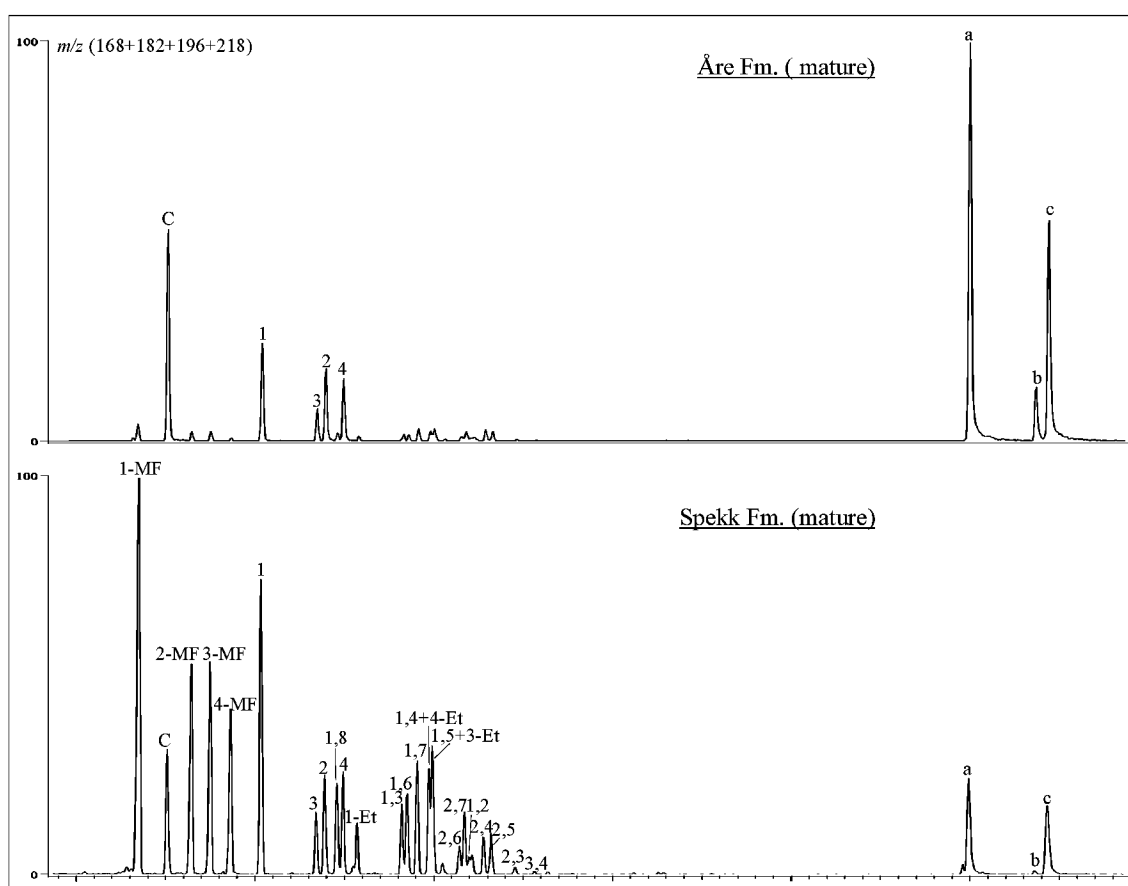


Fig. 5.2.4 Mass chromatograms illustrating the distribution of carbazoles in the extracts from mature Åre and Spekk Fm. source rocks from the Haltenbanken area (measured in CI mode); C = carbazole; x-MF = methylfluorenones; x-Et = ethylcarbazoles; x = methylcarbazoles; x,y = dimethylcarbazoles; a, b, c = benzocarbazoles; numbers indicate alkylcarbazoles with alkyl group position.

The relatively high signals of methylfluorenones (MF) [$M^+ + 1 = m/z$ 195] in the extracts from the Spekk Formation, illustrated in the lower mass chromatogram of

Figure 5.2.4, are due to the ^{13}C satellite (m/z 196) of the methylfluorenones and reflect the high abundance of these compounds in this sample.

The predominance of the benzo-carbazoles in the source rock extracts from the Åre Formation and of the methylcarbazoles in those from the Spekk Formation is illustrated in the triangular plot of carbazole, sum of methylcarbazoles and benzocarbazoles (Fig. 5.2.5). The Spekk and Åre Fm. samples remain clearly distinguishable from each other over the broad maturity range covered by the suite of samples.

The second important difference between these two potential source rocks is the higher relative abundance of benzo[*b*]carbazole compared to total benzocarbazoles in the coaly Åre Formation, as illustrated in Figure 5.2.6. A similar observation has been reported for Westphalian

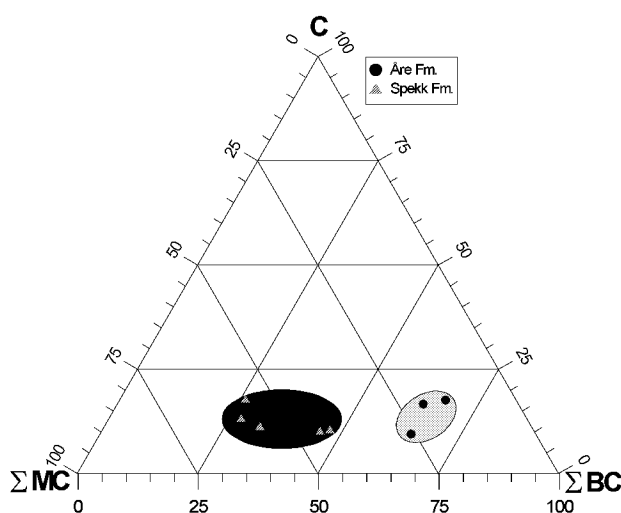


Fig. 5.2.5: Triangular plot showing the differences of the carbazole group distribution of the two potential source rocks from the Haltenbanken area.

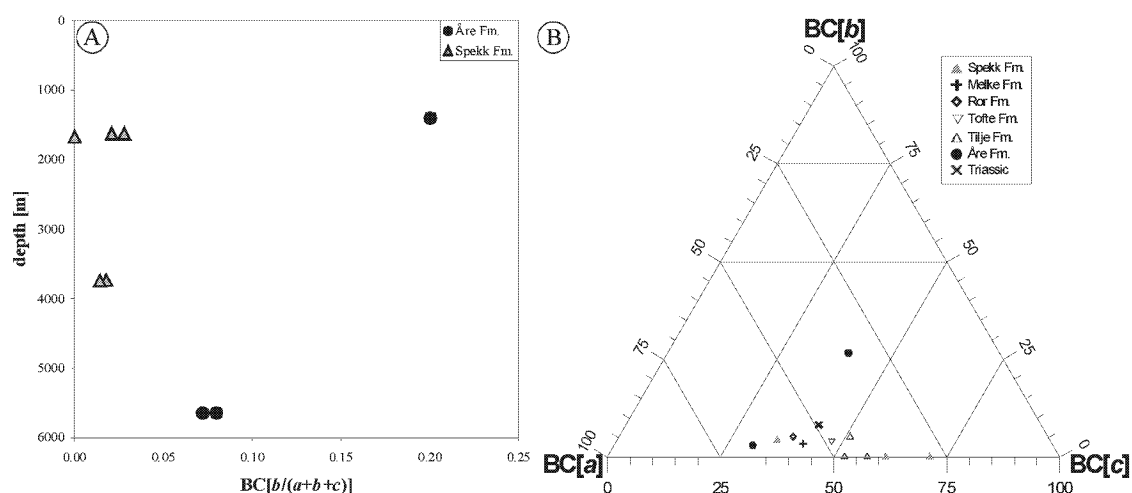


Fig. 5.2.6: A: Relative abundance of benzo[*b*]carbazole in the two potential source rocks; B: Triangular plot showing the relative abundance of benzocarbazoles in additional samples from other source rock formations in the Haltenbanken area.

coals (Harrison et al., 1997). The decrease in the relative abundance of the *b*-isomer with increasing maturity, seen especially for the Åre Fm., is in accordance with the relative stabilities of the three isomers (i.e. $c > a > b$) as derived from molecular mechanics calculations (Harrison et al., 1997). As the *b*-isomer is the most unstable one, it is remarkable that high relative abundances of this isomer were detected in the very mature source rocks of the Åre Formation. Whereas the *a*- and *c*-isomers occur in both marine and terrigenous organic matter the *b*-isomer seems only to be associated with terrestrial organic matter (Oldenburg et al., 1999), and a contribution from terrestrial sources should be recognisable in the geochemical composition of the crude oils.

Additional source rock samples from other formations (Upper Jurassic to Triassic) in the Haltenbanken area were analysed in order to exclude other possible contributors to the expelled crude oils. The ternary diagram in Figure 5.2.6.B shows the percentage of benzo[*b*]carbazole in the different formations. Apart from the Spekk Fm. the *b*-isomer was generally either absent or occurred in very low concentrations in the other formations, the exception being one source rock from the Åre Fm. in which benzo[*b*]carbazole occurred with a relative abundance of more than 26%. This supports the assumption that higher relative amounts of this isomer are associated with terrigenous organic matter.

A comparison of the methylcarbazole isomer distributions for the two source rocks is shown in the ternary plot (Fig. 5.2.7) first published by Li et al. (1995) in order to distinguish NH-shielded (1-MC) and NH-exposed (2-, 3-, 4-MC) carbazoles. The diagram reveals clear differences between the two source rocks. The relatively low abundance of 1-methylcarbazole in source rock bitumens compared to crude oils has been attributed to the selective retention of non-shielded isomers during petroleum expulsion (Li

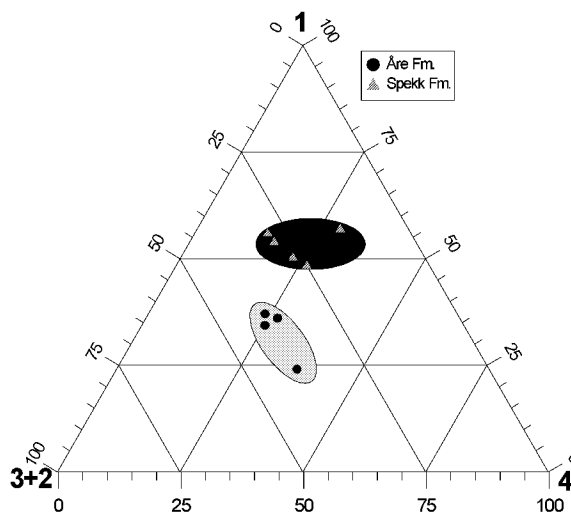


Fig. 5.2.7: Ternary plot illustrating the distribution of the methylcarbazole isomers in the potential source rocks from Haltenbanken (diagram after Li et al., 1995).

et al., 1995), but later investigations (Clegg et al., 1997, 1998a; Horsfield et al., 1998) did not support this hypothesis, but instead facies and maturity influences were recognised. Whereas the Spekk Fm. samples are enriched in (shielded) 1-methylcarbazole, the source rocks from the Åre Fm. have higher abundances of the 3- and 2-isomers. A clear maturity dependence of the methyl carbazole distributions is not observed for the two source rocks analysed in this study although the most mature source rocks in both formations are slightly depleted in 4-methylcarbazole. As the sample suite is limited and comprises a wide maturity range, catagenetic processes could compensate an earlier increase in the abundance of the shielded isomer.

The relative abundance of 1-methylcarbazole to carbazole also discriminates the two source rocks. As illustrated in Figure 5.2.8, the concentration of the 1-isomer is higher than that of the unsubstituted carbazole in all samples from the Spekk Fm. whereas the source rocks from the Åre Fm. are enriched in carbazole. The influence of maturity seems to be opposite for the two source rocks, the relative abundance of 1-MC decreasing with increasing maturity

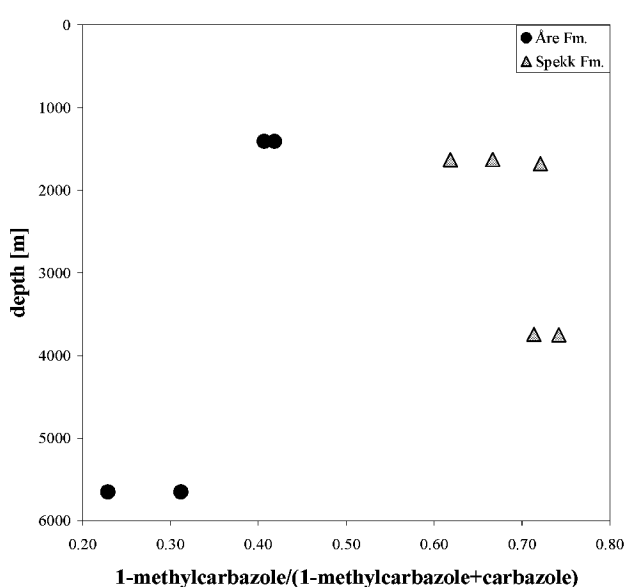


Fig. 5.2.8: Discrimination of the two source rocks using the relationship of 1-methylcarbazole to carbazole.

in the Åre Fm. and increasing slightly in the Spekk Fm. A more detailed discussion of maturity effects on carbazoles distributions will be given in the next section.

The two source rocks can also be discriminated by the relative abundances of the dimethylcarbazoles. Figure 5.2.9 shows a triangular plot of the relative abundances of selected C₂-carbazoles. Clegg et al. (1998b) reported an increase of 1,8-dimethylcarbazole with increasing maturity for the clastic Posidonia Shale. In the present study, the three samples from the Spekk Fm. with highest T_{max} values also contain the highest abundances of the 1,8-isomer whereas such a maturity effect could not be observed for the Lower Jurassic coaly samples. Irrespective of maturity, the Upper Jurassic source rock contains slightly higher concentrations of 1,3-

methylcarbazole compared to the coaly samples whereas the extracts from the Åre Fm. are clearly enriched in 2,4-dimethylcarbazole.

These observations will be used to estimate the source of the crude oils in the Haltenbanken area in the next section.

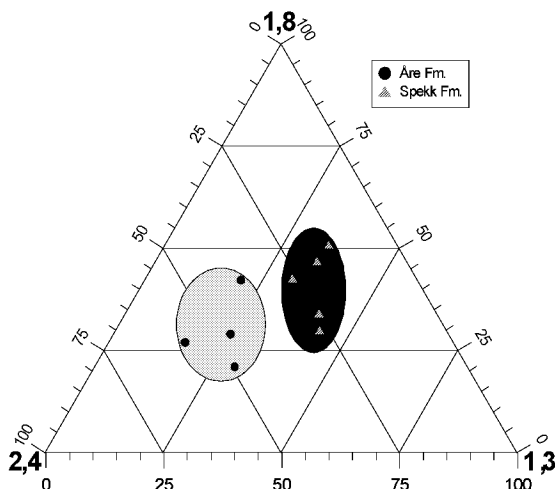


Fig. 5.2.9: Ternary diagram of dimethylcarbazoles illustrating the differences between the two potential source rocks from Haltenbanken.

Crude oils

As described in the previous section the benzocarbazoles are extremely depleted relative to the alkylcarbazoles in all crude oils in comparison to their clastic source rocks (Fig. 5.2.10). This shift to lower relative concentrations of benzocarbazoles is suggested to be a fractionation effect of primary and secondary migration, i.e. the tetracyclic compounds are more strongly retained during expulsion and migration in comparison to the tricyclic compounds. As the relative percentage of benzocarbazoles is less than 3% (with the exception of the Trestakk oil (8%)), it is not possible to determine the relative contribution made by individual source rocks to the reservoired oils.

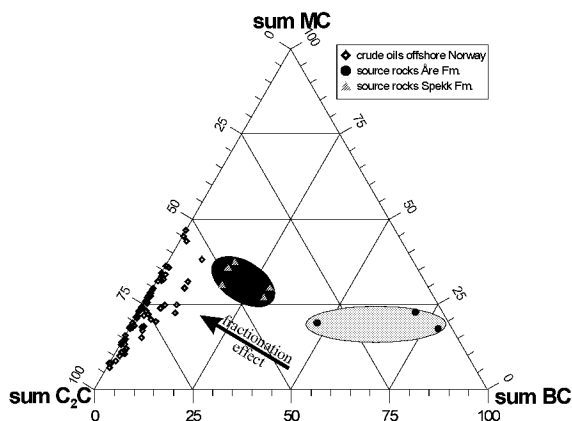


Fig. 5.2.10: Ternary plot illustrating the distributions of alkylated carbazoles and benzocarbazoles.

The *a*- and *c*-isomers of the benzocarbazoles are suggested to be generated from both marine and terrestrial organic matter whereas the *b*-isomer is associated with

terrigenous organic matter as described above. The ternary diagram in Figure 5.2.11 shows the distribution of the benzocarbazoles in the oils from Haltenbanken. Some oils from the Heidrun Field and the oils from the Midgard Field contain very low amounts of benzocarbazoles and are not depicted in the figure. Relatively high abundances of the *b*-isomer were detected in the oils from the Alve Field and the Smørbukk Field, and in some oils from the Heidrun Field. These observations suggest a supply from the coaly Åre Fm.

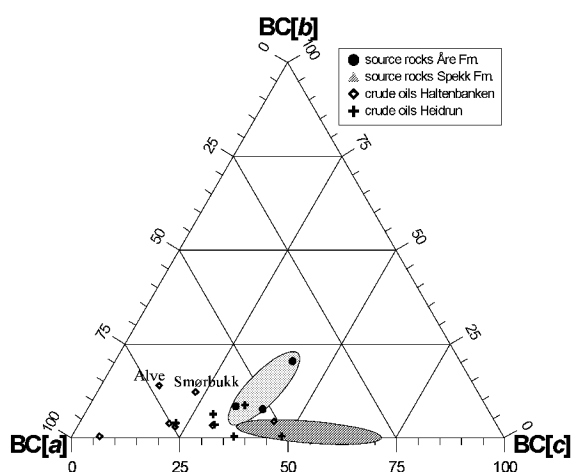


Fig. 5.2.11: Ternary plot showing the distributions of benzocarbazoles in crude oils and source rock extracts from the Haltenbanken area.

As shown in the previous section, the source rocks of the Spekk Fm. are characterised by high relative abundances of the 1-MC isomer whereas the coaly samples of the Åre Fm. are enriched in the 2- and 3-methylcarbazoles. The diagram in Figure 5.2.12.A compares the methylcarbazole compositions of the crude oils and

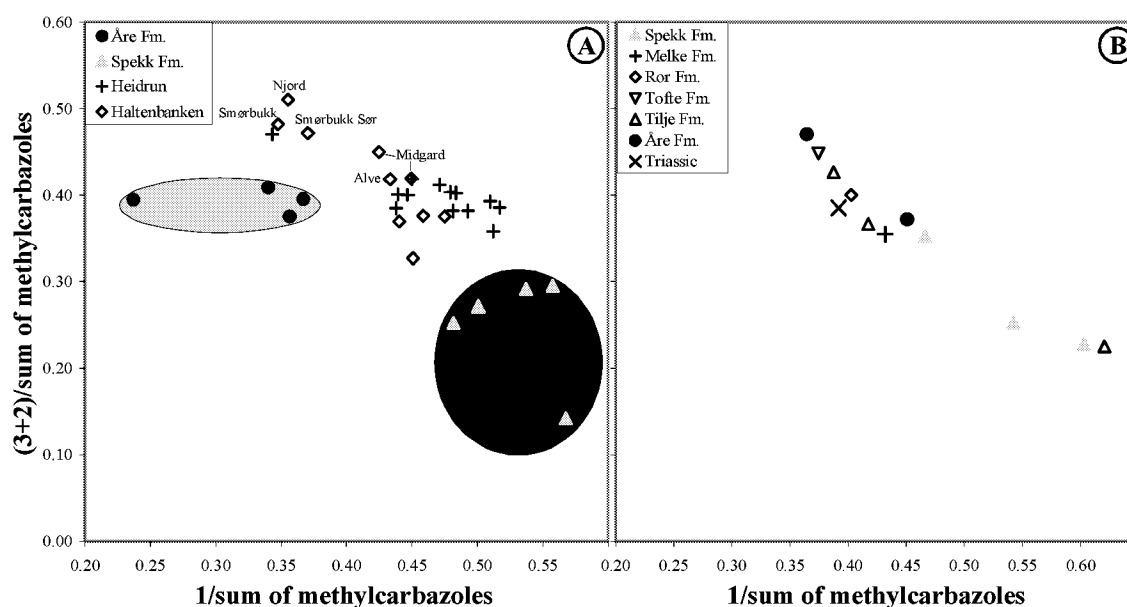


Fig. 5.2.12: Plots showing the relative distribution of methylcarbazoles in crude oils and source rocks from Haltenbanken (A) and in additional source rock samples from other formations (Upper Jurassic to Triassic) (B).

source rocks from the Haltenbanken area. The relative abundance of the sum of 2- and 3-methylcarbazole is higher in all oils in comparison to the source rocks from the Spekk Fm. The highest abundances were observed for the oils from Smørbukk, Smørbukk Sør and Njord, and for one oil from Heidrun. Considering also the relatively low abundance of 1-methylcarbazole, these oils may be sourced at least partly from the coal source rock. In addition, the Åre Fm. may contribute partly to the oils from Midgard and Alve. The methylcarbazole ratios in the pre-Spekk source rocks from Haltenbanken, illustrated in Figure 5.2.12.B, vary between those typical of the Åre Fm. and those typical of the Spekk Fm., but previous studies (Brian Horsfield, personal communication) have shown that only the Ror Fm. is considered a very good oil source locally. The methylcarbazole ratios of the additional samples from the Spekk and Åre Formations confirm previous data.

Correlation of 1,3- to 2,4-dimethylcarbazole and 1- to 4-methylcarbazole ratios with the pristane/phytane ratio for the non-biodegraded oils from the Haltenbanken area (Fig. 5.2.13.A, B) indicates that these carbazole isomer ratios are slightly affected by facies and depositional environment. The partly biodegraded and long-distance migrated oils from the Heidrun Field are characterised by higher carbazole ratios compared to the non-degraded oils from Haltenbanken with similar isoprenoid ratios. Three oils from well 6507/8-4 are not included in Fig. 5.2.13 due to lack of isoprenoids but they also have high values of the carbazole ratios. An explanation as to why biodegraded oils are enriched in shielded isomers in comparison with non-shielded isomers will be given in the following sections. However, it must be remembered that the pristane to phytane ratio is not useful in differentiating the Åre and Spekk Formations (see Figure 5.1.45). The concentration of 1,8-dimethylcarbazole relative to that of 1-ethylcarbazole was reported to increase with increasing maturity both for the Posidonia Shale and the petroleum system of the Sonda de Campeche (Clegg et al., 1998b; Wilkes et al., 1998a). More recently, Bakr and Wilkes (2002) have shown in a study from the Gulf of Suez that this parameter is also sensitive to facies and depositional environment. For the non-degraded oils from Haltenbanken only a weak correlation is observed (Fig. 5.2.13.C) suggesting that other geochemical processes may control this ratio. This will be discussed in the following sections. The 1,8- to 1,3-dimethylcarbazole ratio has been described as a maturity-related parameter in marine carbonate source rocks from the Western Canada Basin (Li et al., 1997). This ratio also shows no facies dependence for

the oils from Haltenbanken (Fig. 5.2.13.D) although a correlation is noted in oils from other areas offshore Norway as discussed below.

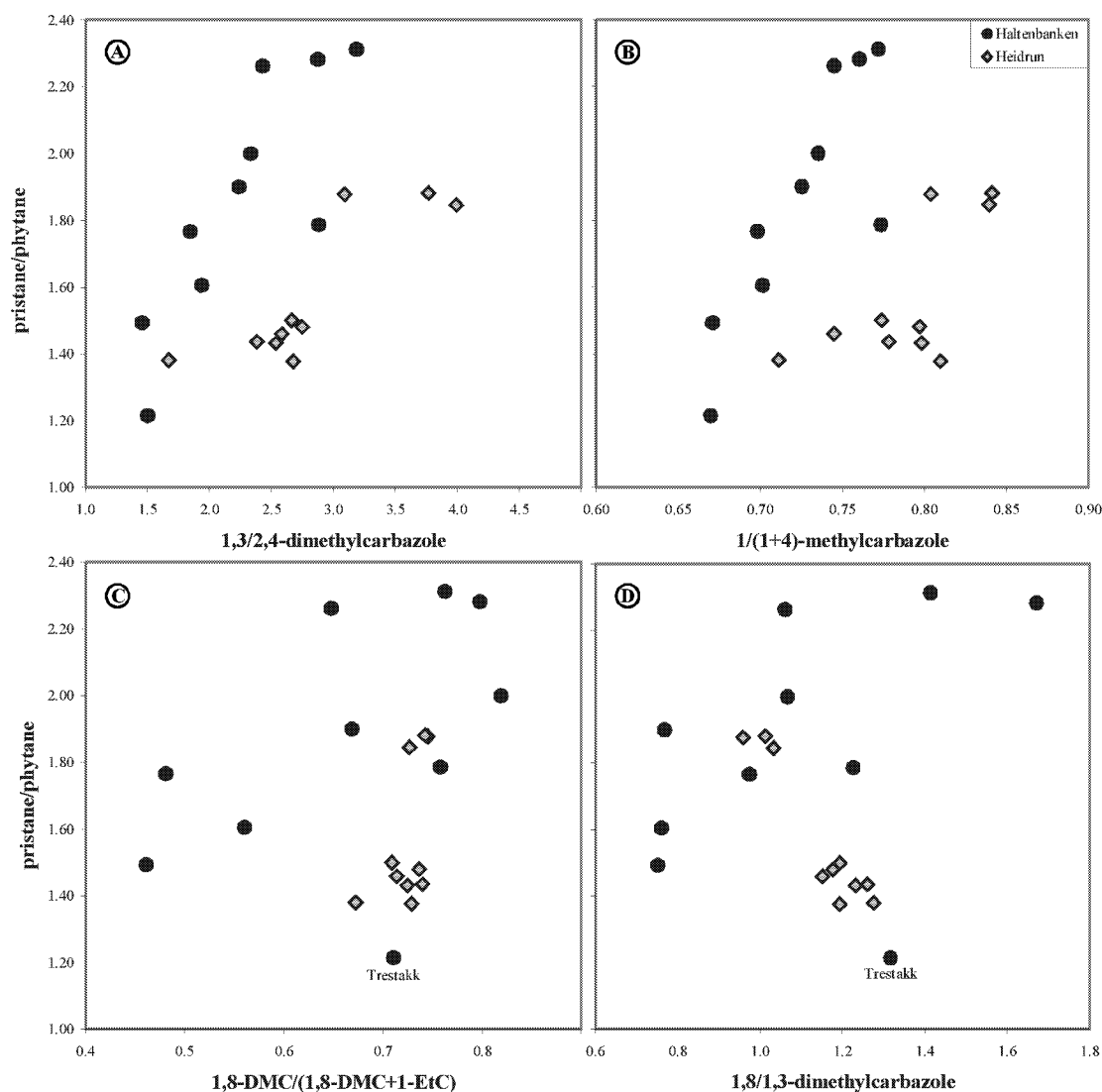


Fig. 5.2.13: Plots illustrating the facies and depositional environment dependence of the carbazole distributions in oils from the Haltenbanken area.

- TAMPEN SPUR -

The 28,30-*dinor*-hopane to 30-*nor*-hopane ratio (DNH/30NH) is a useful tool to differentiate the oil families in the Tampen Spur area, North Sea (Figure 5.1.12). More terrestrially influenced source organic matter is depleted in 28,30-*dinor*-hopane (e.g. Karlsen et al., 1995). The cross plot shown in Figure 5.2.14.A illustrates the facies dependence of the relative abundance of benzo[*b*]carbazole in oils from the Tampen Spur area. Generally, the relative abundance of the *b*-isomer is low. Eight crude oils are

not depicted in the diagram because their *b*-isomer content was below the detection limit, and four oils from the Snorre Field and the Statfjord Nord Field contain only very low concentrations of this isomer. However, some oils, especially those which are thought to be mixed oils from the Heather and Draupne Formations (e.g. Rimbaks, Gullfaks Sør and Visund Fields), are enriched in benzo[*b*]carbazole. For these crude oils the relative abundance of the *b*-isomer increases with increasing terrigenous character.

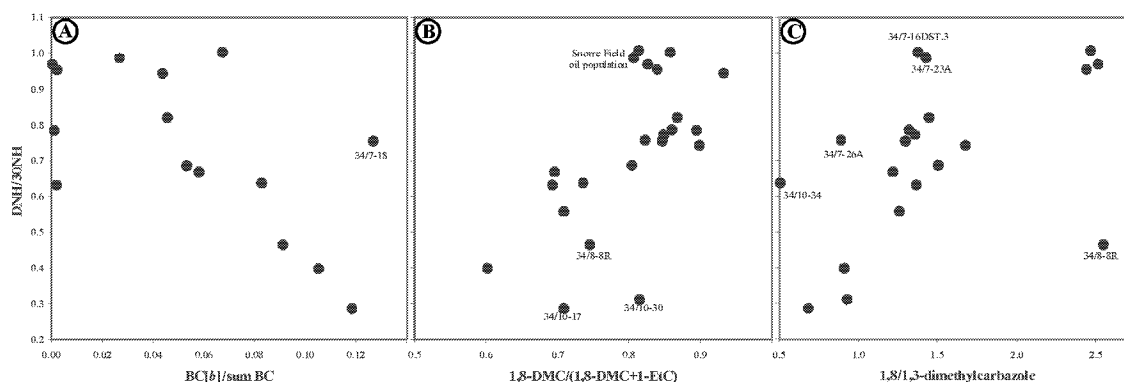


Fig. 5.2.14: Plots showing the facies dependence of different carbazole ratios for crude oils from the Tampen Spur.

With the exception of oils from the Snorre Field and oils from fields located to the south of the Tampen Spur, the ratio of 1,8-dimethyl- to 1-ethylcarbazole increases with increasing relative abundance of 28,30-*dinor*-hopane and, therefore, with increasing marine imprint on the source rocks (Fig. 5.2.14.B). This is in contrast to the tentative trend observed for the oils from Haltenbanken. Thus, it is suggested that this ratio is not controlled by facies in the oils from Haltenbanken. In addition, the abundance of 1,8-dimethylcarbazole decreases relative to that of the 1,3-isomer with increasing terrestrial organic matter supply, as shown in Figure 5.2.14.C. This is also at variance with the tentative trend observed for the Haltenbanken oils. Therefore, it is assumed that the relative abundance of 1,8-dimethylcarbazole in the Haltenbanken oils is not facies dependent. As noted above, the ratio of 1,8- to 1,3-dimethylcarbazole has been described as maturity dependent in marine carbonate petroleum source rock extracts from the Upper Devonian Duvernay Formation in the central Alberta portion of the Western Canada Sedimentary Basin (Li et al., 1997).

– VIKING GRABEN ISOLATED OILS –

The different facies and depositional environments of the Viking Graben are best described by the 25-*nor*-hopane/(25-*nor*-hopane+30-*nor*-hopane) ratio and the pristane to phytane ratio, as shown in Chapter 5.1.1. Whereas the isoprenoid ratio increases with increasing supply of terrigenous organic matter, the *nor*-hopane ratio decreases. The 1,8-dimethylcarbazole to 1-ethylcarbazole ratio correlates strongly with the *nor*-hopane

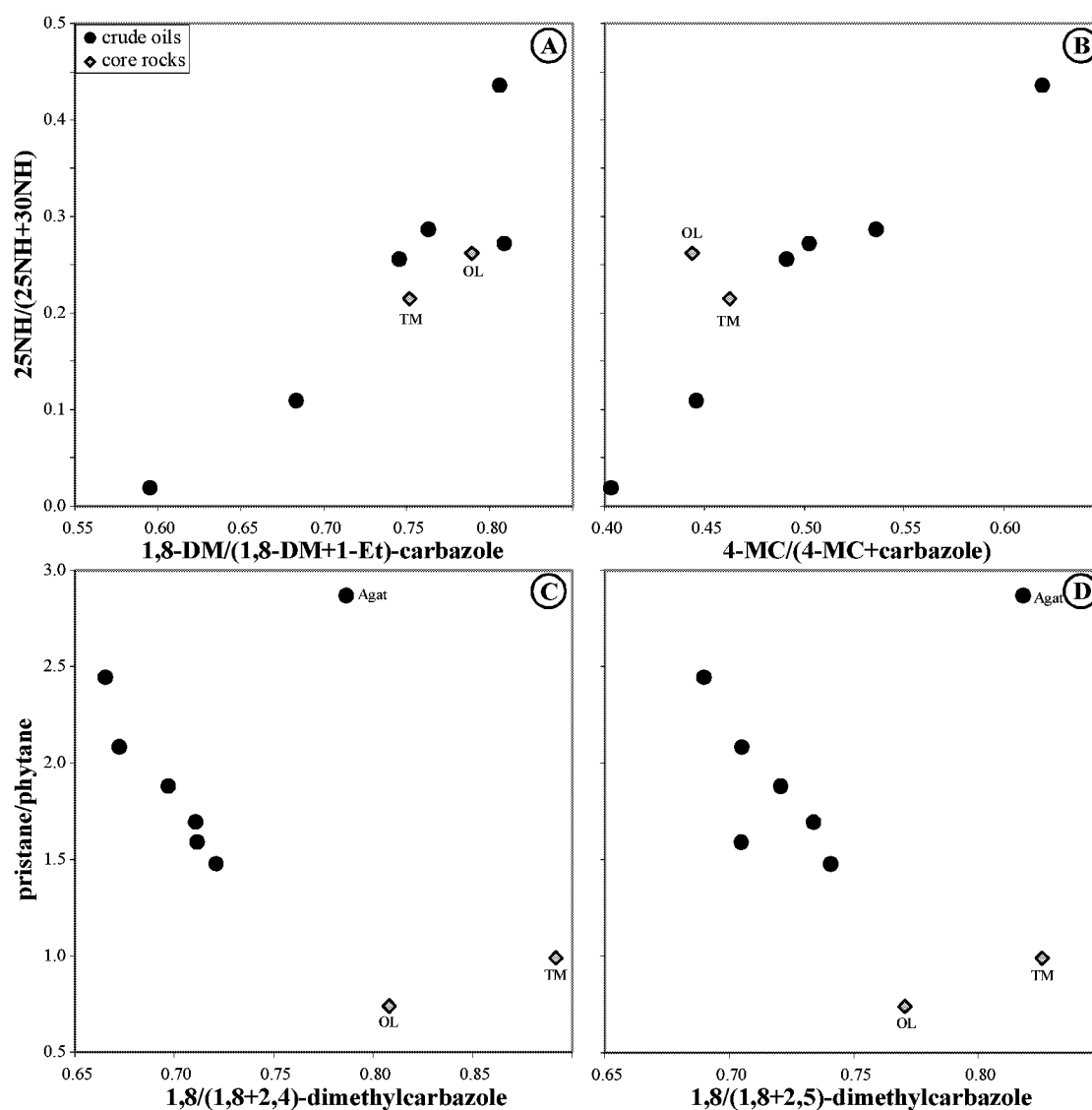


Fig. 5.2.15: Facies dependence of carbazoles in crude oils and reservoir rocks from the Viking Graben satellites.

ratio (Fig. 5.2.15.A) in accordance with the trend observed for the Tampen Spur oils. This C_2 -carbazole ratio has previously been shown to be positively correlated with maturity up to $\sim 1.1\%$ vitrinite reflectance (Clegg et al., 1998b; Wilkes et al., 1998a) both for the Posidonia Shale and the petroleum system of the Sonda de Campeche. A

more recent study from the Gulf of Suez showed that this parameter is also controlled by facies and depositional environment (Bakr and Wilkes, 2002). The ratio of 4-methylcarbazole to carbazole was reported to increase with increasing maturation up to 0.88% vitrinite reflection for the Posidonia Shale (Clegg et al., 1997). The authors suggested that the methyl homologues may be formed through alkylation of the parent compound and interconversion of isomers, as suggested previously for alkyldibenzothiophenes (Radke et al., 1982), phenanthrenes (Alexander et al., 1995) and phenols (Ioppolo-Armanios et al., 1995). As illustrated in Figure 5.2.15.B, this ratio seems also to be influenced by facies and depositional environment.

Whereas no trend was observed between facies dependent parameters and either the percentage of benzo[*b*]carbazole or the ratio of 1,8/1,3-dimethylcarbazole, the dimethylcarbazole ratios (1,8/2,4 and 1,8/2,5) illustrated in Figure 5.2.15.C, D indicate that the relative abundances of 1,8- to 2,4-, and 1,8- to 2,5-dimethylcarbazole correlate strongly with the pristane/phytane ratio. Thus, for the Viking Graben isolated oils these two ratios seem to be dependent on facies and the depositional environment within the Draupne Fm. The condensate from the Agat Field does not follow this trend and may reflect a different source, i.e. a more terrestrially influenced source rock in the Heather Formation. Whereas the oil leg sample fits with the general trend, the tar mat sample is considerably enriched in 1,8-dimethylcarbazole. This could be an effect of water washing and/or biodegradation because the analysed tar mat is located in the Oseberg Field at the top of the Etive Formation in delta front sandstones, close to the oil-water contact (Wilhelms and Larter, 1994a). The presence of the two methyl groups adjacent to the polar function in the 1,8-isomer reduces the polarity in comparison to the non-shielded isomers (2,4- and 2,5-dimethylcarbazole). Therefore, the non-shielded isomers are more water soluble and thus more bioavailable. In addition, proposed biodegradation pathways favour initial dioxygenation adjacent to the polar function, in which case the degradation of 1,8-dimethylcarbazole would be more difficult due to steric hindrance. These effects will be discussed in detail in the following sections.

5.2.4 Influence of maturity on the distribution of carbazoles

- HALTENBANKEN -

Source rocks

The abundances of the different carbazole groups in the source rock extracts from Haltenbanken clearly depend on maturity, there being a log-linear correlation with depth (Fig. 5.2.16). The more mature source rocks of the Åre and Spekk Formations are highly enriched in the carbazole derivatives irrespective of differences in facies. The concentrations of carbazole, the sum of C₁-carbazoles, the sum of C₂-carbazoles, and the benzocarbazoles in the source rocks from the Sonda de Campeche were previously reported to decrease between 0.36 and 0.81% vitrinite reflectance, after which there was an abrupt increase with maximum values occurring at 1.09% R_r (Clegg et al., 1998b).

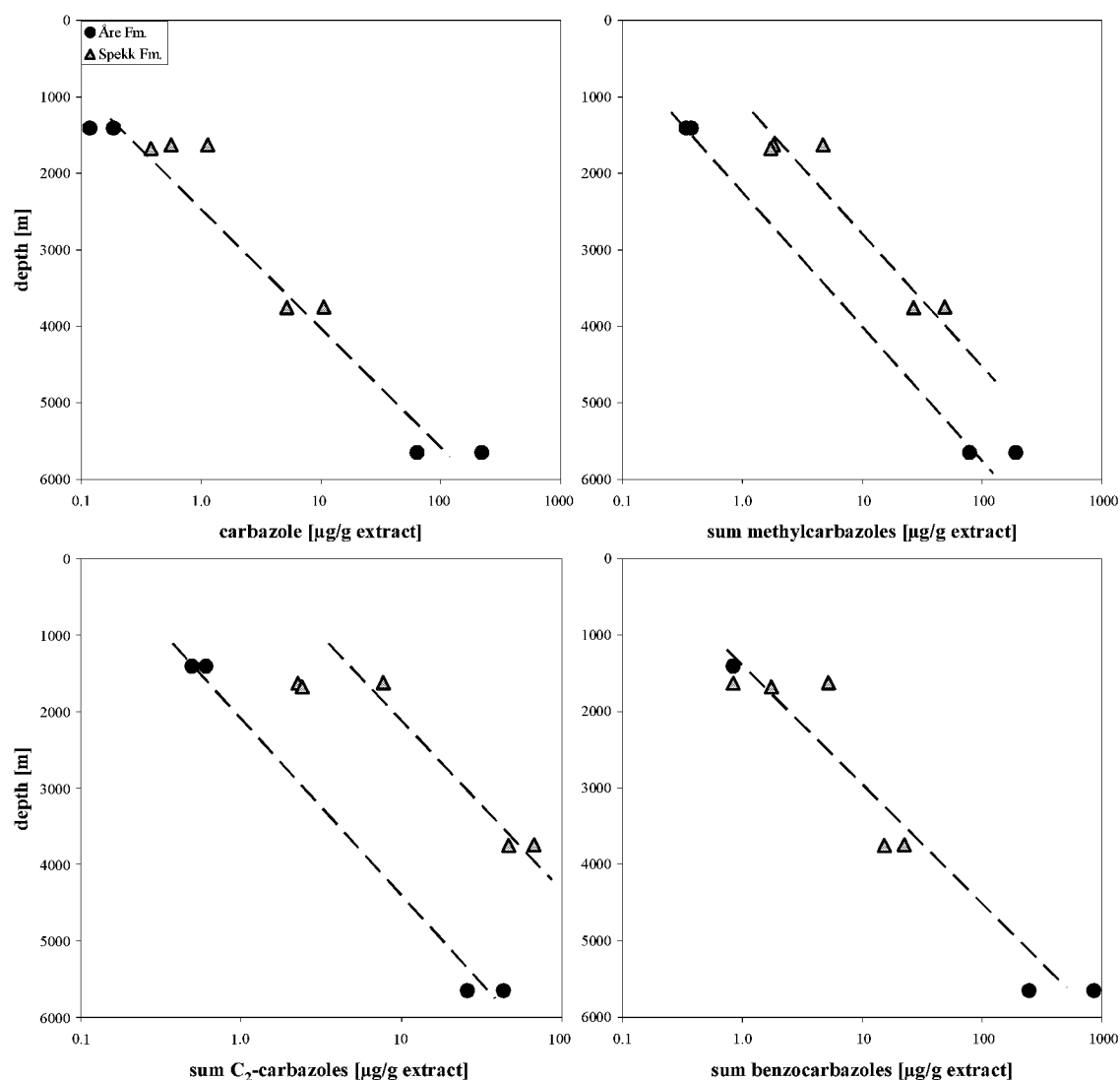


Fig. 5.2.16: Diagrams illustrating the maturity dependence of the different carbazole groups for the source rocks in the Haltenbanken area (note the logarithmic scale on the x-axis).

The authors concluded that intense generation and selective retention of carbazoles occurred between 0.9 and 1.1% R_r . A comparison with the results of the present study is not possible because only the mature samples from the Spekk Fm. fall within this maturity range. Although the sampling frequency over the depth/maturity range is very low, it appears that the concentrations of carbazoles increase steadily with increasing maturity in the range 0.3 to 2.0% R_r (Fig. 5.2.16).

An increase in the abundance of 2-methylcarbazole relative to the 3- and 4-methylcarbazole isomers with increasing maturity is observed for the extracts from mature source rocks from both the Åre and the Spekk Formation as shown in Figure 5.2.17.A, B. Clegg et al. (1997) described a similar maturity-related trend in the

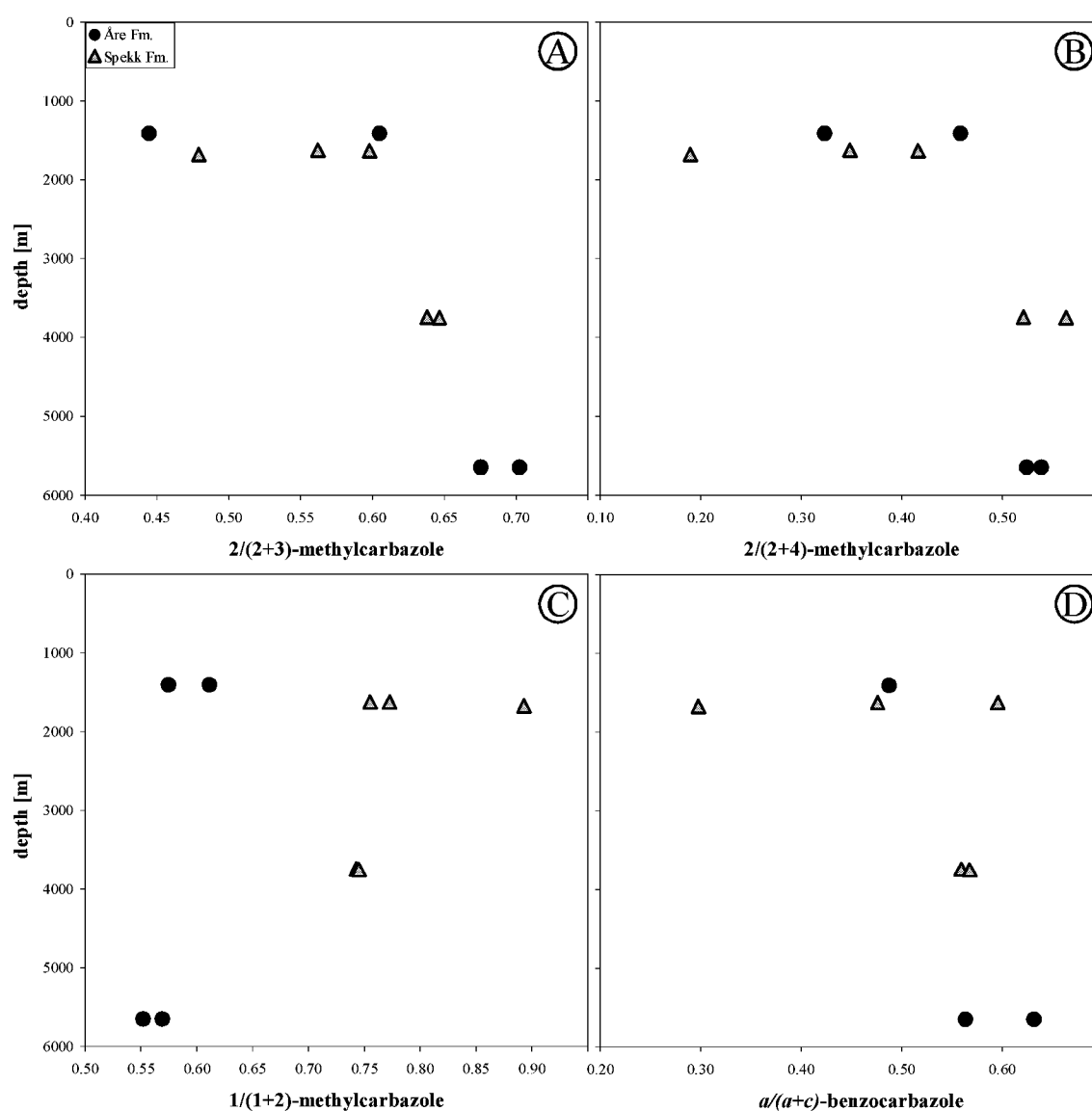


Fig. 5.2.17: Maturity dependence of methylcarbazole and benzocarbazole isomer ratios in source rock extracts from the Haltenbanken area.

2/(2+3)-methylcarbazole ratio for the Posidonia Shale, but they did not find any correlation for the 2/(2+4)-MC isomer ratio. They also observed a positive correlation of the 1/(1+2)-methylcarbazole ratio with maturity but for the source rocks analysed in the present study this ratio reflects more of a facies than a maturity dependence (Fig. 5.2.17.C). Clegg et al. (1997) also described a systematic increase in the benzo[a]carbazole/ (benzo[a]carbazole + benzo[c]carbazole) ratio with increasing maturity. Figure 5.2.17.D shows that this may also be the case for the source rock extracts from the coaly Åre Formation but the isomer ratio for the immature source rocks from the Spekk Fm. is widely variable such that no conclusions can be drawn concerning maturity dependence.

Crude oils

The maturity dependent variation in the concentration of the carbazole groups described for the source rock extracts was not observed for the crude oils from the Haltenbanken area. No trends could be identified using the proven maturity-related parameters discussed in Chapter 5.1.5. Considering the alkylated carbazoles, the increase in the abundance of 2-methylcarbazole relative to the 3- and 4-isomers with increasing maturity observed in the source rock extracts was not apparent in the oils (Fig. 5.2.18.A, B). In about half of the oils from Haltenbanken the abundance of 2-methylcarbazole relative to that of 1-methylcarbazole seems to decrease with increasing maturity, which is in contrast to the observations made for the source rocks. Other geochemical processes could play an important role in determining alkylcarbazole distributions, and these will be discussed later. In the other oils, the abundance of the methylcarbazoles appears to be independent of maturity (Fig. 5.2.18.C). The oils in which there is no correlation with maturity tend to be the partly biodegraded and mixed oils from the Heidrun Field which have higher 1/(1 + 2)-methylcarbazole ratios. The effect of biodegradation will be discussed later.

Clegg et al. (1997) and Horsfield et al. (1998) demonstrated that the benzocarbazole a/(a+c) ratio in crude oils and source rocks from the Sonda de Campeche and the Posidonia Shale depends on maturity. They observed a systematic increase in this ratio with increasing maturity, followed by an apparent reversal at high maturity. Earlier,

Larter et al. (1996a) proposed that secondary migration is a major control on this ratio for crude oils with restricted maturity ranges. The crude oils from Haltenbanken show no systematic change in the benzocarbazole ratio with increasing maturity, as illustrated in Figure 5.2.18.D.

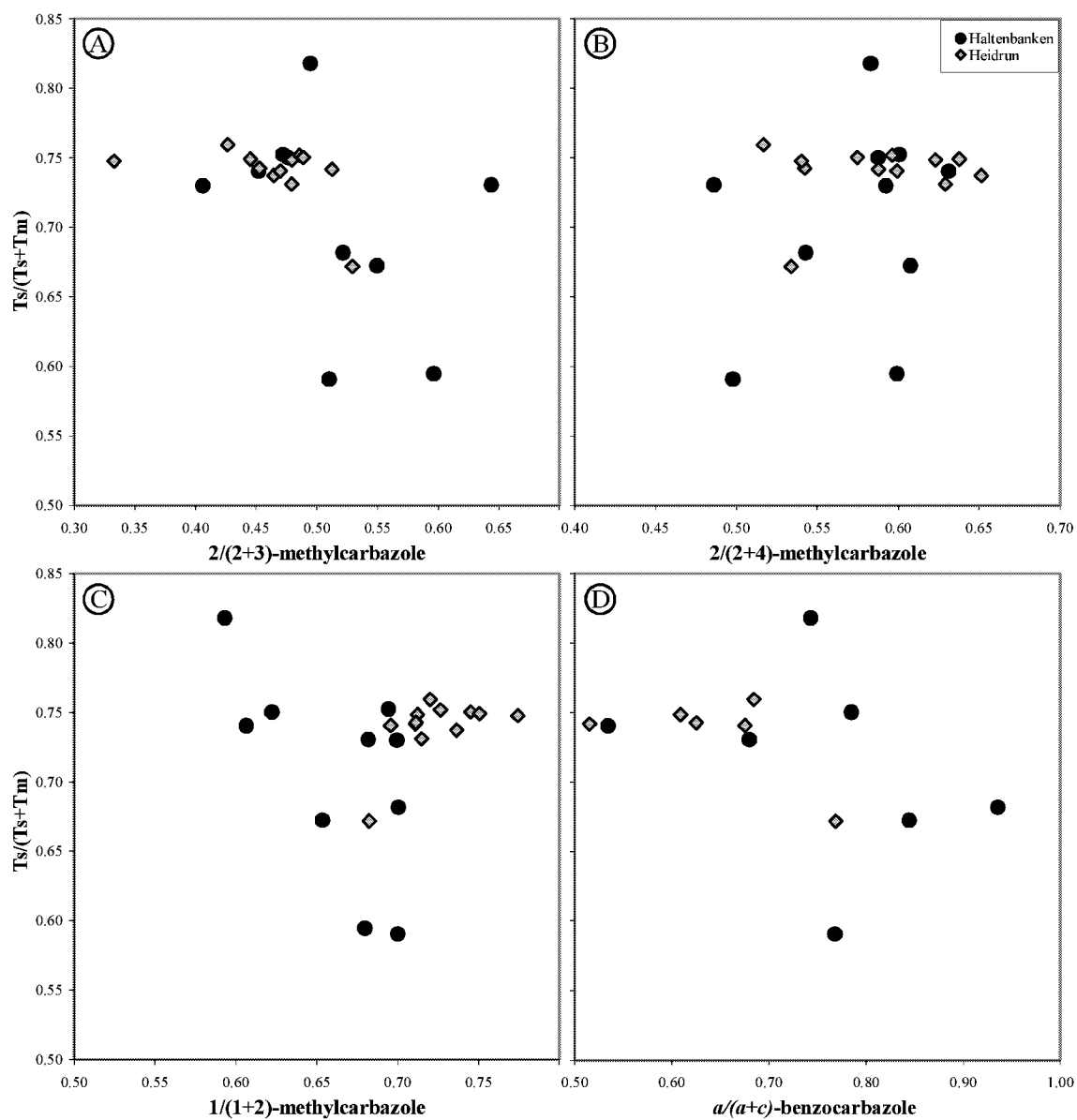


Fig. 5.2.18: Influence of maturity on the carbazole distribution of crude oils from Haltenbanken.

- TAMPEN SPUR -

As revealed in Chapter 5.1.22, the best maturity parameter for the Tampen Spur area are 15α -methyl-27-nor- $17\alpha,21\beta$ -hopane/(15α -methyl-27-nor- $17\alpha,21\beta$ -hopane+30-nor- $17\beta,21\alpha$ -hopane) (DH/(DH+30NM)) and $5\alpha,14\beta,17\beta$ /($5\alpha,14\beta,17\beta$ + $5\alpha,14\alpha,17\alpha$)- C_{29} steranes ($\beta\beta$ /($\beta\beta$ + $\alpha\alpha$) C_{29} steranes). The diagrams in Figure 5.2.19.A, B illustrate the influence of maturity on the concentrations of C_1 - and C_2 -carbazoles in oils from the Tampen Spur area. With the exception of some oils from the southern part of the area (Rimfaks and Gullfaks Sør Fields) which are either sourced from the Heather Formation or are at least mixed oils, and one oil from the Vigdis Field, the concentrations of the alkylcarbazole groups increase systematically with increasing maturity.

The oils from the Tampen Spur showed only a slight increase in the abundance of 2-methylcarbazole relative to 1-methylcarbazole with increasing maturity as illustrated in Figure 5.2.19.C. A similar trend was observed for some of the oils from the Haltenbanken area. Clegg et al. (1997) reported that in source rock extracts of the Posidonia Shale this methylcarbazole ratio increases to a maximum at 0.88% vitrinite reflectance and then decreases. As the oils investigated here are of higher maturity than 0.88% vitrinite reflection the observed negative trend with increasing maturity is in accordance with the previous study.

The Viking Graben isolated oils and the oils from the Central Graben show no correlation between the carbazole distribution and maturity.

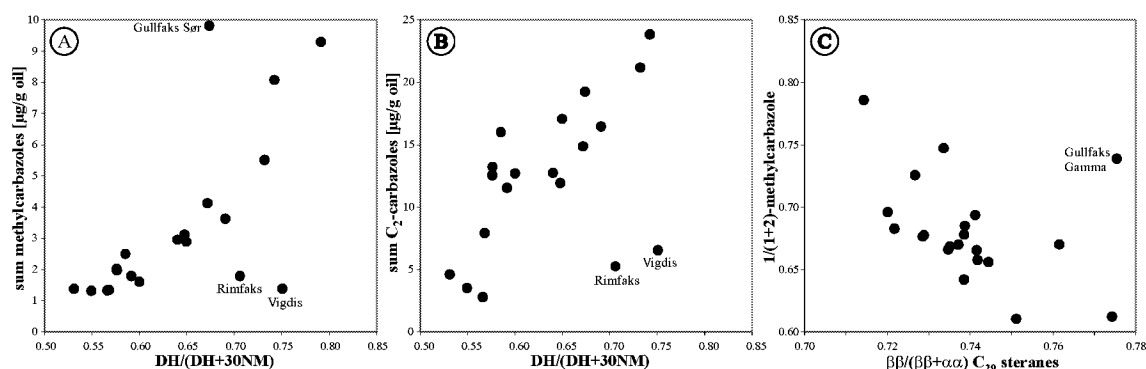


Fig. 5.2.19: Influence of maturity on the distribution of carbazoles in crude oils from the Tampen Spur (DH = $17\alpha,21\beta$ -diahopane; 30NM = 30-nor-moretane; see Table 4.1 and 4.2).

5.2.5 Influence of maturity and primary migration on the carbazole distribution using hydrous pyrolysis experiments

In a previous study Clegg et al. (1998a) investigated the influence of maturity on the carbazole distribution using hydrous pyrolysis experiments. The study was carried out using an immature limestone from the Ghareb Formation at El Lajjun (Jordan), and nine samples were heated isothermally at temperatures from 200 to 360°C (corresponding to *ca.* 0.4 - 1.25% R_r) for 72 h. The authors reported that the concentrations of carbazoles were extremely low in the original sample. At 260°C, along with the first appearance of oil films (Koopmans et al., 1998), higher concentrations were detected but values were still low (Clegg et al., 1998a). From 300°C onwards (*ca.* 0.7% R_r), where the breakdown of kerogen into polar and apolar fractions with subsequent decomposition of the polar soluble fraction and asphaltenes into the apolar fraction takes place (Koopmans et al., 1998), the concentrations of carbazoles increased significantly and

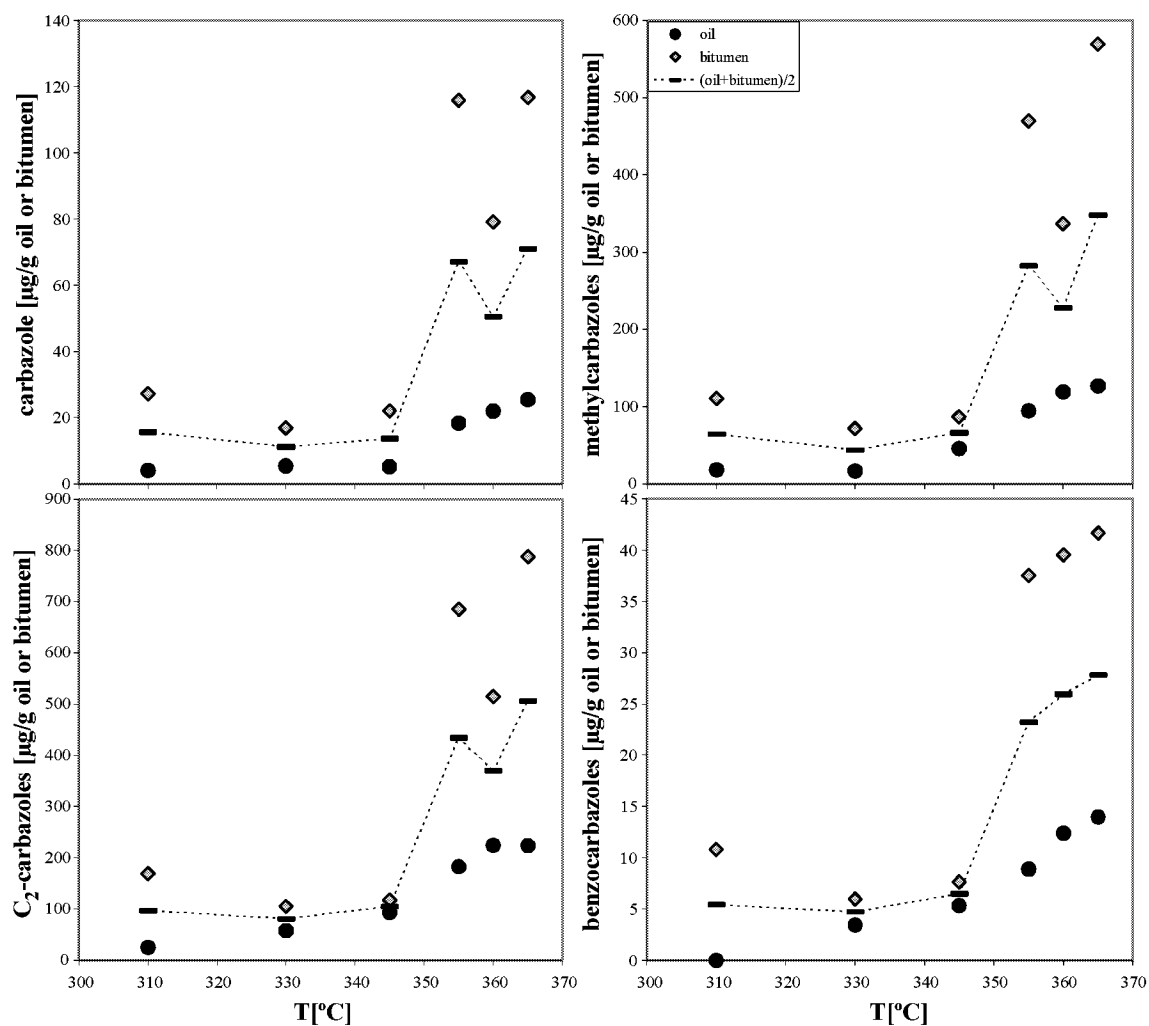


Fig. 5.2.20: Maturity dependence of the concentrations of carbazoles using hydrous pyrolysis experiments.

eventually reached a maximum at 360°C (*ca.* 1.25% R_T) (Clegg et al., 1998a). In the present study the samples were heated from 310 to 365°C (*ca.* 0.8 – 1.3% R_T) at narrower intervals, and the expelled oils and recovered rock extracts were investigated separately. As mentioned in Chapter 5.2.2, the concentrations of the different carbazole groups increased with increasing maturity for both the expelled oils and the recovered rock extracts and amounts were higher in the rock extracts than in the expelled oils (Fig. 5.2.3 and 5.2.20). The summed concentrations of the different carbazole groups in the oils and extracts are very uniform up to 345°C but then abruptly increase to higher values at 355°C. According to Lewan (1985, 1993), the samples heated from 310 to 345°C are at the incipient-oil to primary-oil generation stage whereas the samples heated higher than 350°C are already in the post-oil generation stage. In the post-oil generation stage both the expelled oil and the recovered rock extracts thermally decompose into gas and pyrobitumen. This decomposition of thermally less stable oil and extract components into volatile and macromolecular components (which were not investigated here) may result in a relative enrichment of the thermally more stable aromatic carbazoles. Although the total concentrations of the compound groups are very similar in oils and extracts until 345°C, the differences in the concentrations between the expelled oils and the corresponding recovered rock extracts decrease with increasing temperature. Due to the higher temperatures the pressure within the rocks increases resulting in higher expulsion efficiency.

This effect is strongest for the C_2 -carbazoles, slightly less pronounced for the benzocarbazoles and methylcarbazoles and minor for carbazole. This could indicate a primary migration effect because 8 of the 20 C_2 -isomers analysed (*i.e.* 40%) possess a shielded character whereas only 25% of the monomethyl isomers are shielded, and carbazole itself suffers the greatest retention as it interacts most strongly with the organic matter and mineral matrix of the source rock. The higher the percentage of shielded isomers within a homologue group, the higher is the abundance of the homologue groups in the oil phase. This becomes more obvious looking at the diagrams in Figure 5.2.21. The top diagrams reveal that the concentrations of carbazole and total methylcarbazoles relative to total C_2 -carbazoles are clearly greater in the recovered rock extracts than in the expelled oils. The fractionation effect is greatest at 345°C for the carbazole/total carbazoles ratio whereas fractionation of the alkylated components, as indicated by the C_1/C_2 alkylcarbazole ratio, reaches its maximum at 330°C. The fractionation effect subsequently decreases at higher temperatures due to the strong

increase in the concentrations (Figure 5.2.20) but the ratios continue to be higher in the residual bitumens than in the expelled oils.

The lower diagrams in Figure 5.2.21 show the variation in two ratios of shielded to non-shielded carbazoles. Both diagrams indicate that the oils are enriched in the shielded isomers, with the highest fractionation effect from primary migration occurring at 345°C. After the abrupt increase in the carbazole content of the oils at higher temperatures this enrichment effect disappears. However, in the rock extracts the 1,8-dimethylcarbazole to 4-methylcarbazole ratio increases with increasing maturity above 345°C, indicating a maturity dependence for 1,8-dimethylcarbazole as described by Clegg et al. (1997) and Li et al. (1997). In contrast, the relative abundance of this isomer in the expelled oils decreases or scatters with increasing maturity. The same observation was made for the relative abundance of 1-methylcarbazole. This partly

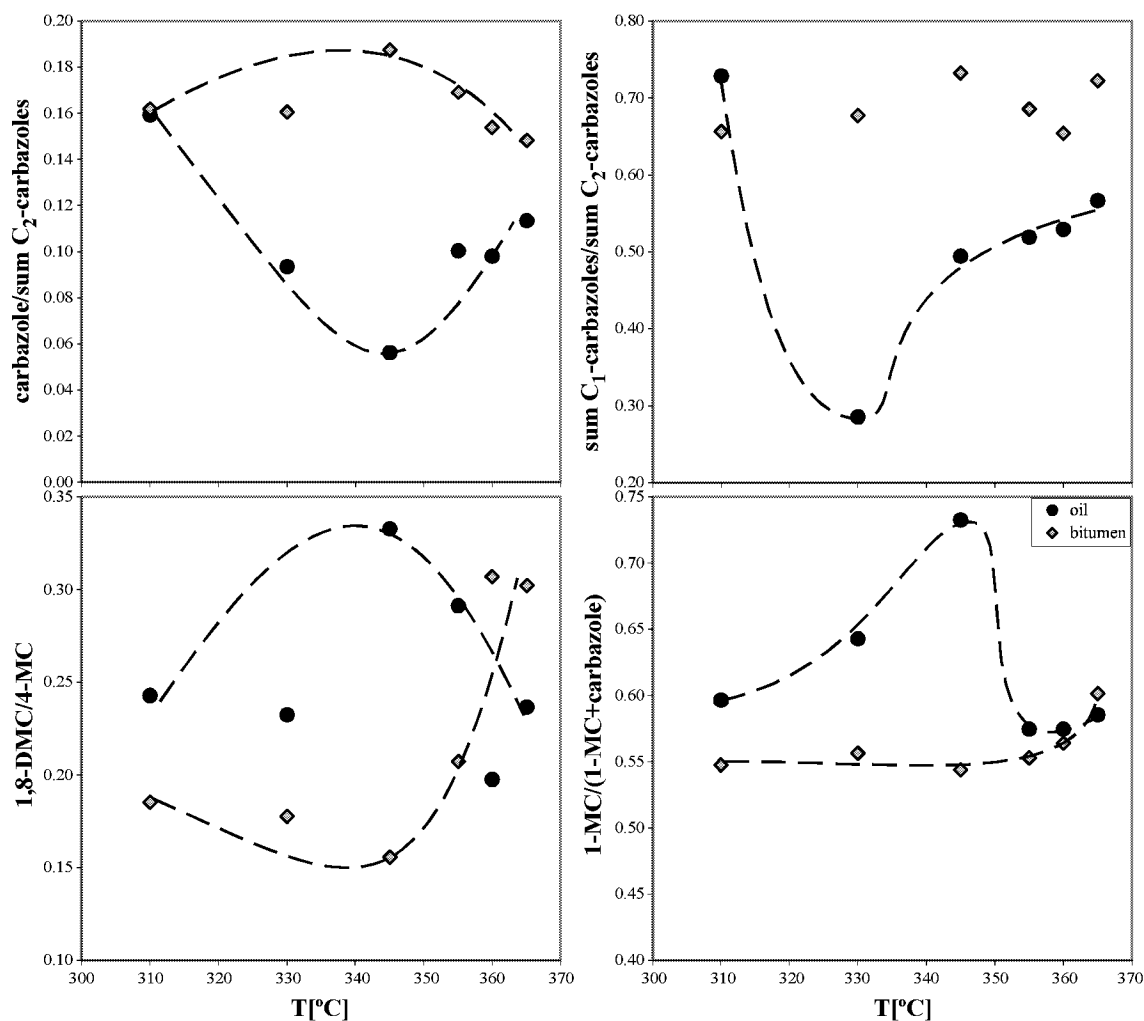


Fig. 5.2.21: Effect of primary migration and maturity on the distribution of carbazoles using hydrous pyrolysis experiments.

shielded isomer is also enriched in the expelled oils compared to the rock extracts. These results support the proposal that primary migration affects the distribution of carbazoles such that shielded isomers are enriched in oils whereas non-shielded, more polar components are more strongly retained within the rock matrix through interactions with the organic matter and minerals.

The 1,8-dimethylcarbazole/(1,8-dimethylcarbazole + 1-ethylcarbazole) ratio has been shown to be positively correlated with maturity up to ~1.1% vitrinite reflectance, both for the Posidonia Shale and the petroleum system of the Sonda de Campeche (Clegg et al., 1998b; Wilkes et al., 1998a). The authors suggested that the systematic increase in this ratio was due to dealkylation of 1-ethylcarbazole as maturity proceeds, a mechanism equivalent to that proposed for 4-ethyldibenzothiophene (Radke and Willsch, 1994). The previous study on an artificial maturity sequence using hydrous pyrolysis, carried out by Clegg et al. (1998a), showed no trend of the 1,8-dimethylcarbazole/(1,8-dimethylcarbazole + 1-ethylcarbazole) ratio. More recently, Bakr and Wilkes (2002) observed that controls other than maturity, such as facies and depositional environment, cannot be excluded.

Figure 5.2.22.B shows the variation in the relative abundance of 1,8-dimethylcarbazole and 1-ethylcarbazole with increasing maturity for the recovered rock extracts and expelled oils analysed in this study. The relative abundance of 1,8-dimethylcarbazole in the bitumens decreases with increasing temperature up to 345°C and then increases, whereas the opposite trend is observed for the expelled oils. Although both 1,8-dimethylcarbazole and 1-ethylcarbazole are shielded compounds this inverse relationship indicates that the shielding effect is greater if both sides of the N-H group are occupied by methyl groups than if there is only one ethyl group shielding the polar function. Surprisingly, similar trends are also seen in the 3/(3+4)-methylcarbazole ratio (Fig. 5.2.22.A). Previous studies involving natural source rock maturity suites have shown a decrease in this ratio with increasing maturity (Clegg et al., 1997; Li et al., 1997). Although both isomers are non-shielded, 3-methylcarbazole has a 'rod-shaped' structure whereas the methyl group situated in position 4 results in a more 'sub-spherical' structure and could interact with the hydrogen at position 5 giving the impression of an additional ring system. This could lead to a greater retention of 4-methylcarbazole in comparison to 3-methylcarbazole during expulsion.

The lower diagrams of Figure 5.2.22 illustrate the influence of maturity on the distribution of the benzocarbazoles. A systematic increase in the benzocarbazole

$[a/(a+c)]$ ratio with maturity (Fig. 5.2.22.C) is observed for the rock extracts, which is in agreement with previously reported studies of both natural maturity sequences (Clegg et al., 1998b; Horsfield et al., 1998) and artificially matured source rock (Clegg et al., 1998a). The concentration of benzocarbazoles is too low to be quantified in the oil expelled at 310°C and at higher maturity levels no correlation is observed with regard to this parameter.

Benzo[*b*]carbazole is thought to be indicative of terrigenous contributions as described previously and as reported by Harrison et al. (1997) and Oldenburg et al. (1999). Surprisingly, the relative concentration of this isomer increases with maturity both in the recovered rock extracts and in the expelled oils (Fig. 5.2.22.D). This may indicate that the *b*-isomer is formed at later stages of maturity than the *a*- and *c*-isomers

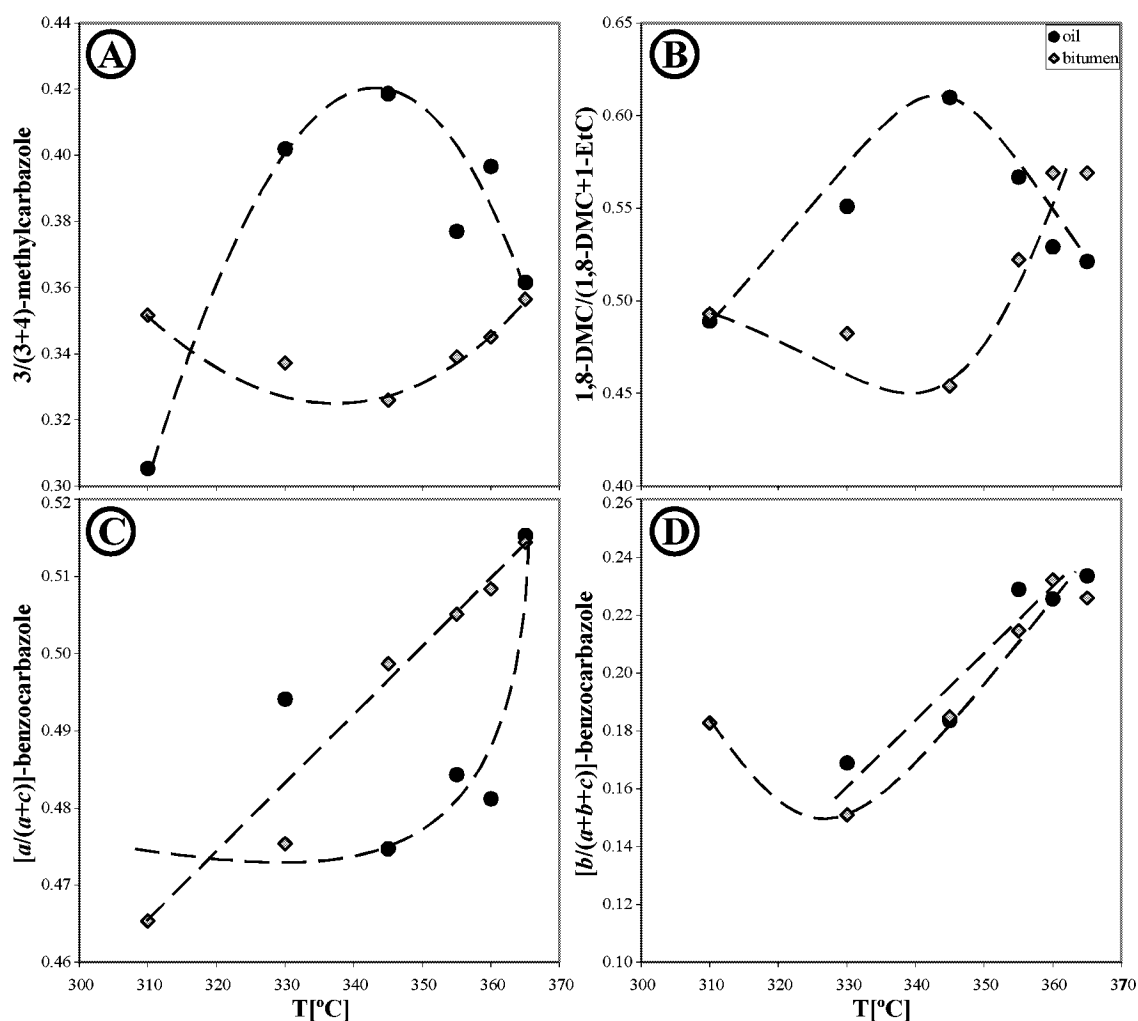


Fig. 5.2.22: Influence of primary migration and maturity on the distribution of alkylated carbazoles and benzocarbazoles using hydrous pyrolysis experiments; benzocarbazole ratios were not determined in the expelled oil at 310°C.

because molecular mechanics calculations have shown that benzo[*b*]carbazole is less stable than the other isomers (Harrison et al., 1997). The limestone from the Ghareb Formation at El Lajjun used in the hydrous pyrolysis experiment is an immature carbonate Type II-S kerogen (Clegg et al., 1998a), and therefore a terrestrial input can be excluded as the source of the *b*-isomer. Previous studies have shown that some compounds, such as alkylbenzothiophenes and alkylnaphthalenes, will be generated under thermodynamic control during hydrous pyrolysis, i.e. these compounds are generated due to the high absolute temperature and do not occur in natural systems (e.g. Eglinton et al., 1987).

5.2.6 Influence of secondary migration on the distribution of carbazoles

Research into the use of the distribution of carbazoles as secondary migration parameters has concentrated mainly on the benzocarbazole parameter (benzo[*a*]carbazole/ (benzo[*a*]carbazole + benzo[*c*]carbazole)). Larter et al. (1996a) proposed this parameter as an indicator of relative petroleum migration distance and charging direction. Some case studies have described successful applications of this parameter as a migration tracer (Li et al., 1997, 1998; Terken and Frewin, 2000). However, there is clear evidence that maturity and/or facies complicates, or even dominates, the picture in several settings (Clegg et al., 1997, 1998b; Harrison et al., 1997; Li et al., 1998; Bakr and Wilkes, 2002; and the present study as discussed above). Although clear maturity-related trends have been seen in several source rock studies, the efficiency with which benzocarbazole concentrations and distributions in maturing source rocks are transferred to the migrating petroleum is still an area of uncertainty (Larter et al., 1996b; Li et al., 1997; and the present study as discussed above). Other investigations have used the distribution of carbazoles to illustrate fractionation effects during primary and secondary migration. For example, Li et al. (1995) reported that in crude oils there is an enrichment of alkylcarbazoles relative to alkylbenzocarbazoles, an enrichment of nitrogen-shielded isomers relative to nitrogen-exposed isomers and an enrichment of more highly alkylated homologues compared to less alkylated homologues with increasing migration distance.

Approximate secondary migration distances have been estimated by Norsk Hydro for the Haltenbanken oils investigated in the present study. Oils from a second known

migration route within the Tampen Spur area were described by Karlsson (1986) and Horstad et al. (1995).

Initially it is important to determine whether the estimated migration distances for the Haltenbanken oils correlate with maturity. Therefore, the migration distances were plotted against the maturity parameters established in Chapter 5.1.5 (Fig. 5.1.37) for the oils from the Haltenbanken area. As illustrated in Figure 5.2.23, there is no correlation between the maturity ratios and migration distance, and a relationship between maturity and migration distance can be excluded.

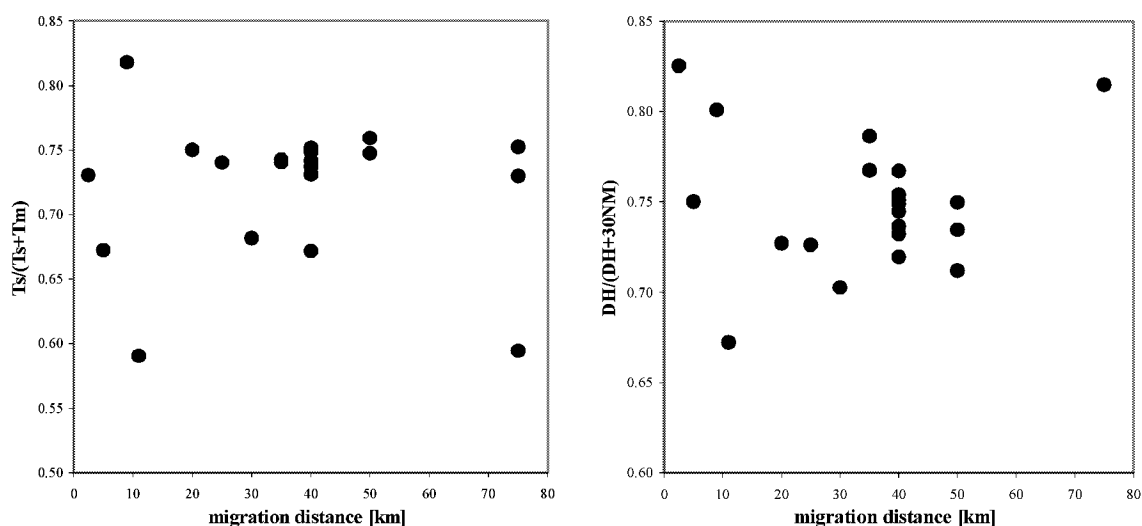


Fig. 5.2.23: Plots showing maturity parameters versus estimated migration distances for oils from the Haltenbanken area (DH = 17 α ,21 β -diahopane; 30NM = 30-nor-moretane; see Table 4.1).

The benzocarbazole ratio of the so-called 'rod-shaped' benzo[*a*]carbazole to the 'sub-spherical' benzo[*c*]carbazole was reported to decrease with increasing migration distance in some secondary migration settings (Larter et al., 1996a). As illustrated in Figure 5.2.24.A, only a weak general decrease in this ratio with increasing migration distance can be recognised in the Haltenbanken oils, and there is no evidence of a clear, consistent trend.

For the ratios of shielded carbazoles to non-shielded carbazoles there are some interesting observations. The abundance of 1-methylcarbazole clearly increases relative to carbazole and 4-methylcarbazole with increasing migration distance for most of the oils (Fig. 5.2.24.B, C). As the non-shielded carbazoles (carbazole, 4-methylcarbazole) are suggested to be more strongly retained in the source rock by interactions with organic matter and mineral phases than the shielded isomer (1-methylcarbazole), these parameters may be useful as secondary migration distance markers. The oils from the

Midgard Field and the oil from well 6406/11-1S to the south of Haltenbanken deviate significantly from the main trend, and on the basis of these carbazole parameters it appears that the secondary migration distance of the oils from the Midgard Field could be approximately 50 km shorter, whereas that of the 6406/11-1S oil might be approximately 20 km longer. The observed deviation from the general trend may also be due to differences in migration scenario e.g., lateral vs. vertical, fill-spill vs. faulting systems, where the extent of exposure to reactive surfaces may have been different and/or the mineral matrices of the carrier systems may have had different sorptive properties.

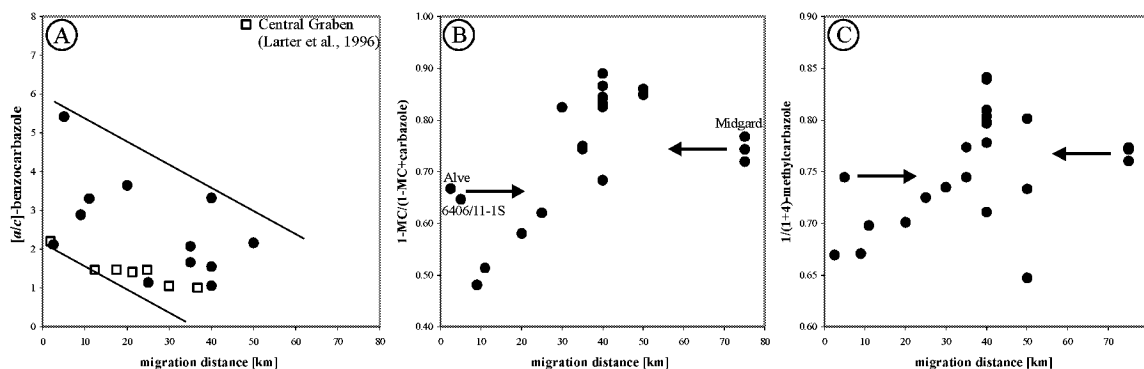


Fig. 5.2.24: Influence of secondary migration on the distribution of carbazoles in the oils from the Haltenbanken area; benzocarbazole ratios from Midgard oils were not determined due to low abundances; filled circles: present study; open squares: data from Larter et al. (1996a); arrows indicate proposed wrong migration distance estimations.

The same effect of an increase in the abundance of the shielded isomer (1,8-dimethylcarbazole) relative to the partly-shielded or non-shielded isomers with increasing migration distance is illustrated in Figure 5.2.25. The parameters correlate well with the estimated migration distances, again with the exception of the oils from the Midgard and Alve Fields and from well 6406/11-1S. For these latter oils, the migration distance may have been wrongly estimated, or different migration effects may have occurred as described above. Figure 5.2.25.B shows the same migration distance effect although 1-ethylcarbazole is a partly shielded isomer. As discussed in the previous chapter, primary migration has a similar effect on the ratio of 1,8-dimethylcarbazole to 1-ethylcarbazole. A comparison of the range in the 1-MC/(1-MC+carbazole) ratio (Fig. 5.2.24.B) with the 1,8-DMC/(1,8-DMC+carbazole) ratio (Fig. 5.2.25.A) demonstrates the difference between alkyl substitution on one side of the polar group and substitution on both sides. Whereas the 1-MC/(1-MC+carbazole) ratio

ranges from 0.45 to 0.90, the values of the 1,8-DMC/(1,8-DMC+carbazole) ratio vary between 0.20 and 0.95.

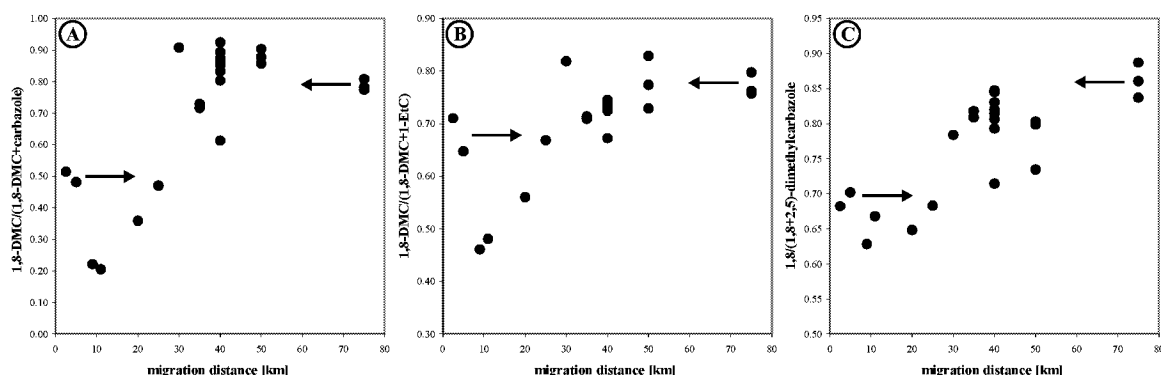


Fig. 5.2.25: Influence of migration distance on the relative enrichment of 1,8-dimethylcarbazole in oils from the Haltenbanken area; arrows indicate proposed wrong migration distance estimations.

Results for the sample sequence from the Alwyn, Brent, Statfjord, H-Central migration route within the Tampen Spur are presented in Figure 5.2.26, with migration distances estimated from the fill-spill route proposed by Horstad et al. (1995) and the migration route to the east of the main fill-spill route proposed by Karlsson (1986). Plots of the benzocarbazole and the dimethylcarbazole ratio against migration distance shown in Figure 5.2.26 indicate that the oils from Tordis and Tordis Øst follow the general trend in a better way if migration distance is based on the shorter pathway as proposed by Karlsson (1986) rather than the long distance pathway proposed by Horstad et al. (1995). The observations described above indicate that partitioning processes occurring during secondary migration lead to an increase in the relative abundance of shielded carbazoles compared to non-shielded isomers.

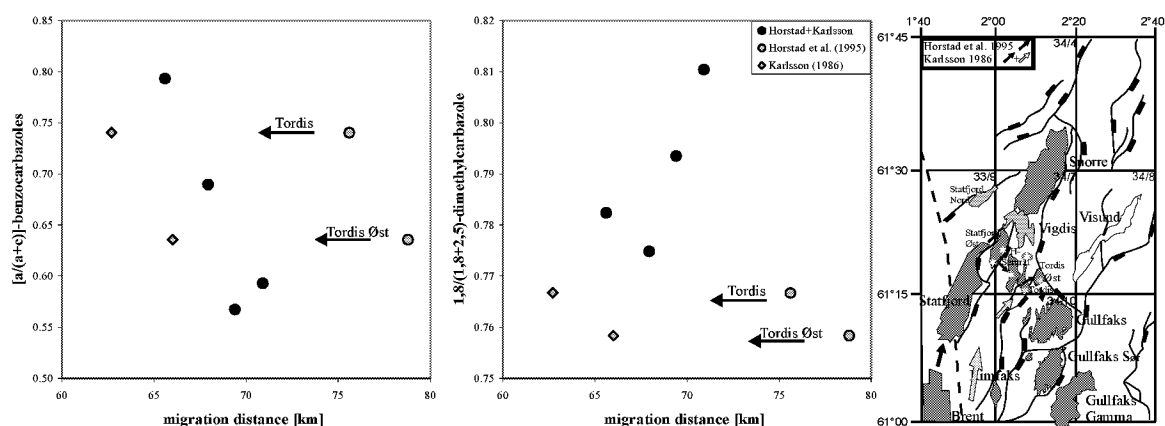


Fig. 5.2.26: Comparison of different proposed migration pathways of a fill-spill route within the Tampen Spur area using migration dependent carbazole ratios.

5.2.7 Influence of biological degradation and/or water washing on the distribution of carbazoles

Although carbazole is relatively resistant to microbial attack, several groups have reported the isolation of carbazole-degrading bacteria (Grosser et al., 1991; Ouchiya et al., 1993; Hisatsuka and Sato, 1994; Kobayashi et al., 1995; Gieg et al., 1996; Millette et al., 1998; Nojiri et al., 1999). A comparison with the pathways for the transformation of aromatic compounds by bacteria reveals some general similarities. The initial enzymatic conversion steps for many compounds yield dihydroxylated intermediates. These intermediates then follow either a *meta*- or an *ortho*-pathway (named according to the location of the initial ring cleavage) both of which lead to intermediates of central metabolic pathways, such as the tricarboxylic acid (TCA) cycle. This arrangement of pathways implies that microorganisms have extended their substrate range by developing peripheral pathways that allow the transformation of initial substrates into one of the central pathway intermediates (Richard and Junk, 1984). The proposed degradation pathway for carbazole (Fig. 5.2.27) begins with

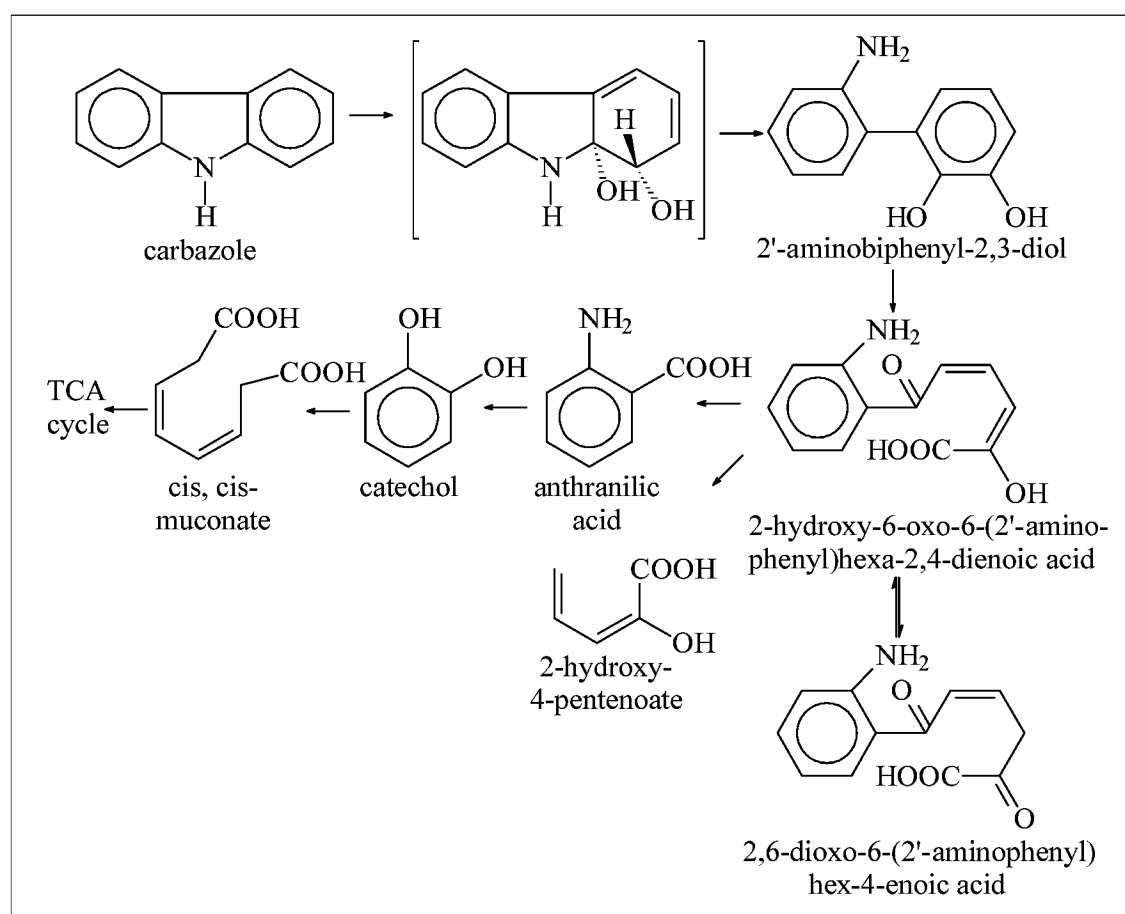


Fig. 5.2.27: Proposed pathway of Ouchiya et al. (1993) for the microbial degradation of carbazole.

dioxygenation at the angular position adjacent to the nitrogen atom to form (via an unstable intermediate) 2'-aminobiphenyl-2,3-diol, which is further degraded by meta cleavage of the diol ring to form 2-hydroxy-6-oxo-6-(2'-aminophenyl)hexa-2,4-dienoic acid. Further degradation of carbazole occurs through hydrolysis to form 2-hydroxy-4-pentenoate and anthranilic acid; the latter then enters the TCA cycle after conversion to tryptophan or catechol (Hisatsuka and Sato, 1994). An alternative microbial oxidation of carbazole to form 3-hydroxycarbazole has been described, but the carbazole was not degraded beyond the initial oxygenation (Resnick et al., 1993). Although cases of anaerobic degradation have been noted, the initial attack by most species is aerobic and consistent with other well-characterised aromatic degradation systems (Resnick et al., 1993; Benedik et al., 1998). Anaerobic biodegradation mechanisms for carbazoles are not yet known, but the initial conversion steps could be similar to those of aerobic degradation.

The sample sequence of the Gullfaks Field was used to investigate the influence of biological degradation on the distribution of carbazoles in oils. The degree of biodegradation increases from the east to the west of the field, and quantitative modelling calculations of biological petroleum degradation carried out by Horstad et al. (1991) have shown that the aerobic degradation process occurred in the reservoir and not during migration into the reservoir. As discussed in Chapter 5.1.3, the best established parameter to describe the degree of biodegradation in this oil sequence is the

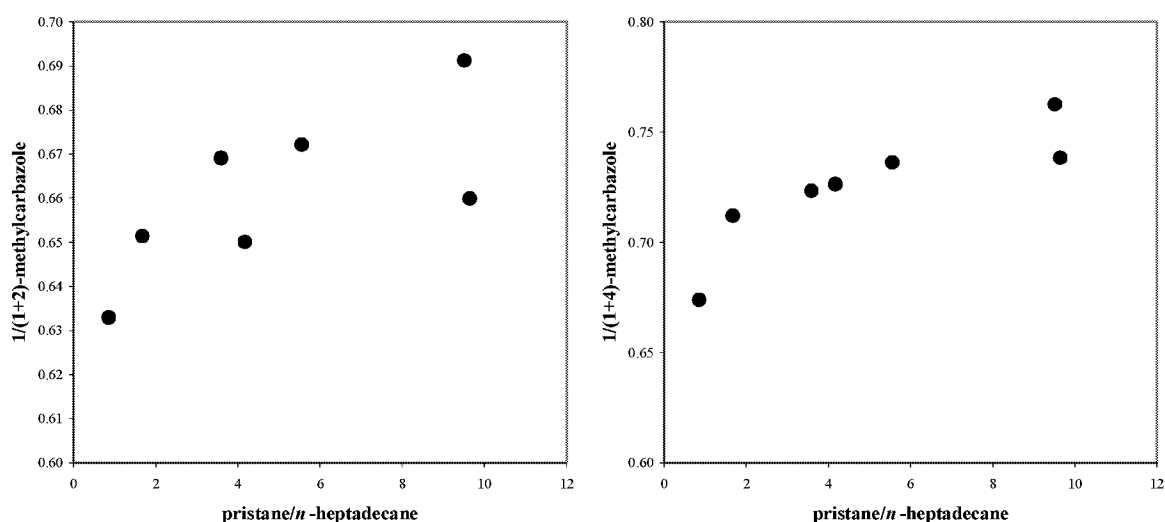


Fig. 5.2.28: Influence of biological degradation on the distribution of methylcarbazoles using a biodegradation sequence from the Gullfaks Field.

pristane (pr) to *n*-heptadecane (*n*-C₁₇) ratio. Good correlations are observed between the pr/*n*-C₁₇ ratio and the ratios of 1-methylcarbazole to 2-methylcarbazole and 1-methylcarbazole to 4-methylcarbazole (Fig. 5.2.28). The proposed aerobic catabolic pathway for carbazole shown in Figure 5.2.27 suggests that a methyl group in position 1 might provide a steric hindrance to degradation which would lead to a relative increase in abundance of 1-methylcarbazole with increasing biodegradation.

The same effect is observed with 1,8-dimethylcarbazole: As both positions adjacent to the nitrogen atom are occupied by methyl groups, the abundance of this isomer increases with increasing biodegradation compared with the non-shielded isomers 2,5-dimethylcarbazole and 4-methylcarbazole, as illustrated in Figure 5.2.29. These examples suggest a preference for dioxygenation adjacent to the heteroatom leading to a relative enrichment of carbazoles with methyl groups at these positions. However, as demonstrated for the influence of primary and secondary migration on the distribution of carbazoles (Sections 5.2.5 and 5.2.6) these results may also indicate an effect of partitioning processes since most biodegraded oils are also exposed to water. The reduced polarity of the shielded isomers results in reduced interaction with water. Additionally, due to the higher affinity of the non-shielded compounds for water, these isomers would be more bioavailable than the shielded isomers.

Although the observed effects accord well with the known aerobic mechanisms they do not provide evidence that aerobic degradation actually takes place. Steric hindrance could also influence anaerobic degradation.

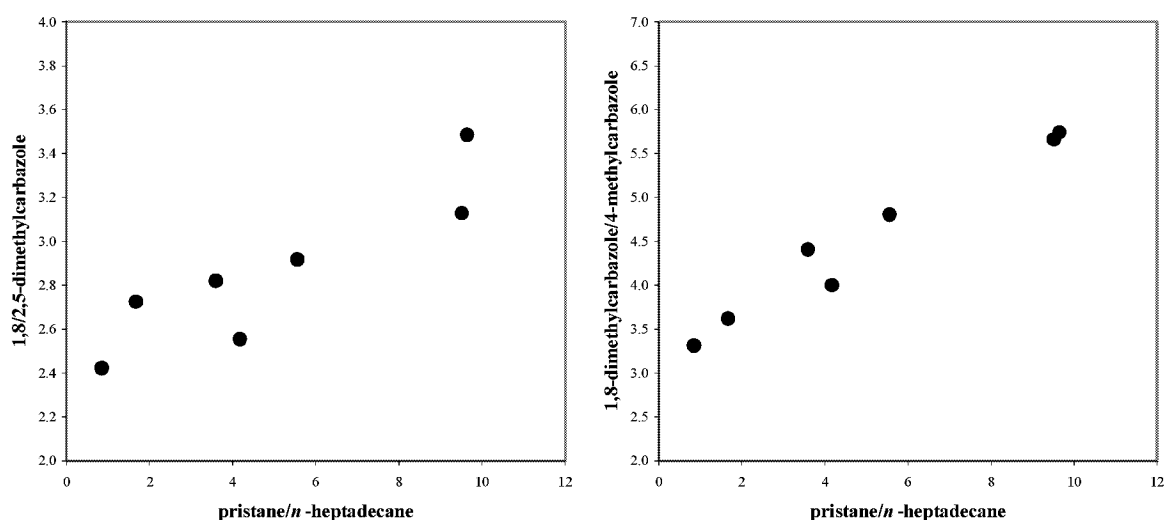


Fig. 5.2.29: Influence of biodegradation on the relative abundance of 1,8-dimethylcarbazole using the biodegradation sequence from the Gullfaks Field.

5.2.8 Conclusions

Carbazole and its derivatives were found in 71 crude oils, two reservoir core samples and nine source rock samples from the Haltenbanken area, offshore Norway. They were also found in expelled oils and recovered rock extracts after hydrous pyrolysis of an immature source rock from Ghareb, Jordan.

Higher amounts of carbazoles are observed in source rocks compared with expelled oils both for the natural samples from offshore Norway and for the artificially matured samples. The absolute concentrations of carbazoles increase with increasing maturity.

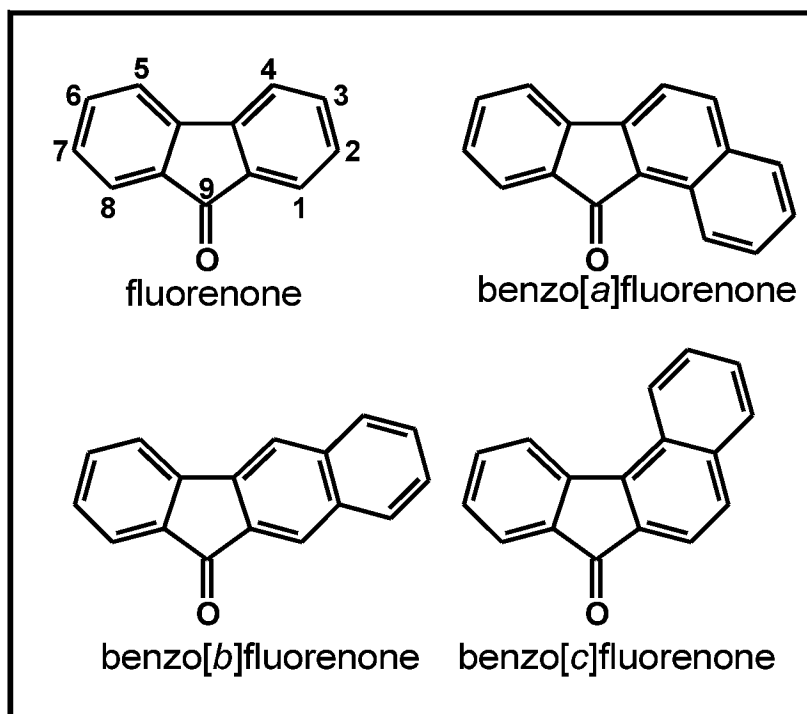
The investigation of two different potential source rocks from the Haltenbanken area reveals that they can be differentiated by the relative abundance of carbazole homologue groups and of individual alkylcarbazole isomer ratios independent of maturity. It was also found that benzo[*b*]carbazole seems to be exclusively associated with a supply of terrigenous organic matter to the source rock. Correlations between carbazole parameters in source rocks and crude oils can give indications as to the source of the oils, but fractionation during expulsion or partitioning plays an important role in controlling carbazole distributions.

Apart from a significant increase in abundance of the different carbazole alkylhomologue groups with increasing maturity, some isomer ratios in the C₁- and C₂-carbazoles and the ratio of *a*/(*a*+*c*)-benzocarbazole also show a maturity dependence, both in the natural source rock and in recovered extracts of artificially matured rocks. In contrast, the natural crude oils and (artificial) expelled oils do not show good correlations between these ratios and maturity, suggesting that the carbazole distribution in oils is controlled by primary and secondary migration. Fractionation during expulsion is impressively demonstrated by hydrous pyrolysis experiments. NH-shielded carbazoles are clearly enriched relative to non-shielded carbazoles in the expelled oils in comparison to the recovered rock extracts. This implies stronger interaction between the more polar non-shielded compounds and the organic matter and minerals in the rock matrix, and the stronger retention of these compounds by the source rock during expulsion.

The primary migration fractionation effects are enhanced during secondary migration as revealed by two sample sequences from the Haltenbanken and Tampen Spur areas. With increasing estimated migration distance, the abundances of non-shielded isomers decrease in comparison to those of the shielded isomers, which again reflects the difference in ability to interact with the components of the rock matrix.

Biological degradation could also result in an increase in the abundance of the shielded isomers relative to the non-shielded isomers due to steric hindrance by the methyl groups restricting access to the nitrogen functionality as demonstrated by a biodegradation sequence from the Gullfaks Field.

5.3 Fluoren-9-ones and Benzofluoren-9-ones



5.3.1 Introduction

Oxygen compounds have long been known as constituents of crude oils and source rocks. The first detailed investigation of oxygen compounds in crude oils was made by Snyder et al. (1968). In addition to aliphatic carboxylic acids, phenols, benzo-, dibenzo- and benzonaphthofurans and phenylketones they identified compound classes containing an additional heteroatom (sulfur or nitrogen) such as sulfoxides, pyridones and quinolones. Subsequently, many detailed molecular characterisations of oxygen compound classes in crude oils and source rocks have been carried out; including studies of carboxylic acids (e.g. Seifert, 1975; Grimalt et al., 1990; Jaffé and Gardinali, 1990; Jaffé and Gallardo, 1993; Azevedo et al., 1994; Barakat and Rullkötter, 1995), chromans (Sinninghe Damsté et al., 1987; 1993), aliphatic ketones and aliphatic aldehydes (Anders et al., 1975; Grimalt et al., 1990; George and Jardine, 1994; Leif and Simoneit, 1995; Wang and Rullkötter, 1997).

Aromatic ketones and aldehydes are usually among the minor constituents of fossil fuels. Latham et al. (1962) identified alkylated fluoren-9-ones in Wilmington petroleum, and these compounds have also been reported to occur in Athabasca oil sand bitumen (Mojelsky and Strausz, 1986) and Posidonia Shale bitumen (Wilkes et al., 1998a). 1-Indanones and 1-tetralones were detected in the Green River Formation oil shale

(Anders et al., 1975). Costa Neto et al. (1980) identified 1-indanones, naphthaldehydes and acetophenones in Brazilian oil shales from the Irati, Tremembé and Maraú Formations. A detailed account of the distribution of several types of aromatic ketones and aldehydes, such as indanones, tetralones, naphthaldehydes, acetylnaphthalenes, benzaldehydes and acetophenones, in the low-polarity NSO compound fractions of the Posidonia Shale bitumens was provided by Wilkes et al. (1998b).

Fluoren-9-ones are oxygenated polycyclic aromatic compounds which occur in diesel engine combustion products (Erickson et al., 1979; Jensen and Hites, 1983), urban aerosols (König et al., 1983; Fernandez and Bayona, 1992; Lewis et al., 1995; Allen et al., 1997), cigarette smoke condensate (Bell et al., 1969) and as products from burning wood and cereal (Ramdahl and Becher, 1982). Fluorenones are produced during aerial oxidation of diesel fuels (Bahn et al. 1987) and upon flash thermolysis of anthraquinone and phenanthraquinone (De Champlain and De Mayo, 1972). The benzylic carbon of fluorenes undergoes facile reactions under mild oxidising conditions to form fluorenones (Choudary et al., 1992; Harvey et al., 1992).

Fluorenones are also constituents of source rocks and crude oils. They were first identified in Wilmington petroleum by Latham et al. (1962). Subsequently, a series of alkylated fluorenones was detected in Alberta oil sand bitumens (Mojelsky and Strausz, 1986), kerogen pyrolysates from the Toarcian shales of the Paris Basin (van Graas et al., 1981), weathered, surface-retorted oil shales (Pereira et al., 1981), and in marine sediments (Fernandez and Bayona, 1992). The formation and fate of polycyclic aromatic hydrocarbons (PAH) during the pyrolysis and fuel-rich combustion of primary tar from an Australian bituminous coal, generated under rapid heating conditions, revealed that fluorenone is produced only under oxidising conditions (Ledesma et al., 2000). Wilkes et al. (1998a) identified fluorenones and benzofluorenones in the Posidonia shale bitumens from the Hils Syncline, northwest Germany. Apart from the artificial oxidation of fluorenes, they suggested alternative precursors (e.g. 2-carboxybiphenyls) which may give rise to the fluorenones in the Posidonia shale via clay-catalysed condensation or simply at high temperatures in the subsurface. The authors also described a systematic increase in abundance of fluorenones and benzofluorenones, and a linear decrease in the 1-ethylfluorenone/(1-ethylfluorenone + 1,8-dimethyl-fluorenone) ratio with increasing maturity over the maturity range (0.48-1.45% R_r). A detailed reservoir study involving both fluids and core extracts carried out by Bennett and Larter (2000) showed that the concentrations of fluorenones in reservoir

core extracts are often very high, which may reflect sorption processes after fluorenone production. However, fluorenone abundance in flowed oils seems to be sporadic and may be related to sample age and storage history.

Biodegradation of fluorenes in artificial soils contaminated with diesel fuel and lubricating oil also resulted in the production of fluorenones (Langbehn and Steinhart, 1995). Biological degradation experiments with a PAH/creosote-contaminated soil from an old gas works site resulted in accumulations of metabolites/degradation products such as fluorenone and 4-hydroxyfluorenone, but it was not clear whether the detected metabolites were dead-end products or not (Eriksson et al., 2000). It was proposed that the environmental chemical/physical conditions probably have a strong influence on whether these compounds persist or not, since the results varied with different nutrient and inoculum conditions. Fluorenone accumulation was observed during the degradation of fluorene by *Arthrobacter* sp. Strain F274 (Grifoll et al., 1994) and *Arthrobacter* sp. Strain F101 (Grifoll et al., 1992; Casellas et al., 1997). 30 strains of micromycetes, known to be good degraders of polychlorinated aromatic compounds, were investigated with regard to their ability to degrade fluorenes (Garon et al., 2000). The authors observed the accumulation of fluorenone during the degradation of fluorene. Twelve of the strains were considered as “best degraders” having a rate of degradation of 60%, whereas three strains from the Genus *Cunninghamella* were classed as “very efficient” with a mean rate of degradation of 96%.

The broad variety of origins of fluorenones, including combustion, geochemical, storage or biochemical suggests that interpretation of their occurrence in the geosphere may be problematic.

For this investigation, the following pathways were considered:

1. primary generation of fluorenones in source rocks (direct formation from the kerogen within the source rock),
2. secondary formation by mineral- and/or water-mediated oxidation of kerogen-derived fluorenes within the geosphere (e.g., in source rocks, carrier beds, reservoirs),
3. secondary formation as artefacts by oxidation of fluorenes in oils and source rock organic matter during sample handling, processing and storage (e.g., atmospheric oxidation, photo-oxidation).

5.3.2 Occurrence and origin of fluorenones

Fluorenone and the alkylated homologues were detected in all of the crude oils from offshore Norway, whereas the abundances of benzofluorenones were too low for quantification in 20 of the 72 samples analysed. High amounts of fluorenones were detected in the nine source rock samples from Haltenbanken, the core rock sample, the tar mat sample and in the recovered rock extracts from the hydrous pyrolysis experiments, whereas the abundances of fluorenones were below the detection limit in the expelled oils from the artificial maturation sequence.

Source rocks

The concentrations of fluorenone, the sum of C₁-fluorenones, the sum of C₂-fluorenones and the sum of benzofluorenones in the nine source rocks from Haltenbanken ranged between less than 2 µg/g extract for the immature coaly samples from the Åre Formation and 650 µg/g extract for the mature samples from the Spekk

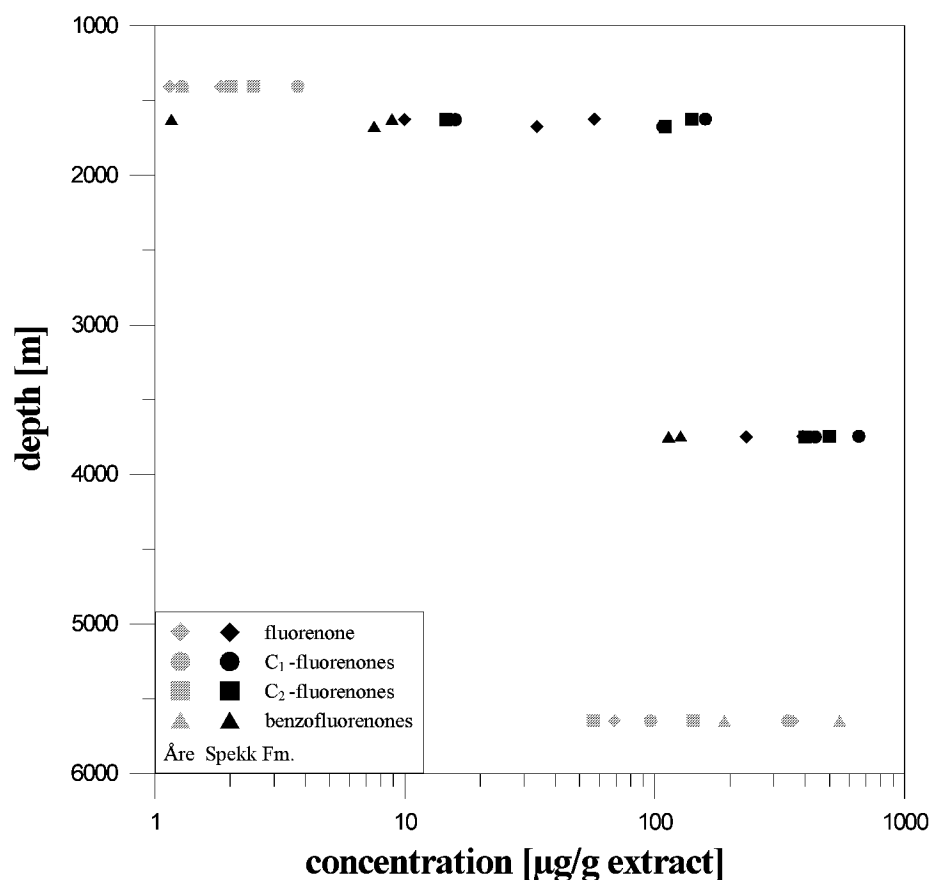


Fig. 5.3.1: Concentrations of fluorenones in source rocks from the Haltenbanken area (note the logarithmic scale on the x-axis).

Formation (Fig. 5.3.1). As observed with the carbazoles, the concentrations of fluorenones are controlled by maturity. This is in accordance with a previous study of a maturity sequence from the Posidonia shale (Wilkes et al., 1998a) and will be discussed in detail in the following sections.

In the Spekk Formation, the concentrations of the compound groups increase in the order benzofluorenones < fluorenone < C₂-fluorenones < methylfluorenones, independent of maturity. In contrast, the distribution of these compound groups in the source rock extracts from the mature Åre Formation is characterised by a dominance of the benzofluorenones and a relatively low abundance of the C₂-fluorenones, analogous to the carbazoles. In addition, the concentrations of fluorenones and benzofluorenones are an order of magnitude higher than those of the carbazoles and benzocarbazoles (see Fig. 5.2.1) in the Spekk Formation, whereas these compounds occurred in similar abundance in the Åre Formation.

In the oil leg sample, the concentrations of the four compound groups increase in the order benzofluorenones < fluorenone < methylfluorenones < C₂-fluorenones (27.5, 45.3, 186.7, 246.4 µg/g extract, respectively). In the tar mat extract the concentrations increase in the same order but the abundances are about 20% higher than in the oil leg sample.

Crude oils

As observed for carbazole and benzocarbazoles, the concentrations of fluorenone and benzofluorenones were very low (<2 µg/g oil) in most of the oils analysed from offshore Norway (Fig. 5.3.2). However, some oils are enriched in fluorenone (up to 65 µg/g oil), the sum of methylfluorenones (up to 172 µg/g oil) and the sum of the C₂-fluorenones (up to 278 µg/g oil) (Appendix 5). These are oils from the Midgard Field, the Heidrun Field and some samples which have been stored and worked with for several years at the Research Centre Jülich. Surprisingly, these oils are depleted in benzofluorenones, with concentrations below the detection limit. This could be an important fact because Bennett and Larter (2000) have proposed that fluorenone abundance in flowed oils seems to be sporadic and may be related to sample age and storage history, with recent production oils having lower fluorenone concentrations than corresponding older Drill Stem Test (DST) oils.

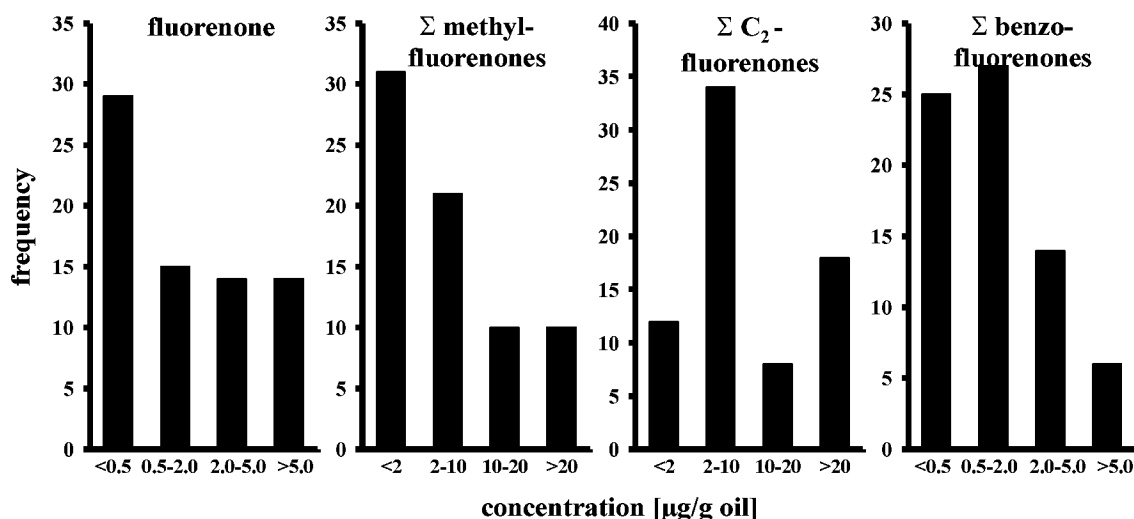


Fig. 5.3.2: Histograms showing the quantitative occurrence of fluorenones in crude oils from offshore Norway.

If fluorenones originate from fluorenes by oxidation in the reservoir or during sample handling a relationship between the distributions of these two compound groups should be observed. To test this, a comparison of the methylfluorenone distribution with the methylfluorene distribution was carried out on selected samples. The methylfluorene isomers are dominated by 1-methylfluorene in all oil samples. 1-Methylfluorenone is dominant among the ketones but generally to a lesser extent compared to 1-methylfluorene to its homologues as illustrated by the oil from well 34/10-3 shown in Figure 5.3.3. It is possible that steric hindrance of the methyl group in position 1 impedes oxidation at the neighbouring C-9. In some oils, the 1-methyl-substituted isomer is predominant in both the methylfluorenes and methylfluorenones, suggesting a precursor-product relationship between fluorenones and fluorenes, i.e. fluorenones are oxidation products of fluorenes. All three benzofluorenes were also detected in the oils but their elution order could not be determined.

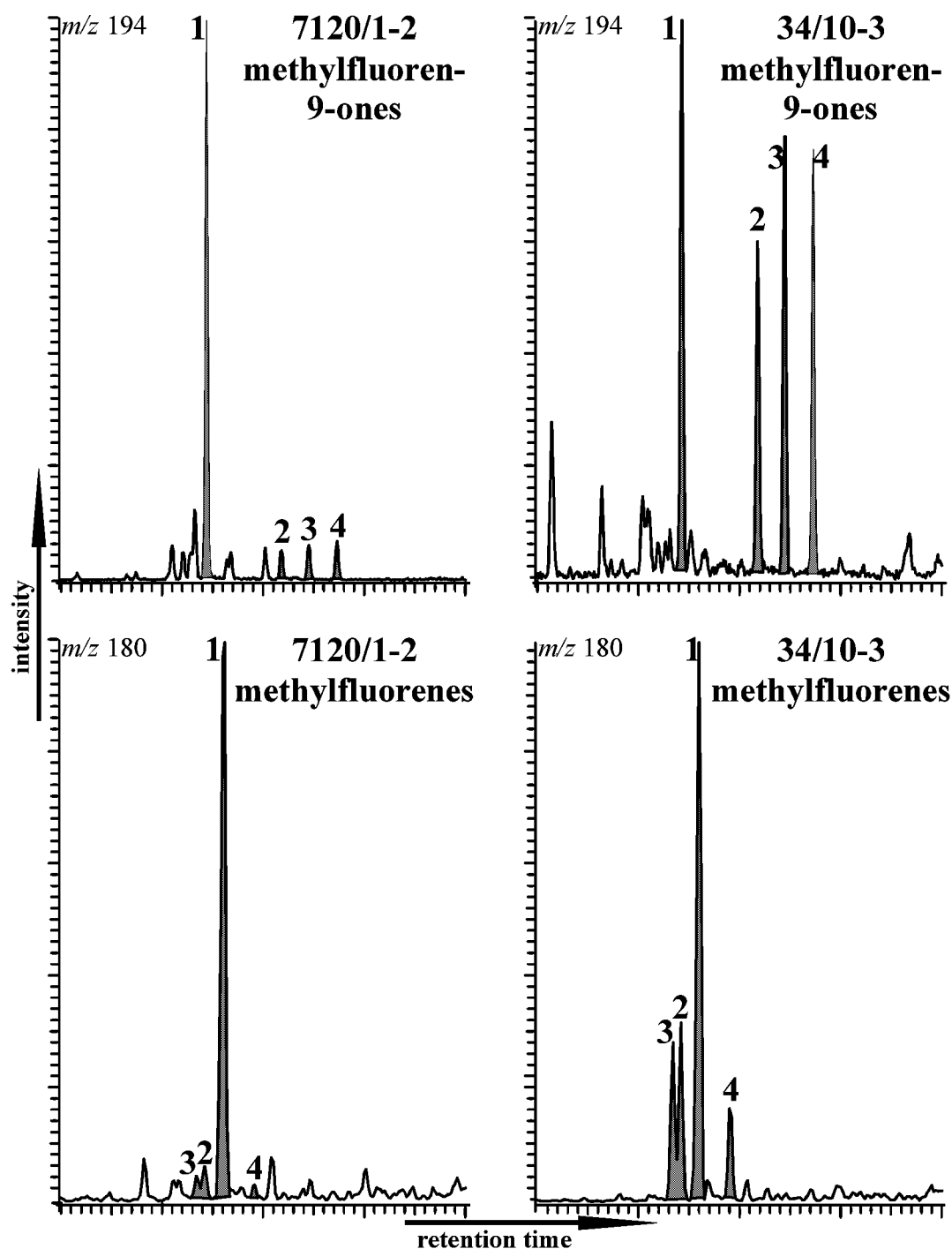


Fig. 5.3.3: Mass chromatograms showing the distribution of methylfluorenones and methylfluorenes in two oils from offshore Norway illustrating the relationship between these isomer groups; labels indicate the position of the methyl group; elution order after Wilkes et al. (1998a) for ketones, and Willsch and Radke (1995) and Bennett and Larter (2000) for fluorenes.

In order to determine the effect of oxidation during sample storage a window-sill experiment was carried out. Oil from well 34/10-32R, which has low concentrations of fluorenones, was put into a clear glass vial and exposed to sun and air for a period of six months. As illustrated in Figure 5.3.4, a strong increase in abundance of the fluorenones

was observed afterwards. The concentrations of the fluorenones are two orders of magnitude higher after six months compared to those in the initial oil.

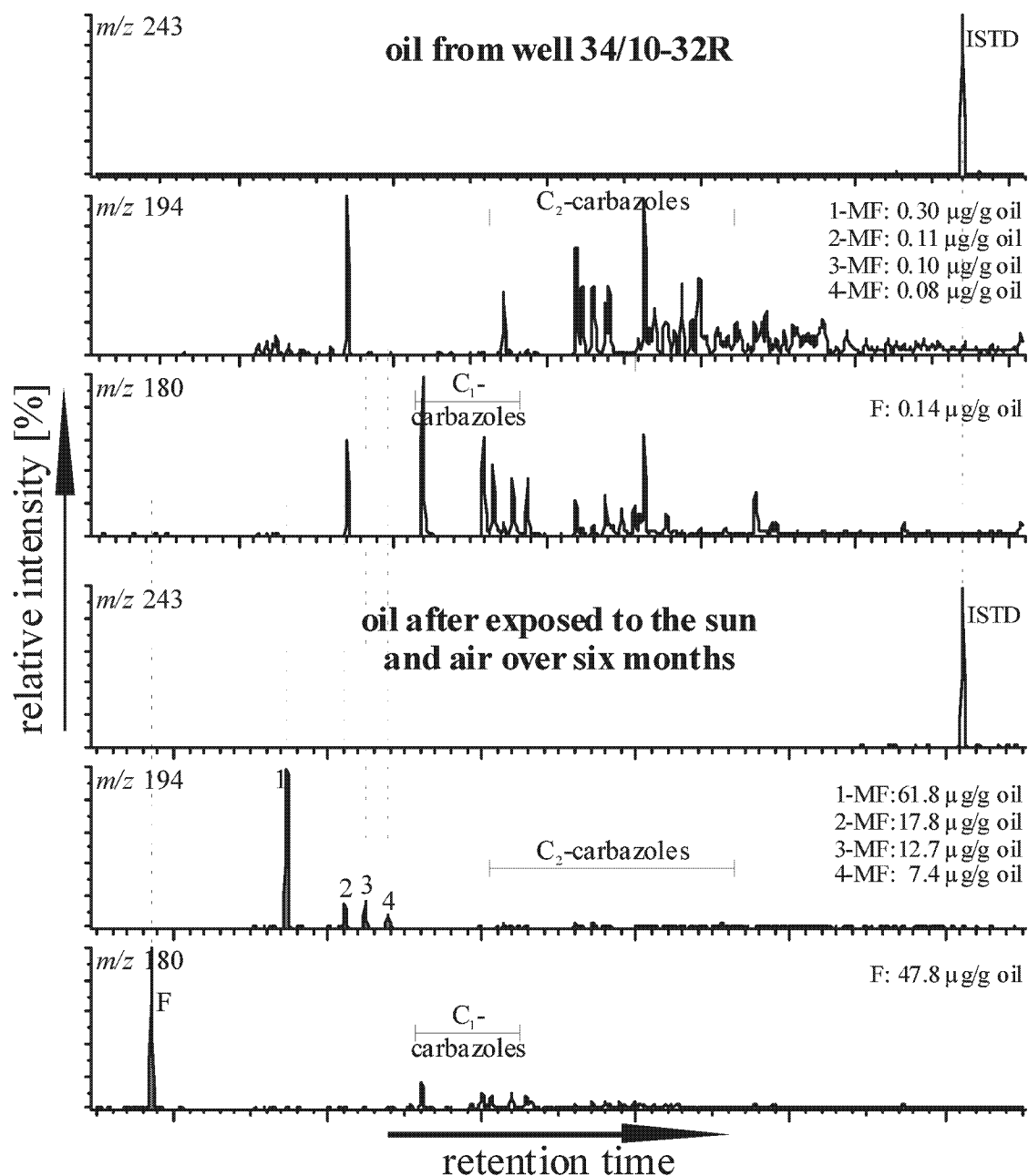


Fig. 5.3.4: Mass chromatograms of fluorenone (m/z 180) and methylfluorenones (m/z 194) illustrating the increase in abundance of these compounds during exposure to air and sunlight; ISTD = 9-phenylcarbazole.

The relationship between the distributions of fluorenes and fluorenones, and the results from the window-sill experiment indicate that oxidation during sample storage and handling is an important factor which can influence the occurrence of fluorenones.

The comparison of fluorene and fluorenone distributions in oils indicates that alkyl groups adjacent to position 9 of the fluorene structure appear to hinder oxidation.

Hydrous pyrolysis experiments

Fluorenones occurred in all of the recovered rock extracts from the hydrous pyrolysis experiments, but their concentrations were below the detection limit in all of the expelled oils. The order of relative abundance of the different isomer groups in the extracts was benzofluorenones < fluorenone < C₁-fluorenones < C₂-fluorenones. The concentrations of fluorenones were about an order of magnitude lower than those of the carbazoles in the extracts, in contrast to the observations made for the source rocks from offshore Norway. The concentrations of fluorenones in the extracts decreased after 355°C (see Figure 5.3.5), again in contrast to the abundance of the carbazoles which increased significantly with increasing temperature after 345°C.

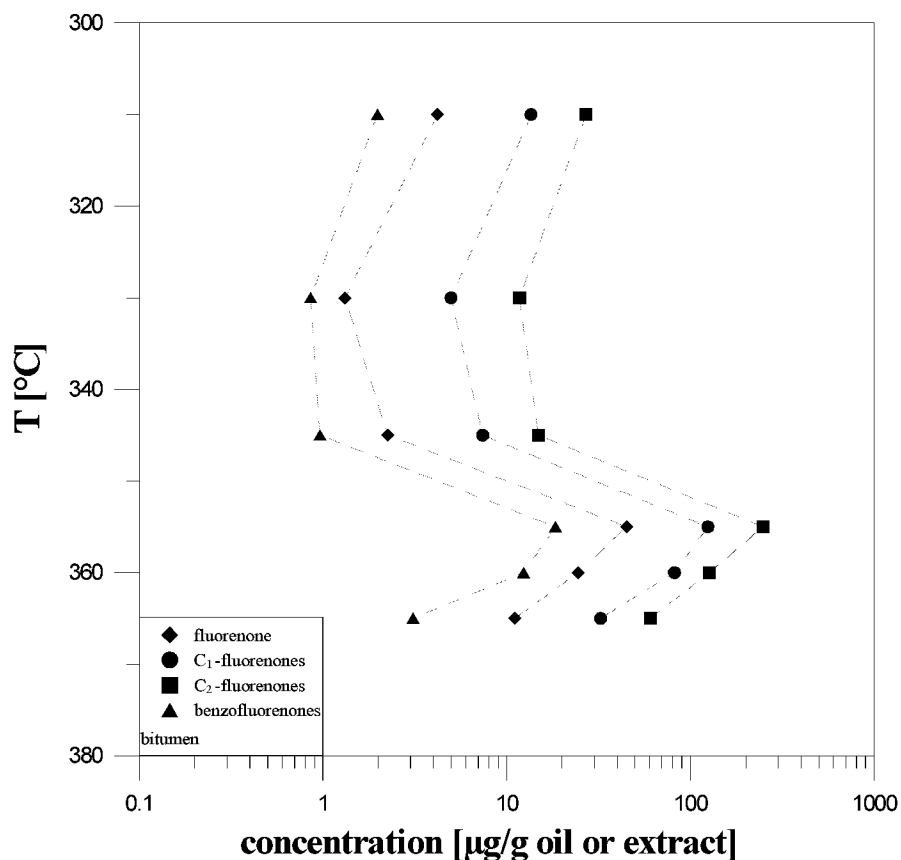


Fig. 5.3.5: Concentrations of fluorenones in the extracted bitumens from the hydrous pyrolysis experiments (the amounts in oils were too low for quantification).

Two possible reasons may explain the differences between fluorenone occurrence in recovered rock extracts and in expelled oils. First, the observations actually reflect the influence of sorption processes occurring during primary migration, and as such the results are of geochemical significance. Second, the results may be attributable to oxidation during extraction and analysis of the recovered rock bitumens. The laboratory procedures for the analysis of oils and bitumens differ in that the rock samples require grinding and extraction – thus there may be increased exposure to air. However, it should be noted that extraction experiments comparing the flow blending and Soxhlet methods resulted in the same concentrations of fluorenones in the residual bitumens. The first reason is perhaps more plausible although an influence of oxidation during extraction and analysis cannot be ruled out.

5.3.3 Influence of facies on the distribution of fluorenones and benzofluorenones - HALTENBANKEN -

Source rocks

Although some observations suggest that fluorenones may be oxidation products of fluorenes and the distribution of the ketones may therefore reflect the original distribution of the corresponding fluorenes, this compound class is nevertheless of geochemical interest. With regard to the influence of facies, there are some similarities between the distributions of the carbazoles and the fluorenones. A comparison of the two potential source rocks from Haltenbanken shows that the coaly samples from the Åre Formation are relatively enriched in benzofluorenones and depleted in alkylated fluorenones independent of maturity, as illustrated in Figure 5.3.6 and in the ternary diagram of Figure 5.3.7. Similar observations were made for the carbazoles, as discussed in Chapter 5.2.3. In contrast, the source rocks from the Spekk Formation are dominated by fluorenone and relatively depleted in benzofluorenones (Fig. 5.3.6). The left hand diagram in Figure 5.3.7 shows the differences in the benzofluorenone distribution between the two source rocks. Although there is a maturity influence on the distribution of benzofluorenones, especially on the relative proportion of benzo[*a*]fluorenone, the more terrestrially influenced samples from the Lower Jurassic are slightly enriched in benzo[*b*]fluorenone, as observed for the benzocarbazoles. These observations may indicate that the linear *b*-isomers of both benzocarbazole and

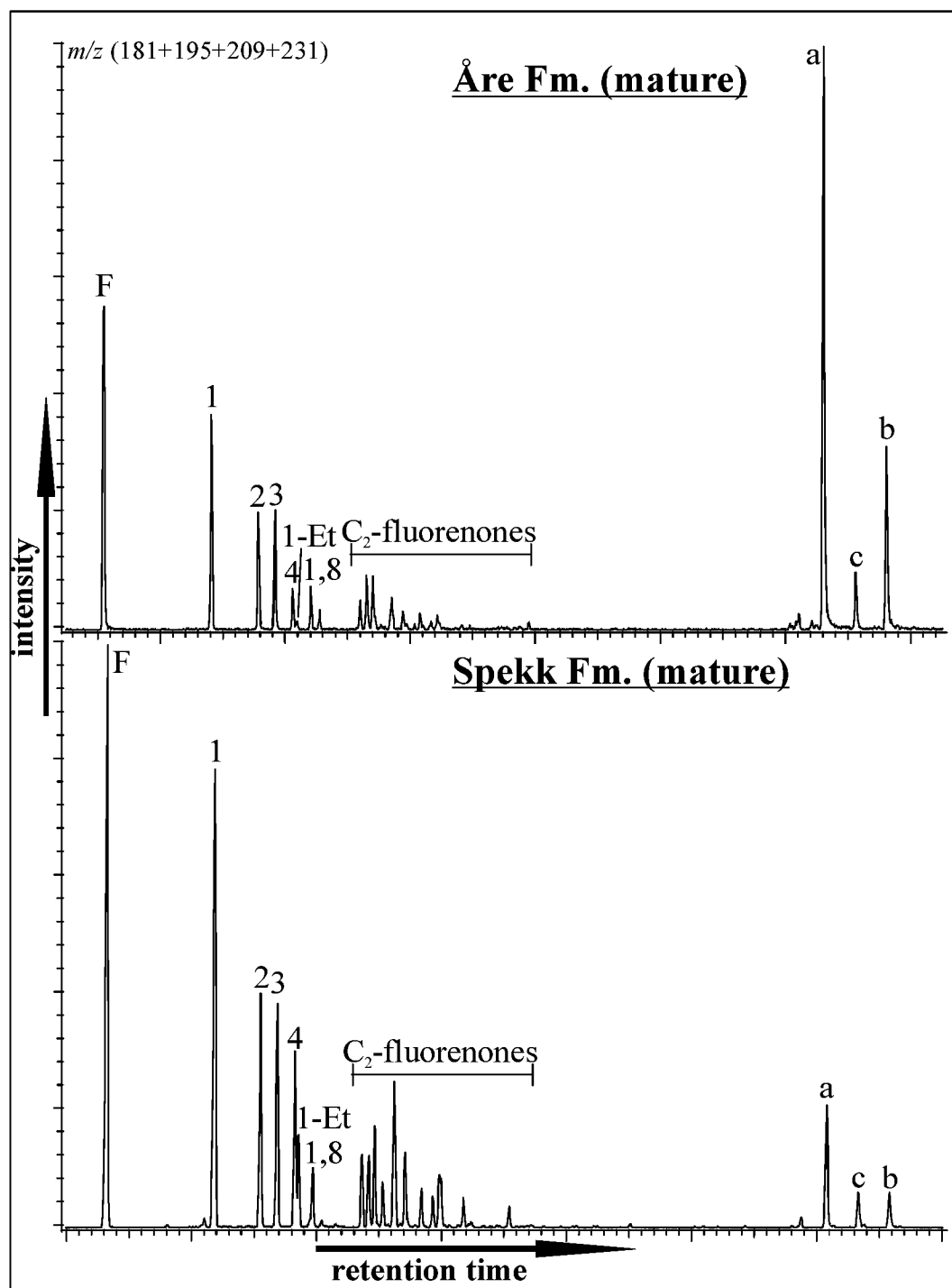


Fig. 5.3.6: Mass chromatograms illustrating the distribution of fluorenones in mature Åre and Spekk Fm. source rocks from the Haltenbanken area (measured in CI-mode); F, fluorenone; a, b, c, benzofluorenones; numbers indicate position of alkyl substitution on the fluorenone structure.

fluorenone occur predominantly in terrigenous organic matter. If proved to be true, from additional analyses, the meaningful geochemical information can also be obtained from the analysis of fluorenones.

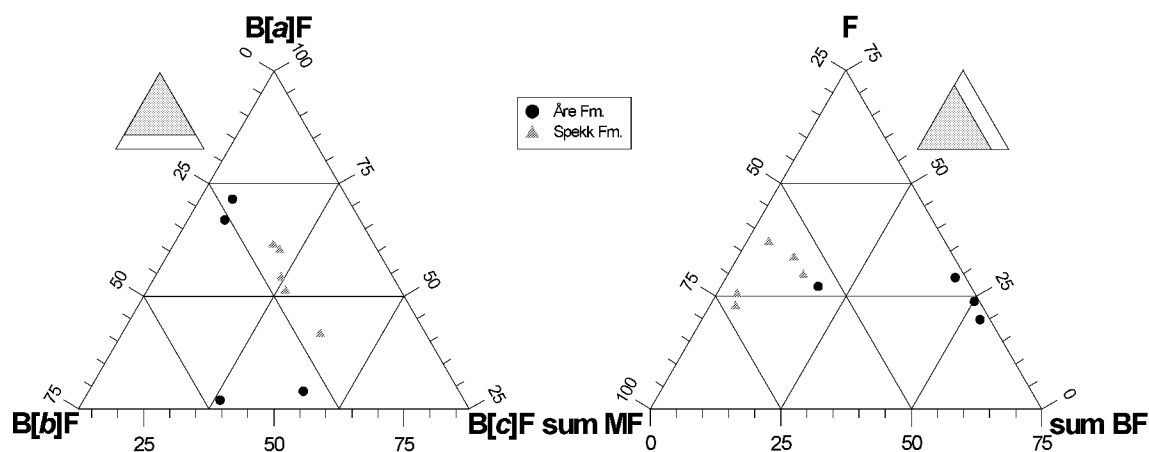


Fig. 5.3.7: Ternary diagrams showing the facies related differences in fluorenone distributions of the two potential source rocks from Haltenbanken; F = fluorenone, MF = methylfluorenone, BF = benzofluorenone.

Wilkes et al. (1998a) reported the ratio of 1-ethylfluorenone to the sum of 1-ethylfluorenone and 1,8-dimethylfluorenone to decrease with increasing maturity in the Posidonia shale. The authors suggested that the observed linear decrease reflects the loss of the longer alkyl chains from the aromatic rings due to thermal stress. The results of the analysis of the source rocks from Haltenbanken indicate that this ratio may also be influenced by facies, as illustrated in Figures 5.3.6 and 5.3.8. The concentration of 1,8-dimethylfluorenone is higher than 1-ethylfluorenone in the extracts from the Åre Formation whereas the inverse applies for most of the source rocks from the Spekk Formation. The mature samples, in particular, of both source rocks are very different from each other. 1-Ethylfluorenone clearly becomes depleted relative to 1,8-dimethylfluorenone with increasing maturity for the coaly Åre samples, as described by Wilkes et al. (1998) whereas there is a slight inverse behaviour for the Upper Jurassic source rocks from the Spekk Formation.

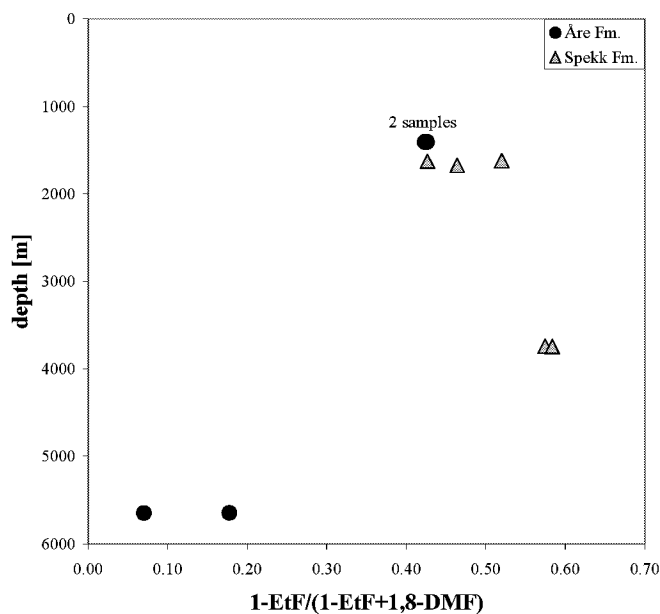


Fig. 5.3.8: Facies influence on the C₂-fluorenone distribution in source rocks from the Haltenbanken area.

Crude oils

There is some degree of scatter in the plot of the concentrations of fluorenone and the sum of C₁-fluorenones against the source facies-related pristane/phytane ratio in the oils from Haltenbanken, as illustrated in Figures 5.3.9a-b. However, if the samples from the Heidrun Field (mainly biodegraded oils) are considered separately from the other oils

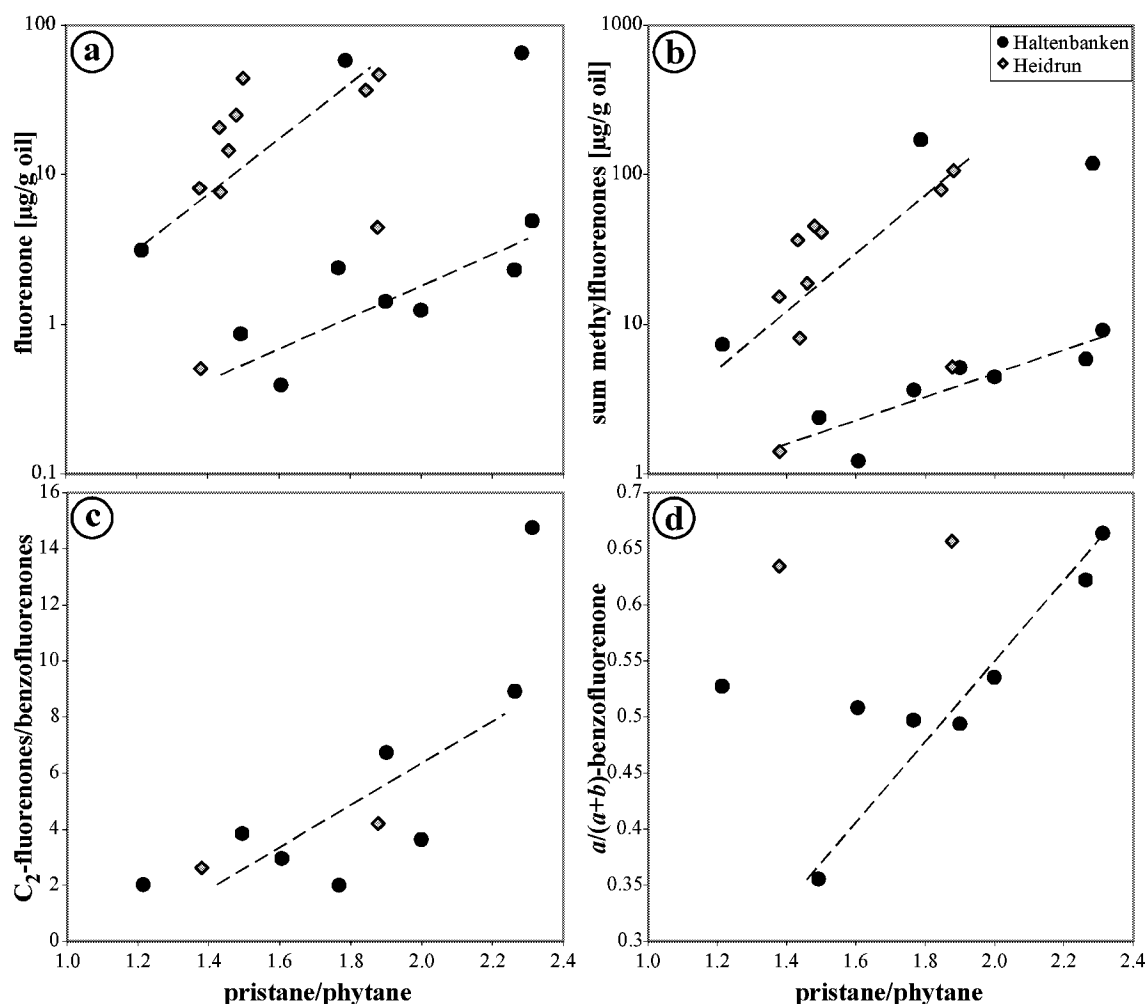


Fig. 5.3.9: Influence of facies on the fluorenone distribution in oils from the Haltenbanken area; concentrations of benzofluorenones in several samples were below the detection limit. (Note the logarithmic scale on the y-axis for the upper diagrams (a-b)).

from the Haltenbanken area then a general increase in the concentrations with increasing pristane/phytane ratio is observed for both sample suites. Fluorenone concentrations were generally higher in the Heidrun oils than in the Haltenbanken oils at any given pristane/phytane ratio; this difference may relate to differences in the degree of biodegradation and will be discussed in Chapter 5.3.7. The abundance of the C₂-fluorenones relative to that of the benzofluorenones also increases with increasing

pristane/phytane ratio, as illustrated in Figure 5.3.9c (data in Appendix 5A). Two reasons could be responsible for these observations. Firstly, aromatic components (including the most probable fluorenone precursors, fluorenes) are more abundant in terrestrial organic matter than in marine organic matter. Secondly, the formation of fluorenes would be minimised in strongly reducing depositional environments (i.e. with low pr/ph values) (Fan et al., 1989) and their oxidation to fluorenones would be limited due to lack of oxygen. It is interesting to note that the trend in the plot of the C₂-fluorenones/benzofluorenones ratio against pristane/phytane is the inverse of that noted for the source rocks. The C₂-fluorenones/benzofluorenones ratio in the predominantly marine source rocks of the Spekk Fm. ranges from 3.5-4.0 (mature samples) to 12.5-16.0 (immature) whereas ratio values for the coaly samples from the Åre Fm. are between 0.25-0.30 (mature) and 0.8-2.0 (immature). This may indicate that a direct correlation between source rocks and crude oils is not possible on the basis of the distribution of fluorenones and that other effects, such as partitioning processes, may control their occurrence in oils.

The $a/(a+b)$ -benzofluorenone ratio is relatively constant at pristane/phytane ratios <1.8 but then increases with increasing pr/ph ratio. If the geochemistry of the *b*-isomers of benzocarbazoles and benzofluorenones is similar, then the opposite correlation would be expected i.e. the relative abundance of the *b*-isomer would increase with increasing terrigenous nature of the organic matter. This again indicates that a simple correlation between the fluorenone distributions in source rock extracts and those in crude oils is not possible.

- TAMPEN SPUR -

Figure 5.3.10 shows the variation in a selection of fluorenone parameters with the 28,30-*dinor*-hopane (DNH)/30-*nor*-hopane (30NH) ratio; this facies-related hopane ratio decreases with increasing terrigenous nature of the organic matter, as described in Chapter 5.1.1. There is some scatter in the fluorenone data, and no clear correlation with facies is apparent. As shown in Figure 5.3.10c, the $a/(a+b)$ -benzofluorenone ratio generally increases with an increase in the ratio of 28,30-*dinor*-hopane (DNH) to 30-*nor*-hopane (30NH). Similarly, the concentration of fluorenone and of 1-methylfluorenone increases relative to that of 1-ethylfluorenone with increasing supply of terrestrial organic matter (Fig. 5.3.10a-b).

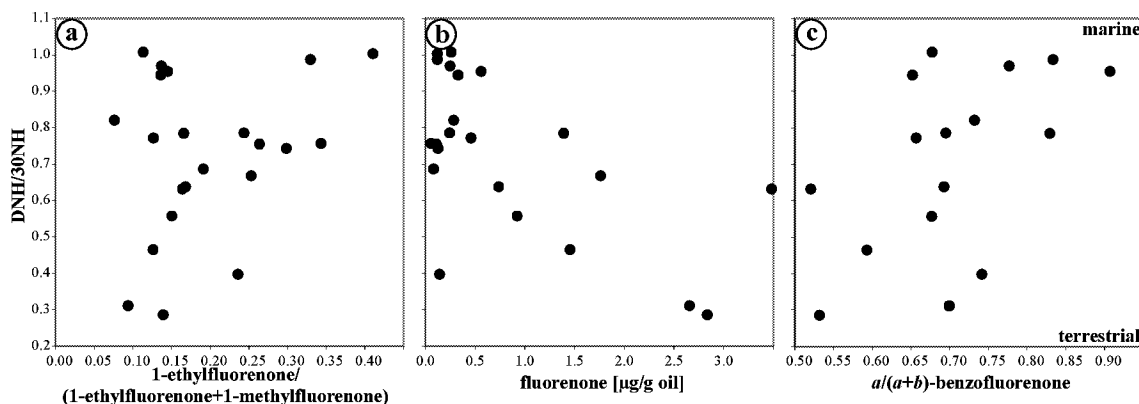


Fig. 5.3.10: Influence of facies on the fluorenone distribution in the oils from the Tampen Spur.

- VIKING GRABEN ISOLATED OILS -

For the isolated oils from the Viking Graben, positive correlations are observed between the abundance of 1-methylfluorenone relative to the other methyl isomers and to fluorenone, and the facies-related 25-*nor*-hopane/(25-*nor*-hopane + 28,30-*dinor*-hopane) ratio (Fig. 5.3.11). A similar trend is observed for the 1-ethylfluorenone/(1-ethylfluorenone + 4-methylfluorenone) ratio. It is apparent that the relative abundances of 1-methylfluorenone and 1-ethylfluorenone in the oils increase with increasing marine supply to the source organic matter. It is remarkable that these parameters give very similar values for the core samples from both the oil leg and the tar mat.

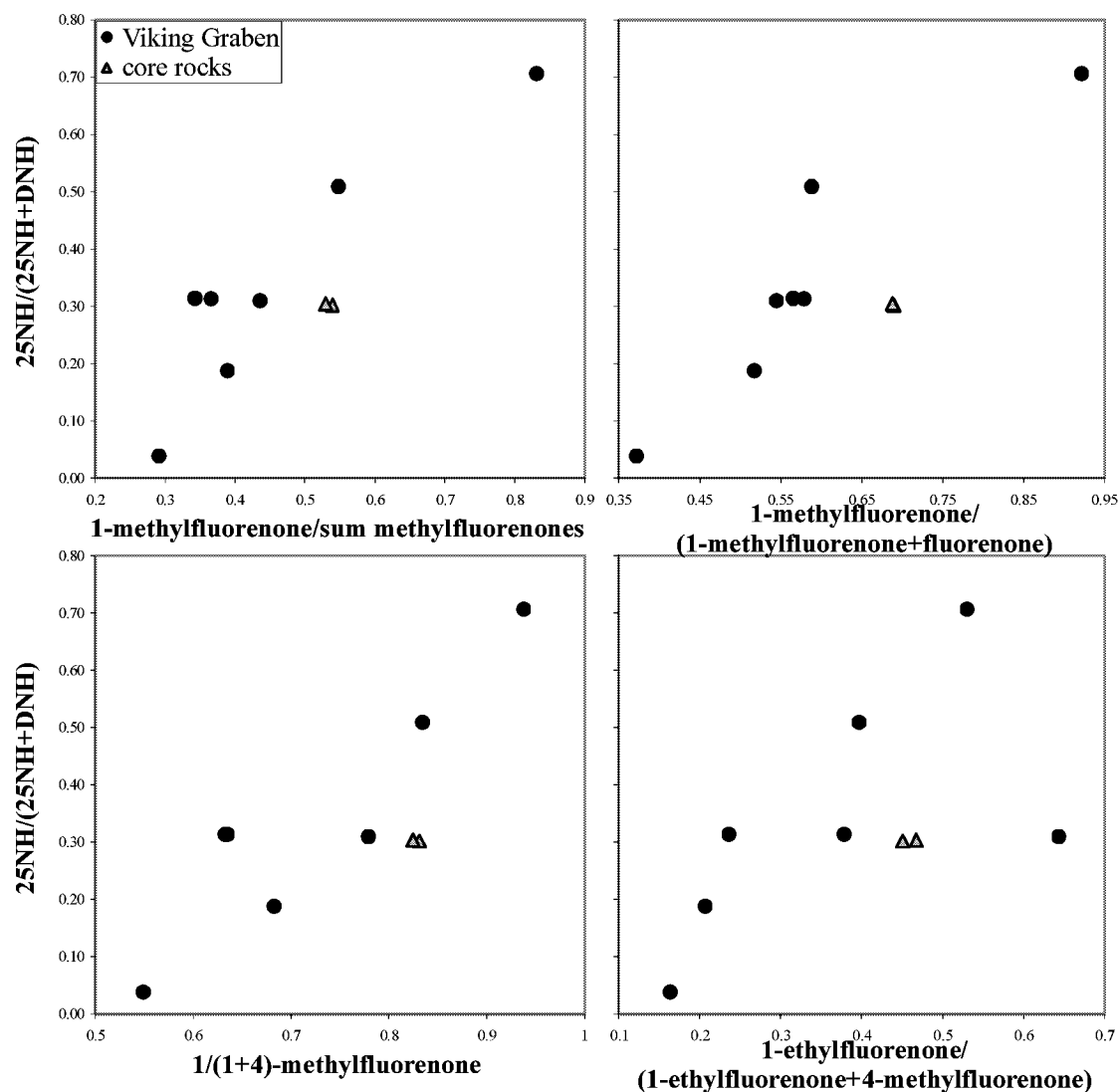


Fig. 5.3.11: Influence of facies on the distribution of fluorenones in the oils and reservoir core samples (oil leg and tar mat) from the Viking Graben.

- CENTRAL GRABEN -

For the oils from the Central Graben, several fluorenone ratios appear to be related to facies and depositional environment, as illustrated in Figure 5.3.12. The ratio of 1-methylfluorenone to the sum of 1-methylfluorenone and fluorenone increases with increasing pristane to phytane ratio whereas the abundance of 1-ethylfluorenone relative to the sum of 1-ethylfluorenone and 1,8-dimethylfluorenone decreases. There is also an increase in the abundance of benzo[*b*]fluorenone relative to the *c*-isomer with increasing pristane/phytane ratio. However, this sample suite is limited in number and some oils do not follow the main trends shown in Figure 5.3.12 .

These observations noted above may suggest that the fluorenone distribution may be influenced by source facies and depositional environment. As described previously, fluorenes are the most probable precursors of the fluorenones. It is therefore likely that the abundances and distribution of the fluorenones are largely determined by and a reflection of the abundance and distribution of the fluorenes, and are also related to the availability of oxygen in the depositional environment. However, the apparent effects of facies variation seem to be inconsistent for the different petroleum provinces, and consequently it is suggested that the interpretation of fluorenone data in the context of source facies must involve caution.

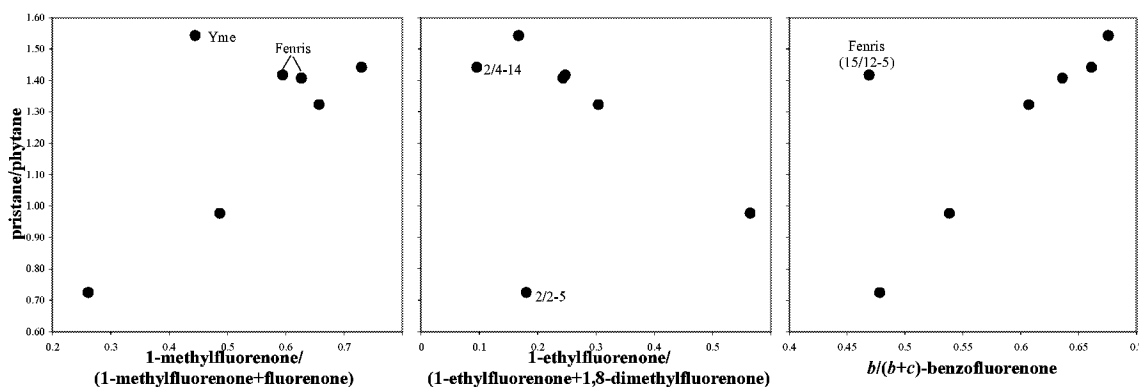


Fig. 5.3.12: Influence of facies on the fluorenone distribution in oils from the Central Graben.

5.3.4 Influence of maturity on the distribution of fluorenones and benzofluorenones

- HALTENBANKEN - *Source rocks*

As discussed in Chapter 5.3.2 and illustrated in Figure 5.3.1 the concentrations of fluorenone, methylfluorenones, C₂-fluorenones and benzofluorenones increase with increasing maturity in both of the potential source rocks from Haltenbanken. This is in agreement with an earlier study on a maturity sequence from the Posidonia shale reported by Wilkes et al. (1998a). As discussed in the previous chapter, the benzofluorenones can be used to differentiate between the source rocks of the Spekk Fm. and Åre Fm. As shown in Figure 5.3.13, the benzofluorenone distribution is also influenced by maturity. There is a systematic increase in all three benzofluorenone ratios with increasing maturity, the increase being especially pronounced in the $a/(a+b)$ -benzofluorenone ratio. The maturity-related variation in benzofluorenone ratios is more

significant for the coaly samples from the Åre Formation than for the marine source rocks of the Spekk Formation.

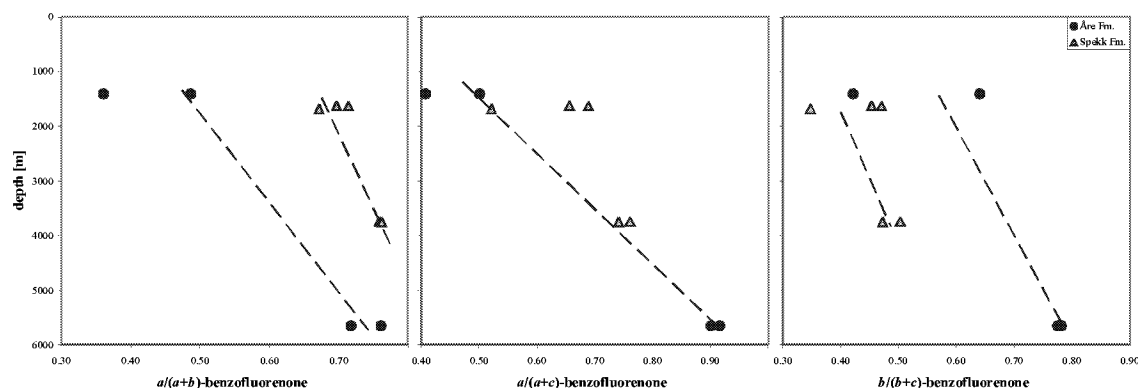


Fig. 5.3.13: Influence of maturity on the benzofluorenone distribution in the source rocks from Haltenbanken.

It is interesting to note that the effect of variation in maturity on the distribution of the alkylfluorenones is different for the two source rocks (Fig. 5.3.14). For example, whereas the abundance of 4-methylfluorenene in the source rocks from the Åre Formation decreases relative to other alkylfluorenones with increasing maturity, the reverse behaviour is observed for the samples from the Upper Jurassic Spekk Formation.

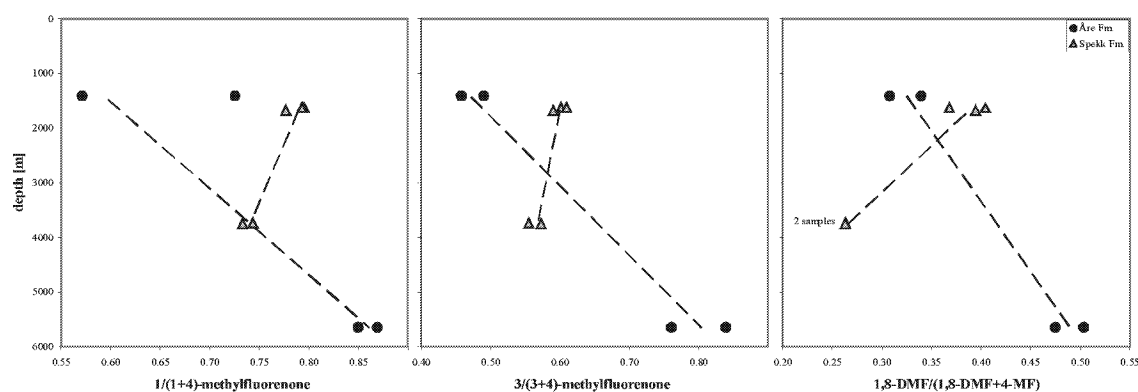


Fig. 5.3.14: Influence of maturity on the alkylfluorenone distribution in the source rocks from Haltenbanken.

- TAMPEN SPUR -

Oils

No clear trends were observed when the fluorenene distributions of the Tampen Spur oils were correlated with the maturity-related parameters established in Chapter 5.1.

Data points were quite scattered although in some cases ‘tendencies’ were apparent, as shown in Figure 5.3.15. The abundance of benzo[*b*]fluorenone relative to the *c*-isomer and to the sum of benzofluorenones increases slightly with an increase in the maturity-related C₂₉-sterane isomerisation parameter. Similar observations were made for the source rocks from Haltenbanken (Fig. 5.3.13). A controversial observation is that obtained for the *a*/(*a*+*b*)-benzofluorenone ratio. Whereas this ratio correlates positively with maturity for the source rock extracts from Haltenbanken, it decreases slightly with increasing maturation in the oils from the Tampen Spur (top right diagram, Fig. 5.3.15).

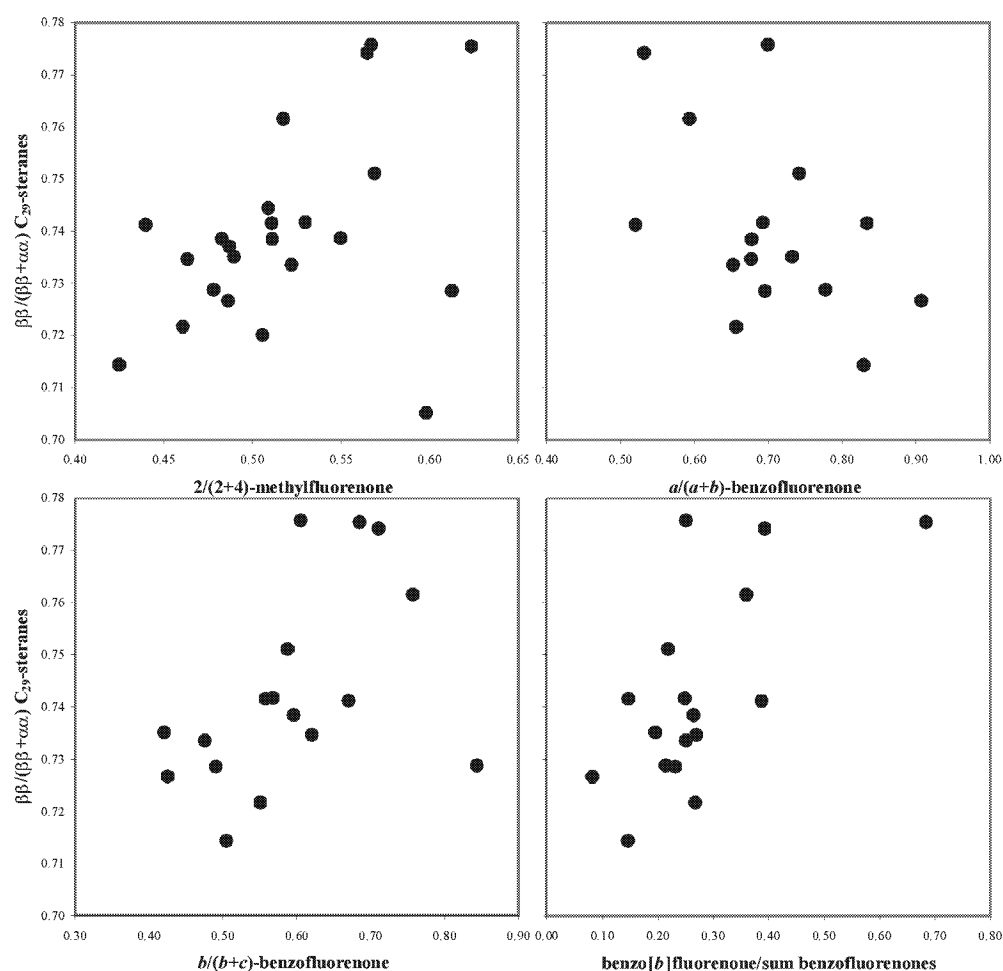


Fig. 5.3.15: Influence of maturity on the fluorenone distribution in oils from the Tampen Spur.

These results point to the difficulties in the general use of fluorenone distributions in oils for facies and maturity assessments. A slight increase in the 2/(2+4)-methylfluorenone ratio with increasing maturity was observed.

5.3.5 Influence of maturity and primary migration on the fluorenone distribution using hydrous pyrolysis experiments

As reported in Chapter 5.3.2, fluorenones could only be quantified in the recovered rock extracts from the hydrous pyrolysis study; the concentrations of fluorenones in the expelled oils were below the detection limit. This could be a primary migration effect, i.e. it may reflect the strong sorption of fluorenone after production within the source rock due to its high dipole moment (2.91 D).

As illustrated in Figure 5.3.5, there is a strong increase of the concentrations of fluorenone, methylfluorenones, C₂-fluorenones and benzofluorenones between 345°C and 355°C. The same trend was observed with the carbazoles. This abrupt increase could reflect the decomposition of thermally less stable components into volatile compounds and (insoluble) macromolecular components resulting in the enrichment of the thermally more stable aromatic fluorenones in the extracts. However, the reason for the subsequent slight decrease in the concentrations at temperatures above 355°C is not clear since it was not reflected in a corresponding increase in concentrations in the expelled oils.

Variations in the relative abundance of the benzofluorenones during artificial maturation were observed. As illustrated in Figure 5.3.16, the $a/(a+b)$ - and $a/(a+c)$ -benzofluorenone ratios increased slightly with increasing maturity. This was also observed for the source rocks from Haltenbanken but is inverse to results obtained for the crude oils from the Tampen Spur. In contrast to the source rocks from Haltenbanken and to the crude oils, the $b/(b+c)$ -benzofluorenone ratio decreases with increasing maturity. As shown in the previous chapter, the benzofluorenone ratios also show a tentative correlation with facies and depositional environment-related parameters.

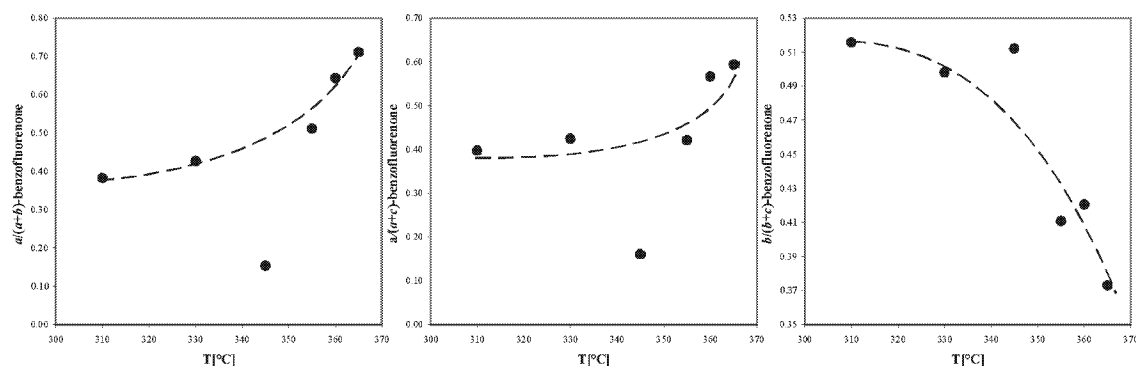


Fig. 5.3.16: Effect of maturity on the fluorenone distribution based on hydrous pyrolysis experiments.

Therefore, the controversial observation for the $b/(b+c)$ -benzofluorenone ratio in the Haltenbanken samples may reflect differences in facies and depositional environments of the source rocks since these factors do not apply to the artificial maturity sequence. However, other processes, such as expulsion and secondary migration, must be considered, and these are discussed in the following sections.

The abundance of 1-methylfluorenone increases with increasing artificial maturation relative to that of its isomers, as depicted in Figure 5.3.17. It is remarkable that the strongest increase in these ratios occurs between 355°C and 360°C. This is most dramatically seen in the ratio of 1,8-dimethylfluorenone/(1,8-dimethylfluorenone + 4-methylfluorenone) which remains stable up to 355°C whereafter there is an abrupt increase.

These observations indicating an apparent influence of maturity on the fluorenone distribution may reflect fluorenone generation in the source rocks. However, it should be noted that fluorenes, as the probable precursors, are also affected by maturity and that the variations in the fluorenones during maturation could reflect variation in the abundance of the fluorenes.

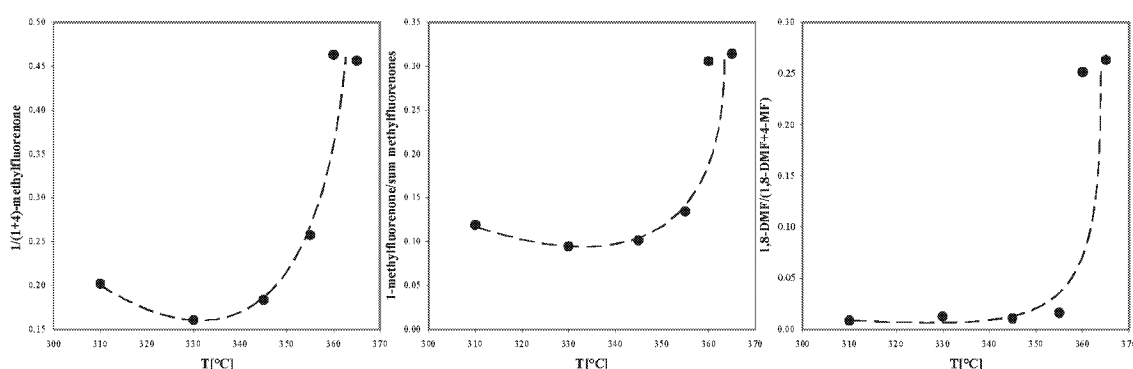


Fig. 5.3.17: Influence of maturity on the alkylfluorenone distribution based on hydrous pyrolysis experiments.

5.3.6 Influence of secondary migration on the distribution of fluorenones

As shown earlier in this chapter, high amounts of fluorenones could be determined in source rock extracts. The hydrous pyrolysis experiments indicated that most of the fluorenones will be sorptively retained during primary migration due to their high dipole moments. However, fluorenes are liberated from the source rock during expulsion. Due to the activation of the methylene bridge by two adjacent benzene rings

these compounds are easily oxidised to the corresponding ketones. Oil-water and/or oil-mineral matter interactions may lead to oxidation of the fluorenes in the expelled oils during migration to the reservoir. Therefore, the effect of secondary migration on fluorenone distributions was tested using the proposed migration sequences from the Tampen Spur and Haltenbanken. As illustrated in Figure 5.3.18, there is some degree of scatter in the data but there is a slight and unexpected decrease in the abundance of 1-methylfluorenone relative to its isomers with increasing migration distances. The abundance of the shielded isomer should increase relative to that of the exposed isomers with increasing migration distance from source to trap due to its reduced polarity, as demonstrated for carbazoles and xanthenes in this study. However, if fluorenes were oxidised during migration then a negative trend would be expected. When oil-water and/or oil-mineral matter interactions lead to the oxidation of fluorenes in expelled oils during migration into the reservoir, the shielded isomer might be less amenable to oxidation compared to the non-shielded isomers due to steric hindrance. This could result in a relative decrease in the shielded/non-shielded ratios with increasing exposure to interactions and a negative trend with increasing migration distance. However, other shielded/non-shielded ratios e.g. with 1,8-dimethylfluorenone, do not support this suggestion, and non of the corresponding ratios obtained from the Tampen Spur oils correlate with migration distances.

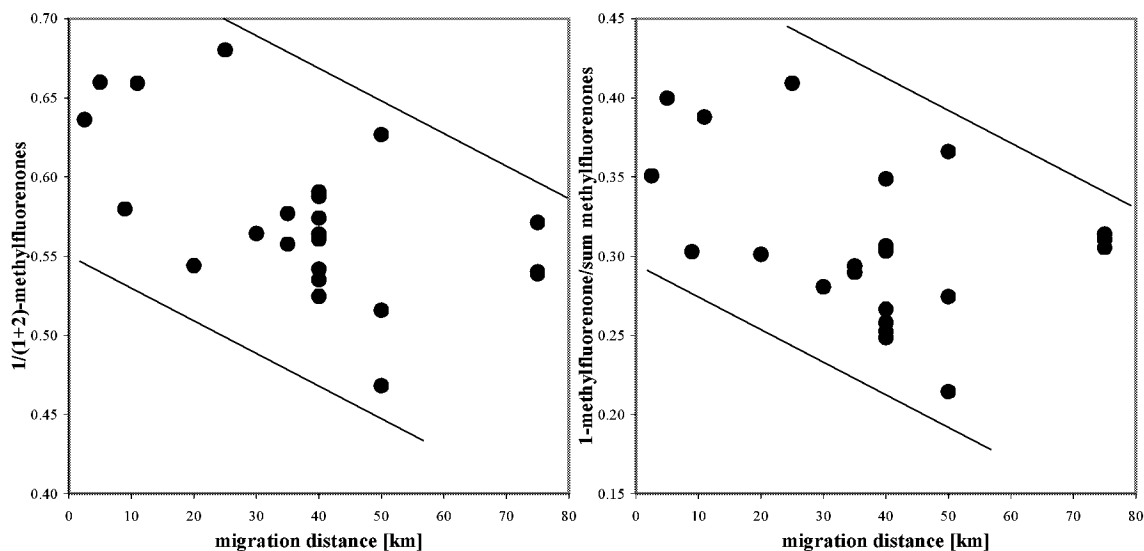


Fig. 5.3.18: Influence of migration distances on the distribution of fluorenones for oils from Haltenbanken.

5.3.7 Influence of biological degradation and/or water washing on the distribution of fluorenones

Fluorenone is one of the main products of the aerobic biological degradation of fluorene. As described previously, Garon et al. (2000) found that 30 strains of micromycetes were able to metabolise fluorene to fluorenone. Other biological degradation experiments involving a PAH/creosote contaminated soil from an old gas works site demonstrated the accumulation of various metabolites/degradation products including fluorenone and 4-hydroxyfluorenone (Eriksson et al., 2000). The authors proposed that environmental chemical/physical conditions probably have a strong influence on whether these compounds remain (as end products) or not, since the results were variable according to nutrient and inoculum conditions. Fluorenone accumulation was reported to occur during the degradation of fluorene by *Arthrobacter* sp. Strain

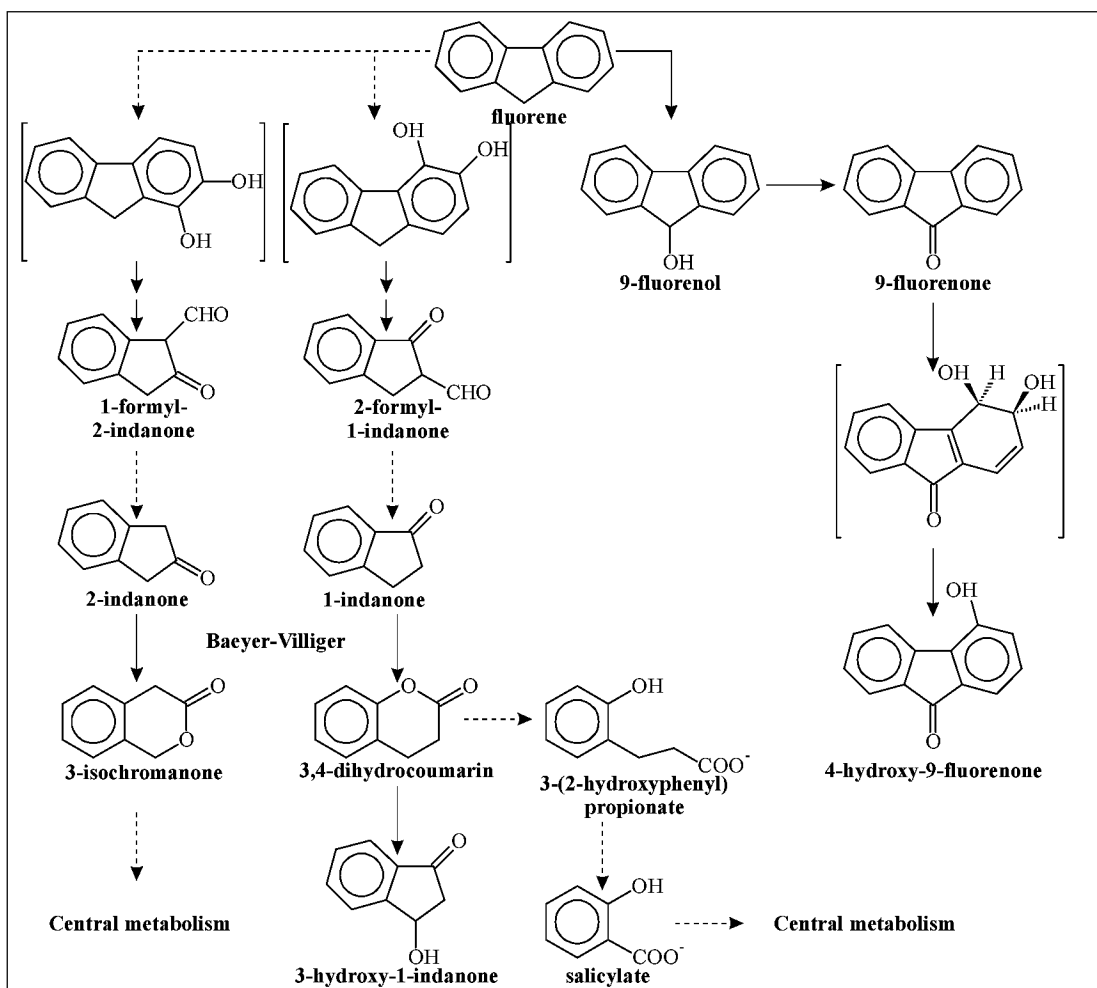


Fig. 5.3.19: Schematic pathway proposed for the degradation of fluorene by an *Arthrobacter* sp. after Casellas et al. (1997); structures in brackets are proposed intermediates and have not been identified; dashed arrows indicate two or more successive reactions.

F274 (Grifoll et al., 1994) and *Arthrobacter* sp. Strain F101 (Grifoll et al., 1992), and it was proposed as a dead-end product in a non-productive route. More recently, Casellas et al. (1997) proposed two pathways for fluorene metabolism in *Arthrobacter* sp. Strain F101, involving monooxygenation at C-9 leading to the accumulation of fluoren-9-one, and dioxygenation at C-1 and C-2 or at C-3 and C-4 as illustrated in Figure 5.3.19. The first pathway involves oxygenation of fluorene at C-9 to give 9-fluorenol, which is then dehydrogenated to the corresponding ketone, 9-fluorenone. The identification of 4-hydroxy-9-fluorenone led to the suggestion that dioxygenation of the ketone does occur (Casellas et al., 1997).

As described in Chapter 5.1.3, a suite of biodegraded oils from the Gullfaks Field was used to investigate the influence of biological degradation on the fluorenone distribution in oils. A slight decrease in the abundance of 1-methylfluorenone relative to 4-methylfluorenone and fluorenone with increasing biodegradation was observed, as illustrated in Figure 5.3.20. Steric shielding of the methyl group adjacent to position 9 of the fluorene structure would hinder the generation of 1-methylfluorenone by the oxidation of 1-methylfluorene. If fluorenones are generated by biological oxidation of the corresponding fluorenes then a depletion of 1-methylfluorenone relative to other compounds would be expected. Unfortunately, this observation was not manifest by the relative abundances of 1-ethylfluorenone and 1,8-dimethylfluorenone which should be affected in the same way. As shown in Figure 5.3.20, the concentration of benzo[*b*]fluorenone increases relative to the [*a*] and [*c*] isomers with increasing biodegradation. Two samples in the data set were omitted due to the low abundances of benzofluorenones. The increase in the relative abundance of benzo[*b*]fluorenone may

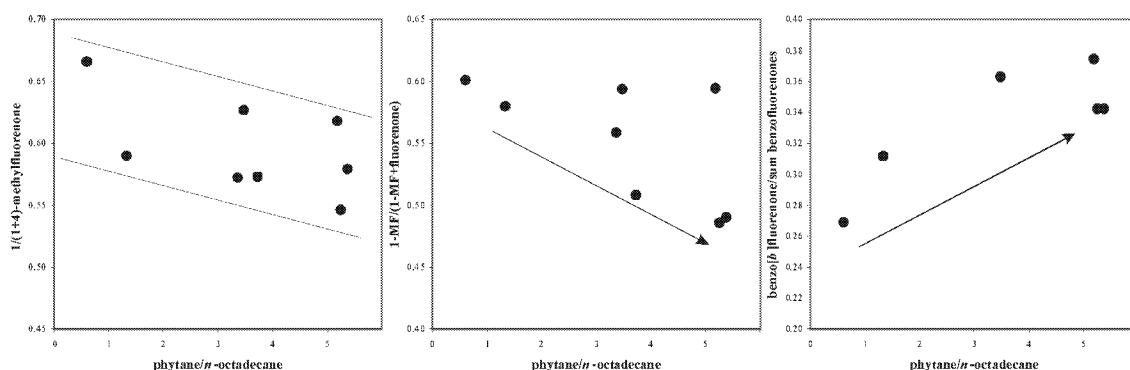


Fig. 5.3.20: Influence of biodegradation on the fluorenone distribution using the biodegradation sequence from the Gullfaks Field.

indicate a preferred enzymatic oxidation of the linear structure relative to other homologues.

5.3.8 Conclusions

Fluorenone and its alkylated homologues were detected in all of the analysed crude oils from offshore Norway whereas the abundances of the benzofluorenones were below the detection limit in 20 of the 72 samples. High amounts of fluorenones were detected in the nine source rock samples from Haltenbanken, a reservoir core sample and a tar mat sample and in the recovered rock bitumens from hydrous pyrolysis experiments. The abundances of fluorenones are below the detection limit in the expelled oils from this artificial maturation sequence. Furthermore, the absolute concentrations of fluorenones increase with increasing maturity, as observed for the source rock extracts.

The two potential source rocks from Haltenbanken are distinguishable on the basis of the distribution of fluorenones independently of maturity; a similar differentiation was noted from the analysis of the carbazoles. The differentiation is evident in the relative abundances of the fluorenone groups, in the alkylated fluorenone isomer ratios and in the distribution of the benzofluorenones.

No direct correlations between source rocks and the probable corresponding crude oils were observed. Factors such as fractionation during expulsion and partitioning during migration or post-sampling oxidation may therefore control the fluorenone distributions in crude oils. A few fluorenone ratios show good correlations with molecular indicators of facies and depositional environment.

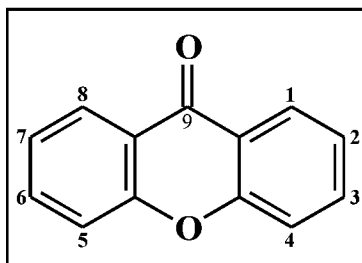
Apart from a maturity-related increase in the absolute concentrations of the different fluorenone groups there is also an influence of maturity on some alkylated fluorenone isomer ratios and on the distribution of benzofluorenones, both for the natural source rocks and for artificially matured recovered rock extracts. Only a slight maturity effect was observed on the fluorenone distributions in the oils from the Tampen Spur, suggesting the influence of other processes, described above, in controlling the fluorenone distribution of oils.

A comparison of the methylfluorenone distribution with the methylfluorene distribution of crude oils reveals similarities between these compound groups which may indicate that the ketones are oxidation products of the fluorenes. This is supported

by window-sill experiments involving an oil contained in a clear glass vial exposed to sunlight and air over a six months period. Concentrations of the fluorenones are two orders of magnitude higher after the sun/air exposure compared with those in the initial oil. These results indicate that oxidation during storage and sample handling is an important factor which could control fluorenone concentrations, especially for oils which usually have naturally low abundances of this compound class. However, the effect on the distribution of fluorenones should be smaller, although a comparison of fluorenes and fluorenones indicates that alkyl groups adjacent to the position 9 of the fluorene structure could hinder oxidation. In this respect, the abundances of the shielded 1-methylfluorenone and 1-ethylfluorenone decrease with increasing secondary migration distance compared to the abundances of the non-shielded methyl isomers. This may indicate oxidation of fluorenes by oil-water and/or oil-mineral matter interactions during migration.

The abundance of 1-methylfluorenone also decreases with increasing degree of biodegradation relative to the abundances of the non-shielded isomers, as shown in the analysis of the biodegradation oil sequence from the Gullfaks Field. As biological degradation of fluorene results in fluorenone production, as a partly dead-end product, steric hindrance of the methyl group adjacent to position 9 of the fluorene structure could reflect the relative decrease in the abundance of the shielded isomer to those of the non-shielded isomers.

5.4 Xanthenes



xanthen-9-one (xanthone)

5.4.1 Introduction

Xanthenes are aromatic oxygen-containing compounds consisting of a tricyclic aromatic structure with an ether and a keto function in the ring system.

Xanthenes have not been reported as constituents of crude oils and source rocks until now. The unsubstituted xanthone ring structure is not known to occur in nature but it does form the basic structure of different natural pigments of plants, e.g. gentian root (Falbe and Regitz, 1989-1992, p. 5078). Highly substituted xanthenes (with hydroxy-, methoxy- and alkylgroups) occur in many different terrestrial plants (e.g. Tomasek and Crawford, 1986; Peres and Nagem, 1997), especially those that prefer tropical or subtropical climates. Xanthenes are synthesized by fungi, lichens, ferns and many higher plants (Devon and Scott, 1975; Culberson, 1969; Chexal et al., 1975; Berti and Bottari, 1968). Many shrubs and herbs, which occur widely in temperate regions of the world, contain xanthenes (Wu et al., 1998).

Xanthone is one of the predominant oxygenated polycyclic aromatic compounds found in the mutagenic fraction of extracts of diesel and gasoline engine exhaust particles (Strandell et al., 1994). Consequently, it has been identified in urban aerosols (Moriske and Rüden, 1988; Fernandez and Bayona, 1992), in water samples from the North Sea and from the estuary of the river Elbe, Germany (Bester and Theobald, 2000), as well as in sewage sludges in Upper Silesia (Bodzek and Janoszka, 1995).

Many of the naturally occurring xanthenes are considered important compounds because they show remarkable pharmacological and other biological activities. Furthermore, they are of chemotaxonomic value (Afzal and Al-Hassan, 1980). The isolation of a neurotrophic xanthone and a number of new antioxidative xanthenes has

been described by Minami et al. (1998) and authors cited therein. Recent biological studies have reported that some xanthenes isolated from *Garcia* species exhibit a wide range of biological and pharmacological activities (e.g. anti-HIV, antihistamine, antiserotonin and anti-MRSA activity as well as topoisomerases I and II inhibitory activity) (Minami et al., 1998). For example, substituted xanthenes contain a potential antiepileptic activity (Marona et al., 1998) and antimycobacterial activity (Pickert et al., 1998; Schaper et al., 1999); they are inhibitors of Epstein-Barr virus activation (Ito et al., 1998) and leading compounds for chemotherapy of human immunodeficiency virus (HIV) infection (Vlietinck et al., 1998). The catabolism of xanthone by an *Arthrobacter* sp. (strain GFB100) capable of growth on this compound as its main source of energy has been described by Tomasek and Crawford (1986).

5.4.2 Identification and synthesis of xanthenes

In this study, the xanthenes were detected in the low-polarity NSO fraction of crude

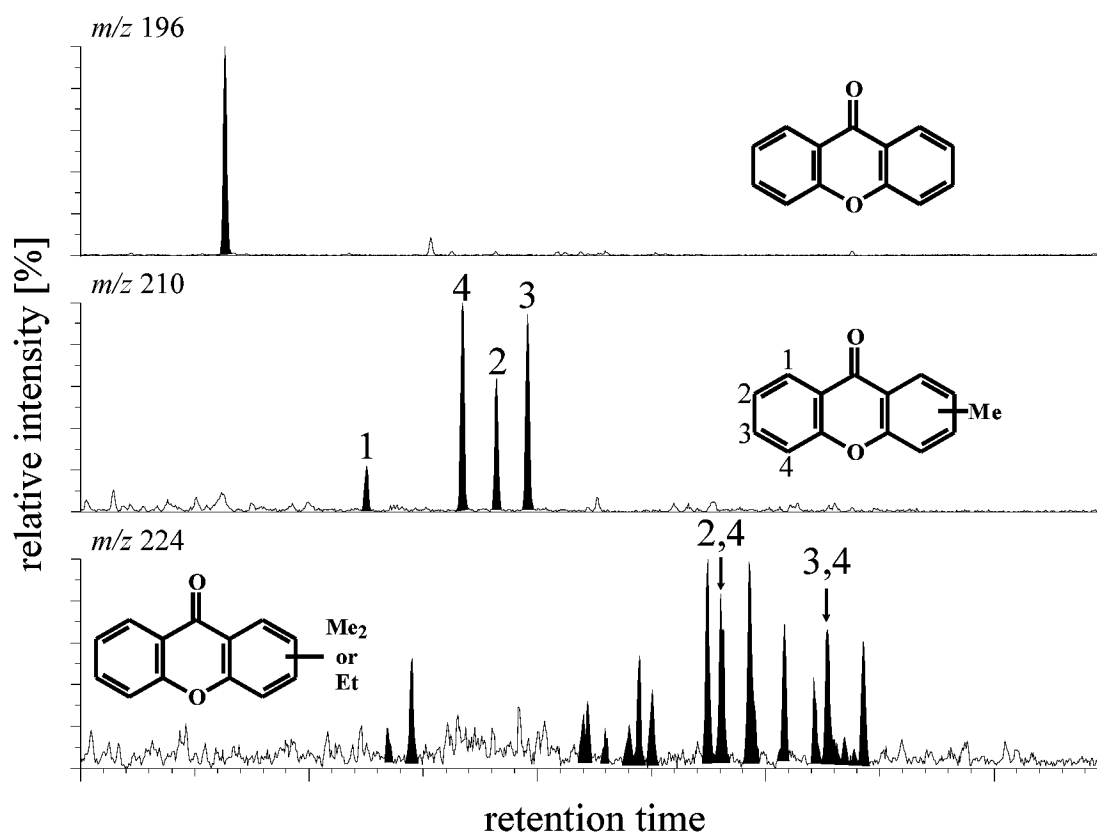
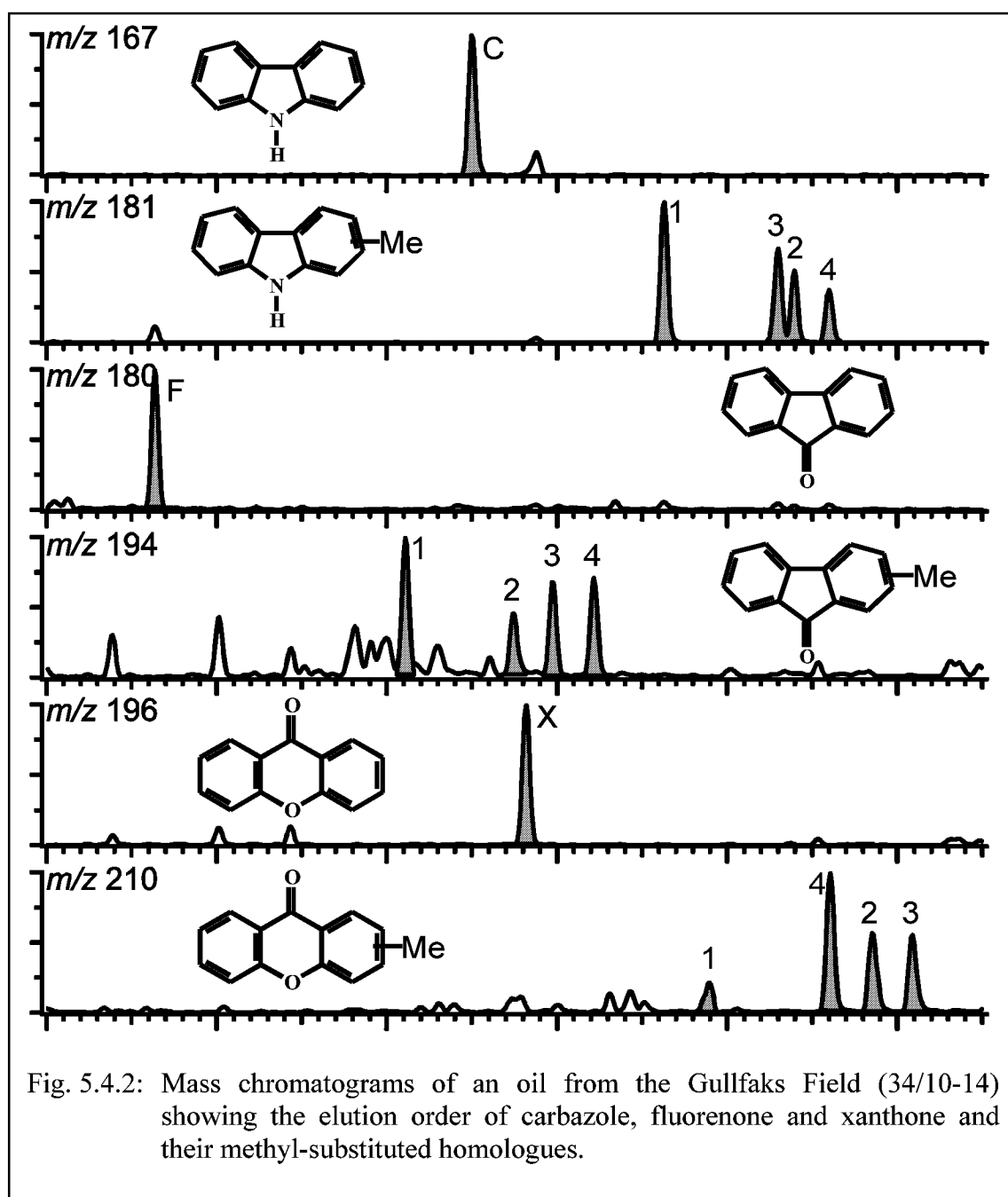


Fig. 5.4.1: Mass chromatograms showing the elution order of xanthone, the four methyl-xanthenes and two of the C₂-xanthenes in a crude oil from the Barents Sea (well 7120/1-2).

oils and rock extracts, i.e., the fraction in which carbazoles and fluorenones also occur. The parent compound, xanthone, the four methylxanthenes and two dimethylxanthenes were identified by comparison of the retention time with those of authentic standards after coinjection on two GC columns of different polarity and from their mass spectra characteristics.

The elution order of the methylxanthenes, reported here for the first time, was established as 1-4-2-3 on a BPX-5 column (Fig. 5.4.1). This elution order reflects the shielding effect of the 1- and 4-methyl substituents on the polar keto- and ether-



functions, respectively. Steric shielding of the keto-function by 1-methyl substitution and, to a lesser extent, shielding of the ether-function by 4-methyl substitution decreases the polarity of the 1- and 4-methylxanthenes, resulting in an earlier elution. The retention times of two dimethylxanthenes (the 2,4- and 3,4-dimethyl isomers) were also determined, as illustrated in Figure 5.4.1.

In comparison with carbazole and fluorenone and their methylated homologues, xanthone and its alkylated derivatives elute relatively late (Fig. 5.4.2). The earlier elution of fluorenone is perhaps due to its lower boiling point (342°C) relative to carbazole (355°C) and xanthone (351°C) (Falbe and Regitz, 1989-1992), and its lower polarity. The influence of polarity on the elution order is recognisable by the comparison of xanthone and carbazole. Although carbazole has the higher boiling point, xanthone elutes later than carbazole due to its higher polarity. In this regard, carbazole has a dipole moment of 2.09 D (Cowley and Partington, 1936) whereas xanthone has a dipole moment of 3.11 D (Le Fèvre and Le Fèvre, 1937).

Different reaction pathways have been described for the synthesis of alkylated xanthenes. The best established method is a two-step reaction illustrated in Figure 5.4.3 for methylxanthenes. The first step is a condensation reaction between a benzoic acid and a cresol under Ullmann conditions (Pickert and Frahm, 1998). The alkylated xanthenes are then formed in a second step by intramolecular Friedel-Crafts acylation of the phenoxybenzoic acid as described by Pickert and Frahm (1998).

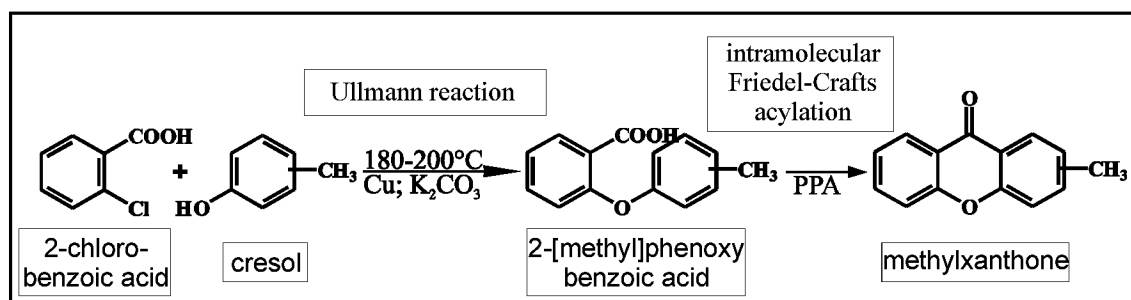


Fig. 5.4.3: Reaction pathway for the synthesis of alkylxanthenes.

5.4.3 Occurrence of xanthenes

Quantitative occurrence of xanthenes in crude oils, offshore Norway

Xanthone and its alkylated homologues were quantified in 67 of the 72 analysed oils from offshore Norway. The exceptions, where xanthenes were either absent or occurred in very low amounts, were two oils from the Central Graben (well 2/2-5 (hypersaline, anoxic source environment) and well 2/4-14 (high maturity condensate)), a condensate from the Gullfaks Gamma Field and two biodegraded oils from the Grane and Troll areas. For the other oils, the quantitative occurrence of xanthone, the sum of methylxanthenes and the sum of C₂ xanthenes is illustrated as histograms in Figure 5.4.4. Most of the oils contain all three compound groups at concentrations of less than 5 µg/g oil, but some oils are clearly enriched. Xanthone occurred in concentrations of up to 38 µg/g oil (Appendix 6a).

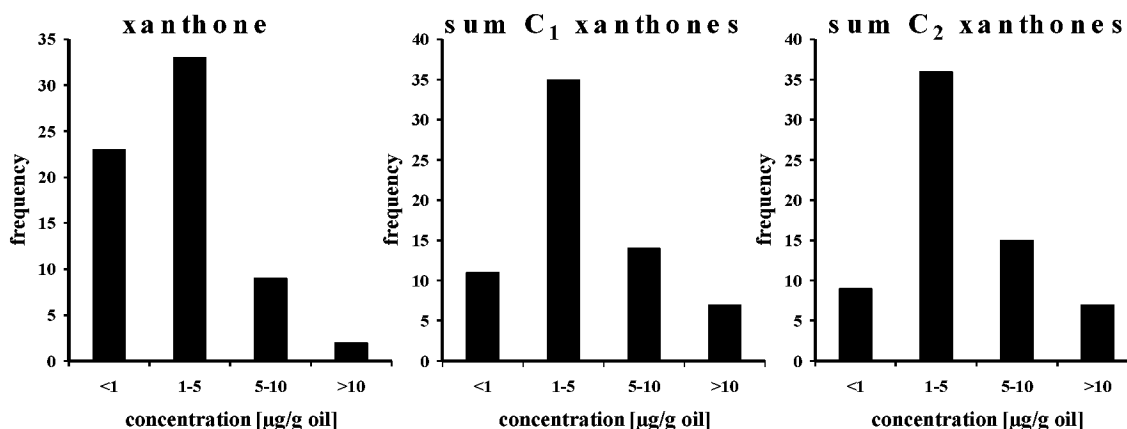


Fig. 5.4.4: Histograms showing the quantitative occurrence of xanthone, sum of C₁ and sum of C₂ xanthenes in crude oils, offshore Norway.

In contrast to the occurrence of the benzocarbazoles and benzofluorenones, benzoxanthenes could not be detected in the oils. This might be an indication of the origin of xanthenes, which will be discussed later. In this connection, it is notable that the source rock extracts from the Spekk and Åre Formations contain only very low (unquantifiable) amounts of xanthenes.

A more detailed examination of the quantitative occurrence of xanthenes with regard to the different sample sequences from offshore Norway shows that the majority of oils exhibit very similar quantitative distribution patterns, as illustrated in Figure 5.4.5. In addition, the concentrations of xanthone, the sum of the methylxanthenes and the sum of the C₂-xanthenes are of the same order of magnitude. The remarkable exceptions to the general picture are the biological degradation sequence from the Gullfaks Field and

the strongly biodegraded oils from the Heidrun Field which are characterised by higher abundances of methylxanthenes and C₂-xanthenes. The higher abundances of the alkylxanthenes relative to that of the unsubstituted xanthone in the biodegraded oils could reflect shielding of the functional groups by the alkyl groups, reducing the polarity of the xanthenes and thereby decreasing their water solubility and susceptibility to water-washing. The reduced solubility in water implies a reduced bioavailability. This will be discussed in detail in the following sections.

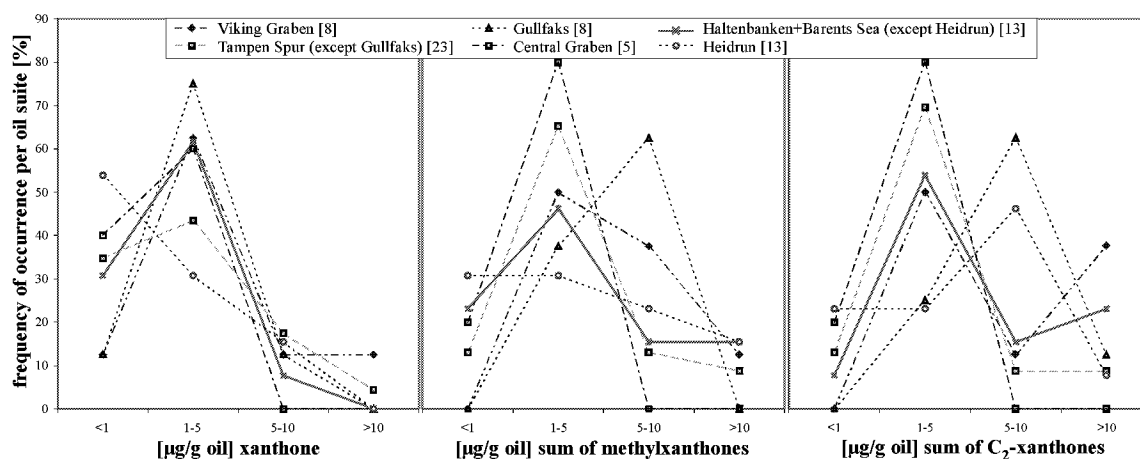


Fig. 5.4.5: Frequency of occurrence of xanthone, sum of C₁ and C₂ xanthenes in 6 crude oil suites from different areas offshore Norway.

5.4.4 Influence of facies changes on the distribution of xanthenes

- HALTENBANKEN -

Crude oils

An influence of facies on the distribution of xanthenes could be observed only for the oils from the Haltenbanken area where it was manifest in the relative abundance of xanthone, the sum of the methylxanthenes and the sum of the C₂-xanthenes. The abundances of the alkylated xanthenes relative to xanthone increase with increasing terrigenous character, as measured by the percentage of the C₂₉ ββ steranes, a terrigenous marker (Fig. 5.4.6). In addition, the concentrations of methylxanthenes decrease relative to those of the C₂-xanthenes with increasing terrigenous supply. Whereas the crude oils from the Heidrun Field indicate a very similar source facies, some strongly biodegraded oils from this field are characterised by low values for these ratios. This could reflect the effect of partitioning processes or it could be the result of biological degradation, a point which will be discussed later. A correlation between

variation in facies and in the distribution of the xanthenes could not be observed for the oils from the Central Graben and the Viking Graben.

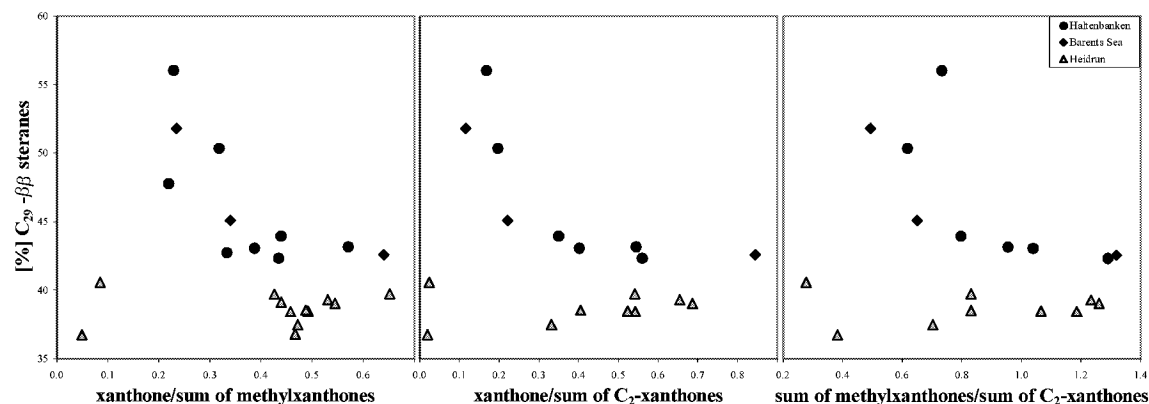


Fig. 5.4.6: Plots illustrating the facies dependence of the distribution of xanthenes in the oils from Haltenbanken and the Barents Sea.

It is interesting to note for the Haltenbanken oils there is also a facies-related variation in the isomeric distributions of the methylxanthenes. Figure 5.4.7 shows how the 4/(4+1)-methylxanthone ratio increases with increasing pristane to phytane ratio. As described in Chapter 5.1.5, an increase in the pristane to phytane ratio of the oils was observed on going from the west to the east within the Haltenbanken area. These observations indicate that the distribution of methylxanthenes is to some extent influenced by source facies variations for some of the oils from Haltenbanken. Only the three oils from the Midgard Field do not follow this trend.

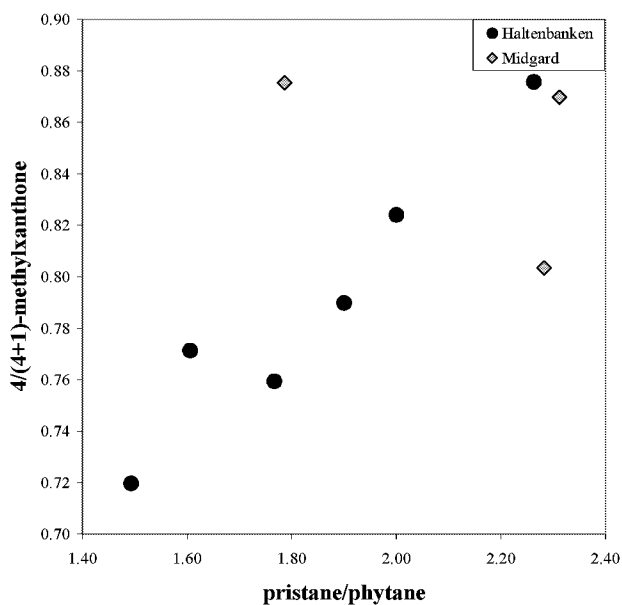


Fig.5.4.7: Plot illustrating the facies dependence of the methylxanthone ratio for oils from Haltenbanken.

- TAMPEN SPUR -

There was no indication of a correlation between the variation in source facies and xanthone distribution in the oils from the Tampen Spur area.

- VIKING GRABEN ISOLATED OILS -

The Viking Graben isolated oils showed some possibility of an influence of source facies on the distribution of xanthenes. As demonstrated in Figure 5.4.8, there is an increase in relative abundance of xanthone homologue groups with increase in the facies-related ratio of 25-*nor*-hopane to the sum of the two *nor*-hopanes for most of the oils, indicating facies and depositional environment influences. The two reservoir core samples are enriched in the alkylated xanthenes relative to xanthone and in the C₂-xanthenes relative to the sum of methylxanthenes. The relative decrease in abundance of xanthone and the methylxanthenes in the tar mat may be due to partitioning processes.

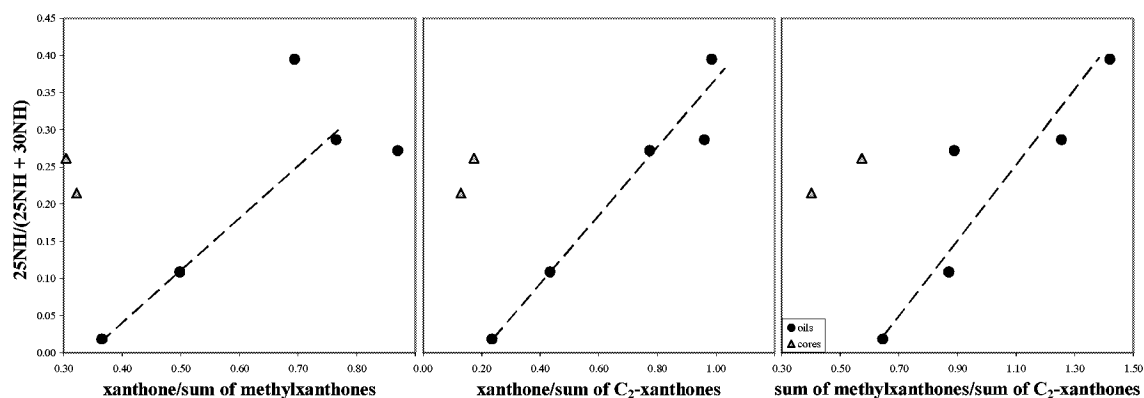


Fig. 5.4.8: Plots illustrating the facies dependence of the distribution of xanthenes in the Viking Graben isolated oils.

5.4.5 Influence of maturity on the distribution of xanthenes

Crude oils

The relative abundance of xanthone, the sum of the methylxanthenes and the sum of the C₂-xanthenes in all of the investigated oils from offshore Norway is shown as a ternary plot in Figure 5.4.9. The crude oils show large variations within the data set, delineated by the curve drawn in the figure. For most oils, especially those from Haltenbanken, the Barents Sea and many from the Tampen Spur area, the xanthone to methylxanthone ratio remains essentially constant (Trend 1), whereas the relative abundance of the C₂-xanthenes varies considerably. The oils from wells 34/10-30, 34/7-10, 34/7-8, 34/8-8R (Trend 2) are clearly enriched in xanthone. The oils from the Central Graben also contain a higher proportion of xanthone than most of the other oils.

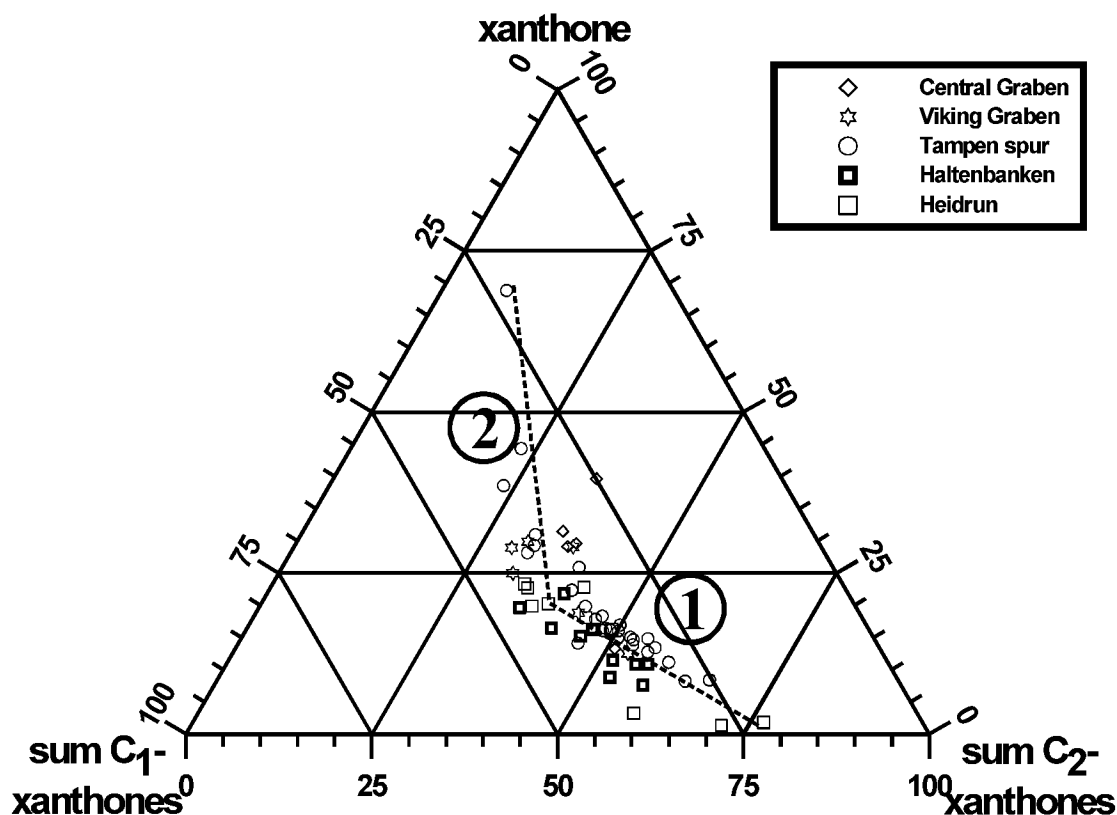


Fig. 5.4.9: Ternary plot showing the relative abundance of the C₀-, C₁- and C₂-xanthenes in all of the investigated oils from offshore Norway.

- TAMPEN SPUR -

Figure 5.4.10 shows the correlation between the ratios of xanthone to the sum of the methylxanthenes, xanthone to the sum of the C₂-xanthenes, and sum of the methylxanthenes to the sum of the C₂-xanthenes and the maturity-related ratio of diahopane to the sum of diahopane and 30-*nor*-moretane. This maturity-related

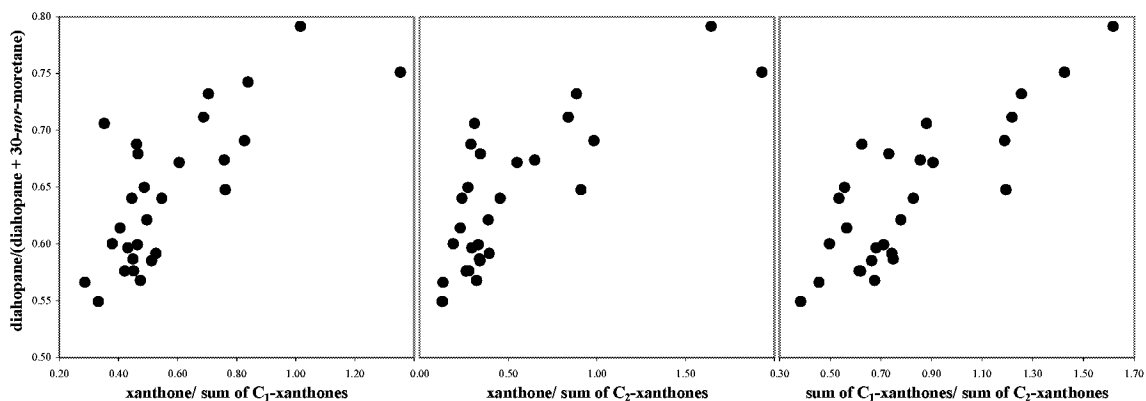


Fig. 5.4.10: Plots illustrating the maturity dependence of the distribution of xanthenes for oils from the Tampen Spur area.

parameter was established by Cornford et al. (1986), further applied by Horstad et al. (1995) and Karlsen et al. (1995), and is used in the present study (Fig. 5.1.14) for the oils from the Tampen Spur area. The three plots shown in Figure 5.4.10 reveal the maturity dependence of the relative distribution of xanthenes. With increasing maturity, the concentration of xanthone increases relative to both the methylxanthenes and the C₂-xanthenes, and the sum of the methylxanthenes increases relative to the sum of C₂-xanthenes. One oil from well 34/7-10 (not depicted in Figure 5.4.10) was unusual in having very low amounts of C₂-xanthenes (not quantifiable) and a very high ratio of xanthone to the sum of the C₁-xanthenes (2.63). A second remarkable oil from well 34/10-30 (also not shown in Fig. 5.4.10) exhibits the highest values of the three ratios described above (3.1, 7.9 and 2.6, respectively), which cannot be explained by maturity effects alone.

An increase in the absolute concentrations of xanthone and the sum of C₁- and the C₂-xanthenes with increasing maturity is observed for the oils from the Tampen Spur but only for some of the oils from the Gullfaks Field, as shown in Figure 5.4.11. The oil sample from well 34/10-30 in the Gullfaks Sør Field (not integrated in the left diagram of Figure 5.4.11) contained remarkably high amounts of xanthone (38.7 µg/g oil).

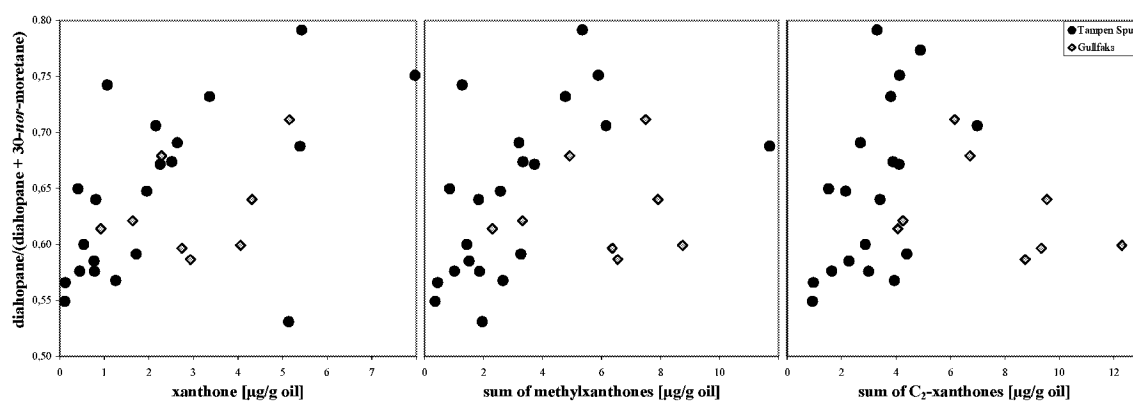


Fig: 5.4.11: Plots illustrating the concentrations of C₀-, C₁- and C₂-xanthenes versus maturity for the oils from the Tampen Spur area.

The effect of maturity on the relative abundance of individual isomers was also investigated. As depicted in Figure 5.4.12, a slight increase in the 4/(4+2)-methylxanthone ratio with increasing maturity is observed for the oils from the Tampen Spur area. Only three oils from the Visund Field (34/8-8R), Rimbaks Field (34/10-17) and the Vigdis East Field (34/7-8) do not follow this trend. Oils from wells 33/9-14, 34/7-10, 34/7-26A, 34/10-34 and 34/10-35 are excluded in Figure 5.4.12 due to the very low quantities of methylxanthenes detected.

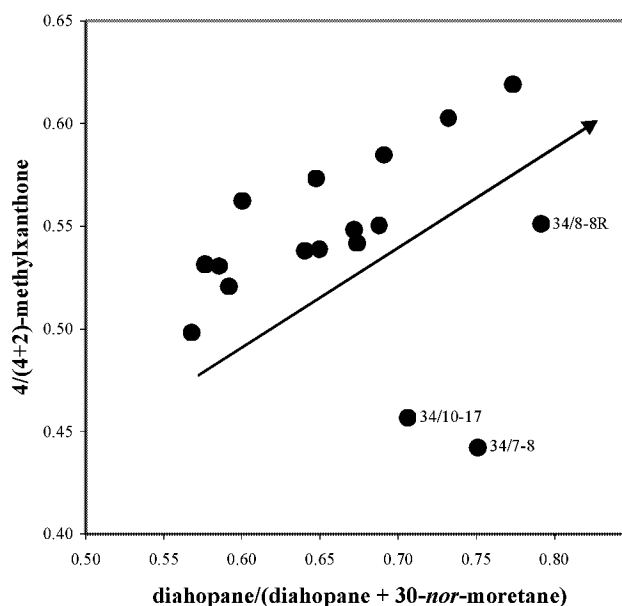


Fig. 5.4.12: Maturity dependence of the 4/(4+2)-methylxanthone ratio for the oils from the Tampen Spur area.

- HALTENBANKEN -

The majority of the oils from the second main study area (Haltenbanken-Barents Sea) also show an increase in the ratios of xanthone and the two alkylated compound groups with increasing maturity, with the exceptions being the oils from Heidrun. Figure 5.4.13 shows these ratios plotted against the *trinor*-hopane ratio $Ts/(Ts+Tm)$, a parameter which is controlled more by maturity than by facies, as demonstrated in Chapter 5.1.5.2. Excluding the oils from the Heidrun Field, two oil groups are distinguishable in the data set on the basis of the ratio of xanthone to the sum of the methylxanthenes ratio, which increases with increasing maturity. The first group contains oils from the south-eastern part of Haltenbanken (Njord, Draugen, Midgard DST.2) and two oils from the Barents Sea (7120/1-2, 7124/3-1), whereas the other group consists of the oils from more western and northern parts of Haltenbanken plus the oil from the Snøhvit Field. This may indicate a possible source facies control on this ratio as described in the previous chapter, although it should be noted that broad ranges in maturity are recognisable across Haltenbanken.

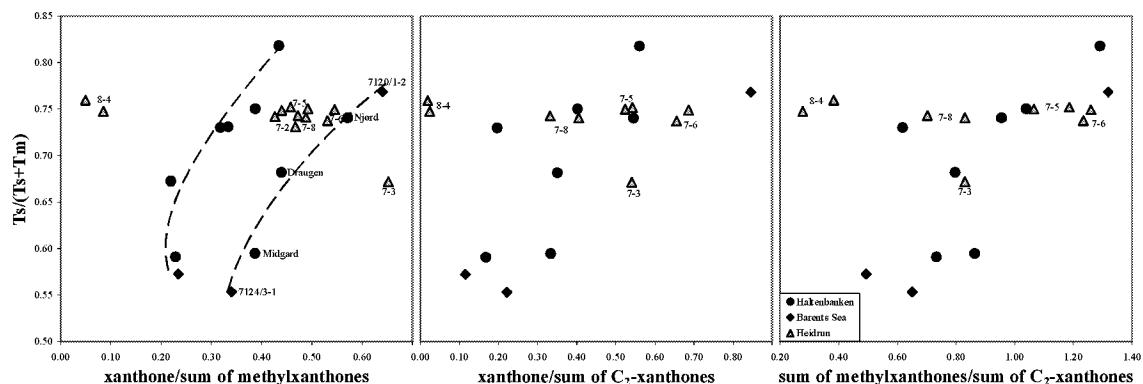


Fig. 5.4.13: Plots illustrating the maturity dependence of the distribution of xanthenes for the oils from Haltenbanken and the Barents Sea.

Large variations in the three xanthone ratios are observed for the oils from the Heidrun Field. The heavily biodegraded oils from the eastern part of the field (well 8-4) are clearly depleted in xanthone and in the methylxanthenes relative to the C_2 -xanthenes, which probably reflects extreme partitioning processes and/or biological degradation. The non-biodegraded oils from the north of the field (wells 7-5, 7-6) are relatively enriched in the lower molecular weight homologues whereas the oils from the south (wells 7-3, 7-8) which are also non-biodegraded are characterised by intermediate values. The oils from the central part of this field (well 7-2) were depleted in C_2 -xanthenes such that they were not quantifiable.

5.4.6 Influence of partitioning processes, secondary migration and biological degradation on the distribution of xanthenes

Partitioning Processes

Partitioning processes occurring during secondary migration and biodegradation of petroleum play a major role in determining the occurrence and distribution of compounds in oils. As described previously, xanthenes are characterised by unusually high dipole moments due to the two polar entities in the structure, the keto and the ether functions. Isomers with shielded functional groups, i.e. 1-methylxanthone and, to a lesser extent, 4-methylxanthone, should show a partitioning behaviour different from that of the non-shielded isomers during contact between the oil and water in the reservoir or along migration pathways. Due to the low solubility of xanthenes in water, experimental measurements of their oil/water partition coefficients ($K_{o/w}$) are unreliable.

Consequently, molecular modelling calculations were carried out in co-operation with Adri van Duin, University of Newcastle, in order to establish the partitioning behaviour of xanthone and the methylxanthenes.

Molecular dynamics (MD) calculations (Allen and Tildesley, 1987; Hale, 1992; Frenkel and Smit, 1996; van Duin and Larter, 1998) describe the movement of molecules in time, including both the intermolecular movement such as the rearrangement of solvent molecules due to interaction with a substrate molecule, and intramolecular movement, describing the conformational freedom of the molecules. Due to the ability to calculate interactions between a solvent and a substrate molecule, MD has found application in predicting the partitioning behaviour of organic compounds between solvent phases (e.g. Jorgensen and Nguyen, 1993; DeBolt and Kollman, 1995; van Duin and Larter, 1998).

In this study, cyclohexane was used to simulate the oil phase because MD calculations on solvation energies work best if the solvent consists of similar, relatively small compounds. Cyclohexane has a density (778.55 kg/m³) and boiling point (81°C) similar to that of oils. Although cyclohexane is probably slightly more apolar than most oils, qualitative differences between the cyclohexane/water and oil/water partition coefficients of compounds should be similar. The MD simulation of the various xanthenes surrounded by either 200 water molecules or 50 cyclohexane molecules provided us with the solvation energies of these compounds in the water and 'oil' phases. As described by van Duin and Larter (1997) the differences between these solvation energies ($E_{\text{oil}} - E_{\text{water}}$) are directly related to the compounds partition coefficient ($K_{\text{o/w}}$) by the following equation (assuming E is measured in kcal/mol):

$$\frac{(E_{\text{oil}} - E_{\text{water}}) * 4.184}{RT} = \ln(K_{\text{o/w}})$$

This theoretical definition of a partition coefficient implies that a higher energy difference between the 'oil' (i.e. cyclohexane) and water phase stability ($E_{\text{oil}} - E_{\text{water}}$) indicates a higher water phase affinity for that compound, which is equivalent to a lower $K_{\text{o/w}}$.

Figure 5.4.14 and the table therein show the results of the MD simulations. MD calculations taking the difference in the phase stability of the methylxanthone in oil and water resulted in a decreasing oil/water partitioning coefficient in the order 1>4>2>3. 1-Methylxanthone has the lowest affinity for the water phase due to the shielding effect of

the methyl group on the more polar keto oxygen. The shielding effect of the methyl group in position 4, closest to the slightly less polar ether oxygen, has a smaller effect on water solubility than methyl substitution adjacent to the keto-group whereas the non-shielded 2- and 3-methylxanthenes have the greatest solubility in water. Interestingly, methyl substitution in position 3 results in a partitioning behaviour very similar to that of the unsubstituted xanthone.

On the basis of these calculations, various methylxanthone ratios were tested as possible indicators of secondary migration distances and biodegradation, in particular the (1+4)/(2+3)-methylxanthone ratio.

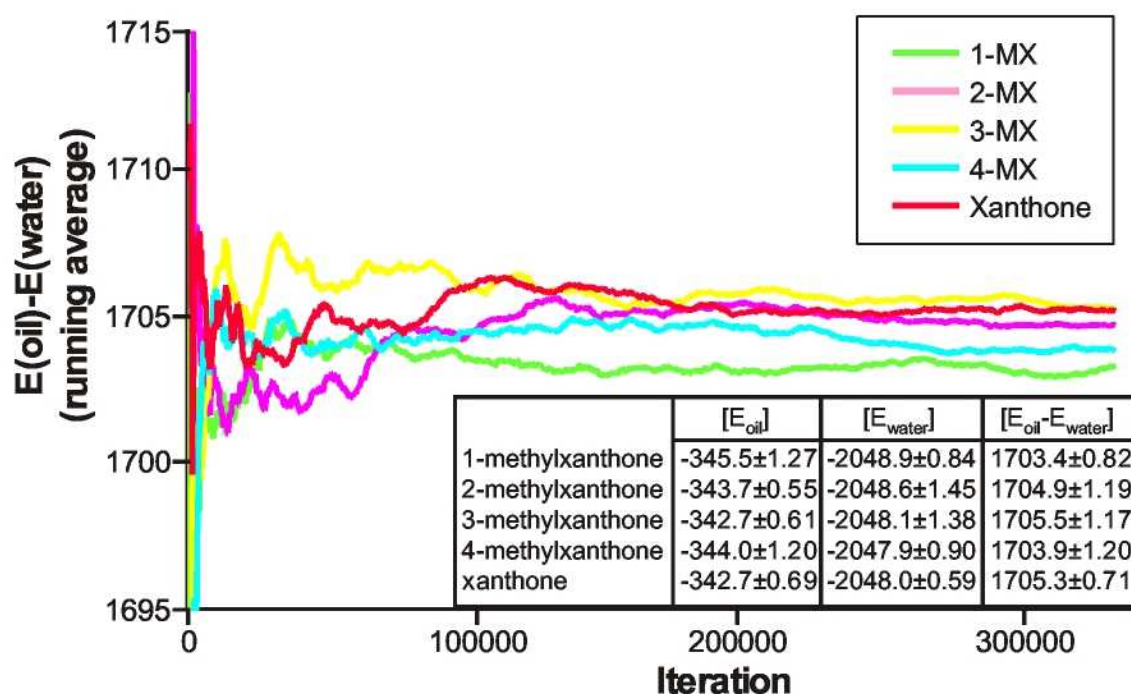


Fig. 5.4.14: Molecular dynamics calculations of the partitioning behaviour of xanthone and the four methylxanthenes.

Secondary migration

If partitioning processes affect the distribution of xanthenes between the oil and the water phase, then their relative abundance in oils might be useful as an indicator of secondary migration distance. The (1+4)/(2+3) methylxanthone ratio would be expected to increase with increasing migration distance, due to greater partitioning of 2- and 3-methylxanthone into the water phase. Unfortunately, the migration route and therefore the migration distance of many of the oils analysed in this study is not well known.

However, an estimation of some migration distances is possible, especially for the oils from Haltenbanken and for some of the Tampen Spur oils, as described in Chapter 5.2.

For many of the oils from the Haltenbanken area, the (1+4)/(2+3) methylxanthone ratio shows a positive correlation with increasing migration distance, as illustrated in Figure 5.4.15. As also noted in Chapter 5.2 for the migration-related carbazole ratios, the oils from the Midgard and Alve Fields and the oil from well 6406/11-1S deviate most from this trend. One explanation for this observation could be that the migration distances estimated for these 3 oils may be incorrect. However, other factors can affect the oil/water partitioning, such as different local hydrodynamic conditions or the proximity of the sampled oil to an oil-water contact. The two oils with highest values for the (1+4)/(2+3) ratio are strongly biodegraded. The influence of biodegradation and/or water washing will be discussed in the following section.

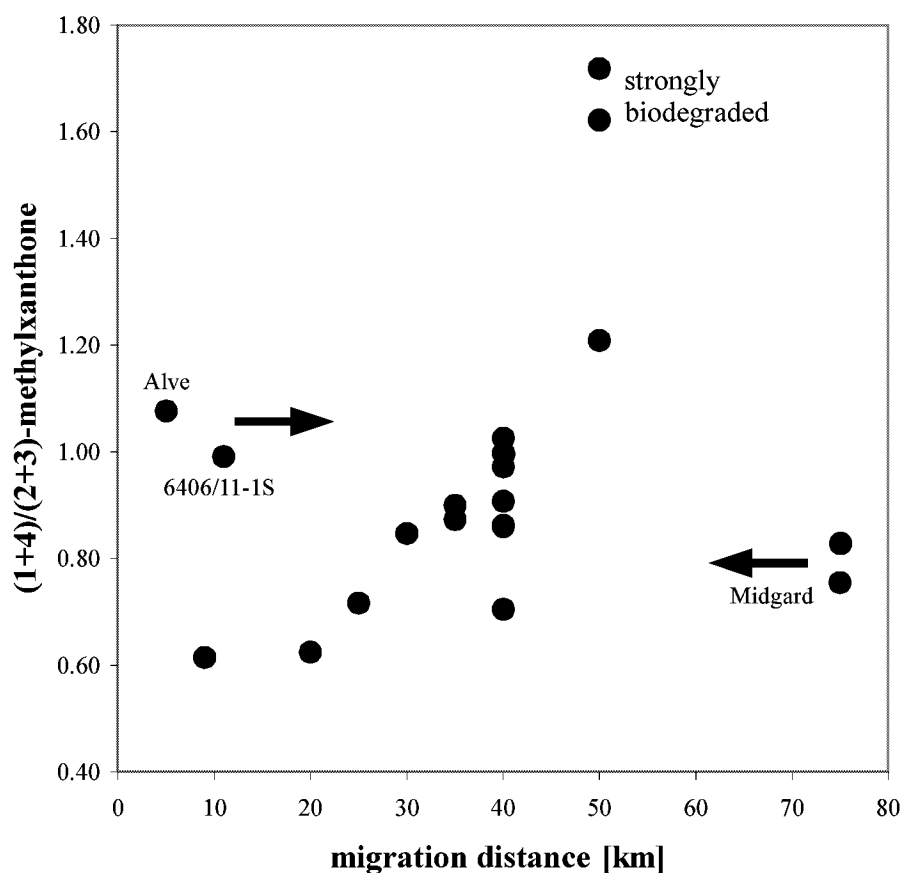


Fig. 5.4.15: Influence of secondary migration on the distribution of methylxanthenes in the oils from the Haltenbanken area.

A comparison of migration distance dependent carbazole ratios (as ascertained earlier in this thesis) with the methylxanthone ratio shows good correlations, as illustrated in the diagrams of Figure 5.4.16. Most of the oils from Haltenbanken follow the same positive trends for the different carbazole ratios. The oils from well 6406/11-

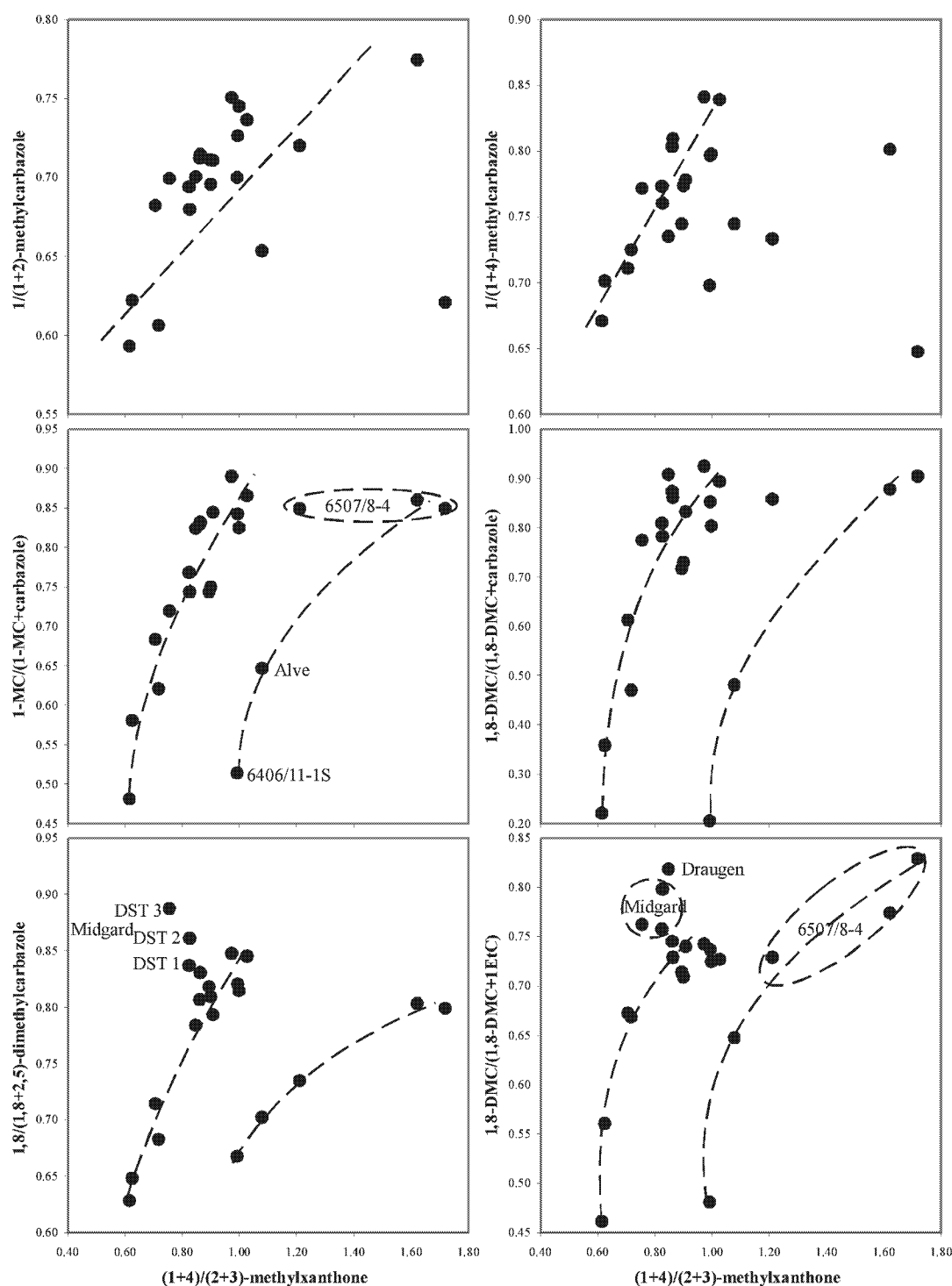


Fig. 5.4.16: Plots of migration dependent carbazole ratios versus the methylxanthone ratio for the oils from Haltenbanken.

1S, the Alve Field and well 6507/8-4, located in the eastern part of the Heidrun Field, are characterised by higher methylxanthone ratios and form a second trend parallel to the main trend. In a few cases, the oils from the Midgard Field show a slightly reduced methylxanthone ratio in comparison to the main trend. The shift to higher methylxanthone ratio values is suggested to reflect a difference in source facies. The oils from the Alve Field and wells 6406/11-1s and 6507/8-4 contain the lowest 28,30-*dinor*-hopane to 30-*nor*-hopane ratios of all the Haltenbanken oils and other biomarker parameters also indicate that these oils are generated from more terrestrially sourced organic matter, as discussed in Chapter 5.1.5. Therefore, these two different trends may reflect oils originated from the two different potential source rocks from Haltenbanken, the Spekk Formation and the Åre Formation. However, some of the oils from the eastern part of the Heidrun Field are highly biodegraded; this might influence the methylxanthone ratio and will be discussed in the following section. Biodegradation may affect the xanthone distribution to a greater extent than that of the carbazoles.

Although the Midgard condensates have high pristane/phytane ratios, they generally follow the main trend. This may indicate that these oils are sourced from the Spekk Formation, with facies changes within this formation reflected by the isoprenoid ratio. Since the Midgard samples follow the main trend it is suggested that the migration distances of these condensates are shorter than previously estimated.

Two different fill-spill routes have been suggested for the second migration distance sequence, the Tampen Spur area (Horstad et al., 1995; Karlsson, 1986). Utilising the migration distance estimates for the route proposed by Horstad et al. (1995), four of the six samples in the suite show progressively increasing (1+4)/(2+3) values with increasing migration distance. An explanation of why the oils from Tordis and Tordis Øst do not fall on the trend can be found in the work of Karlsson (1986), who proposed an additional migration route to the east of the main fill-spill route (Fig. 5.4.17). For these two oils, the results suggest a migration distance of approximately 65 km, indicating that they probably did not migrate along the main fill-spill route.

The methylxanthone ratios in the oils from the Tampen Spur are very low in comparison to the oils from Haltenbanken. Considering the relationship between migration distance and methylxanthone ratio seen for the Haltenbanken oils, methylxanthone ratios in the range 1.3-1.6 would be expected for the Tampen Spur oils,

whereas actual values are in the range 0.7-0.85. This could be the result of a lower system reactivity in the Tampen Spur compared to Haltenbanken, which may be due to differences in mineralogy or availability of formation water, or it may reflect the lower sorption capacity due to the large volumes of the oil which have migrated along this fill-spill route.

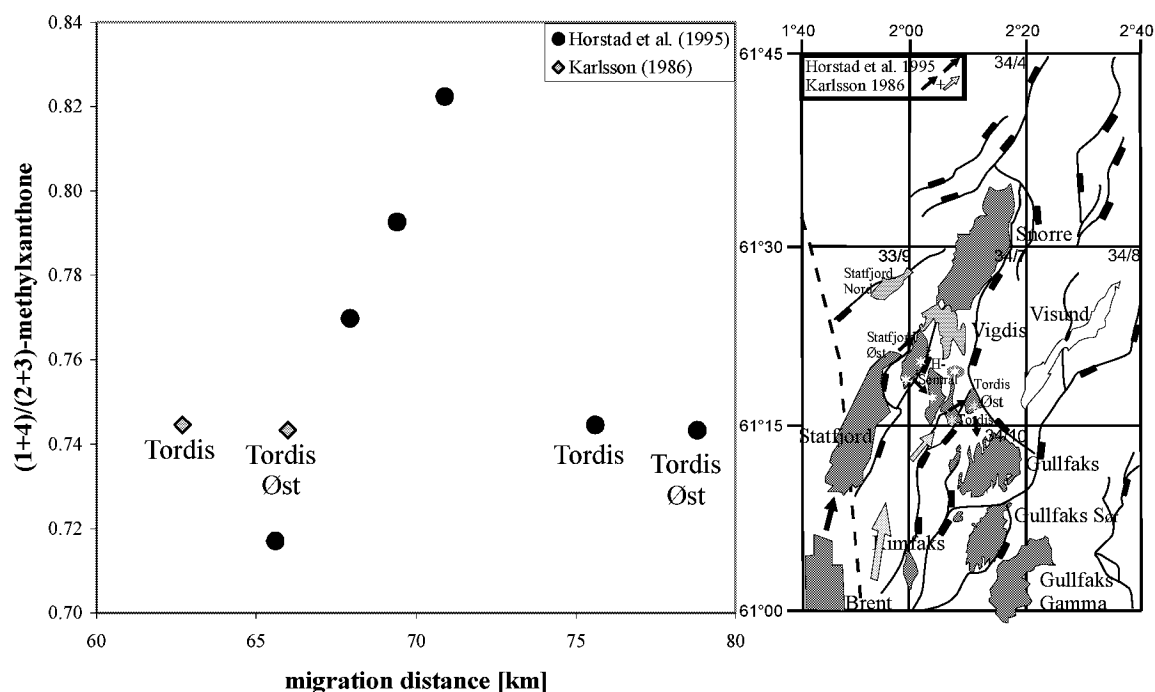


Fig. 5.4.17: Plot illustrating a possible influence of secondary migration on the methylxanthone distribution for oils from the Tampen Spur area.

A comparison of the migration-related carbazole ratios with the methylxanthone ratio also shows good correlations for the oils from the Tampen Spur (Fig. 5.4.18). Although the number of samples is limited and there are some inconsistencies, the carbazole distribution seems to be affected in the same way as that of the xanthenes both for the oils from the Tampen Spur and for those from Haltenbanken.

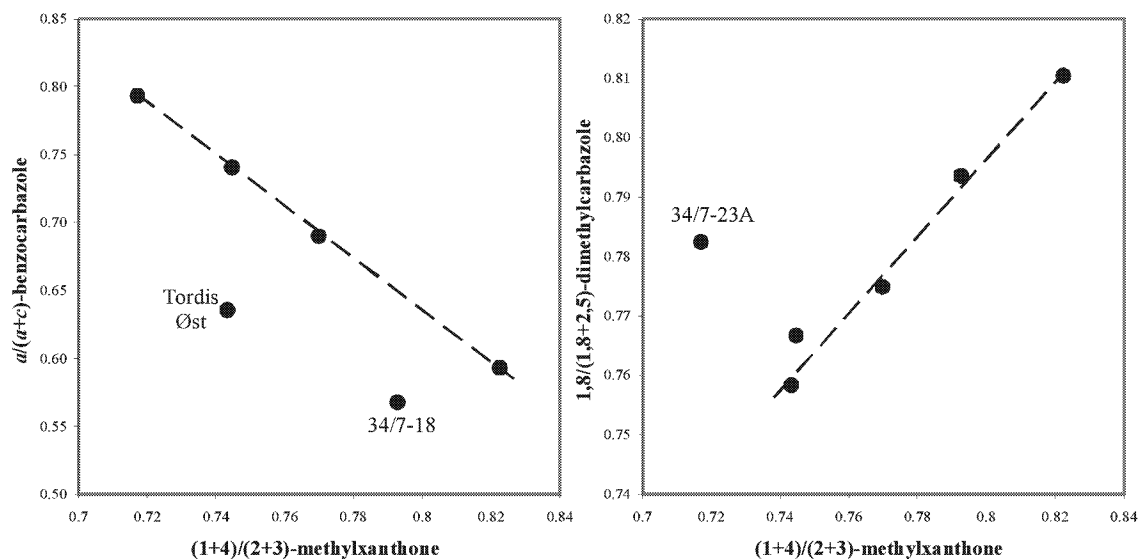


Fig.5.4.18: Plots of migration dependent carbazole ratios versus the methylxanthone ratio for the oils from the Tampen Spur.

Biological degradation

A suite of oils representing a biodegradation sequence from the Gullfaks field was used to study the influence of biodegradation on the distribution of the xanthenes. The degree of biodegradation in the field increases from the east (non-degraded) to the west (level 3-4 on the scale of Peters and Moldowan, 1993). On the basis of quantitative modelling calculations, Horstad et al. (1991) proposed that the degradation process occurred in the reservoir and not during migration into the reservoir. One of the more

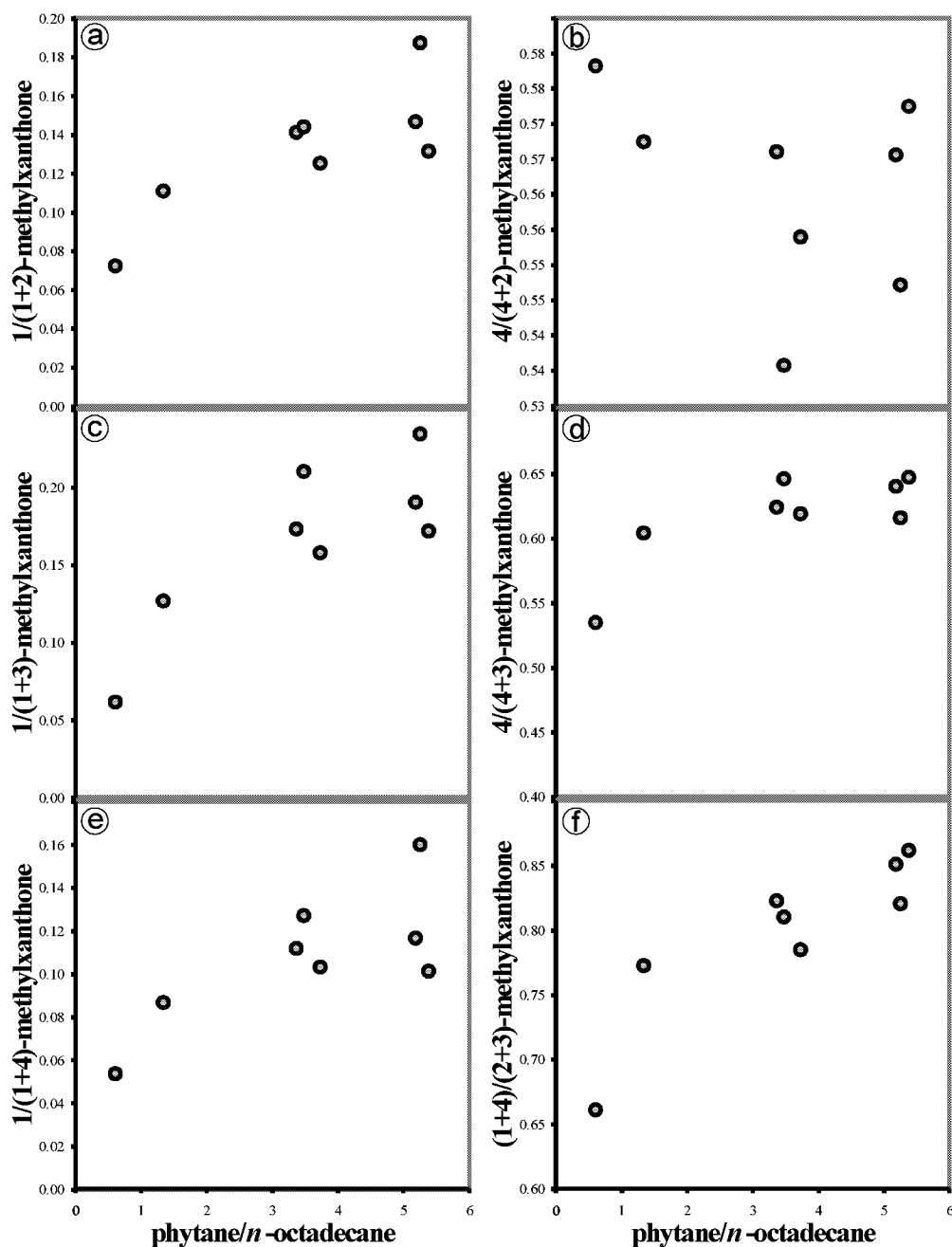


Fig. 5.4.19: Cross plots showing the influence of biodegradation on the methyl-xanthone distribution using the degradation sequence from the Gullfaks Field.

useful parameters illustrating the different grades of (early-stage) biodegradation is the phytane to *n*-octadecane ratio, which increases with increasing biodegradation, as described in Chapter 5.1.4. Figure 5.4.19a-f shows plots of different methylxanthone ratios against this parameter. Good correlations are observed for the ratio 1-methylxanthone to the sum of 1-methylxanthone and to each of the other methylxanthenes (Fig. 5.4.19a, c, e). In addition, the ratio of 4-methylxanthone to the sum of 4-methylxanthone and 3-methylxanthone (Fig. 5.4.19d) and the ratio of the sum of 1- and 4-methylxanthone to the sum of 2- and 3-methylxanthone (Fig. 5.4.19f) correlates well with the biodegradation parameter. All of the plots indicate enhanced preservation of 1-methylxanthone relative to the other methylxanthenes and, to a lesser extent, a better preservation of 4-methylxanthone relative to 3-methylxanthone, which results in the good correlation between the (1+4)/(2+3)-methylxanthone ratio and the phytane to *n*-octadecane ratio. Only the 4/(4+2) ratio, comprising compounds with very similar partition coefficients (see Fig. 5.4.14), shows no correlation with increasing biodegradation (Fig. 5.4.19b).

The effect of biodegradation on the methylxanthone distribution was also studied using the variably degraded oils from the Heidrun Field. Since the *n*-alkanes and isoprenoid hydrocarbons are strongly depleted or absent in the more strongly biodegraded oils, the degree of biodegradation was estimated from the percentage of aromatic hydrocarbons. Figure 5.4.20 shows the variation in the (1+4)/(2+3)-methylxanthone ratio with the percentage of aromatics for the majority of the oils from the Heidrun Field – the exceptions are

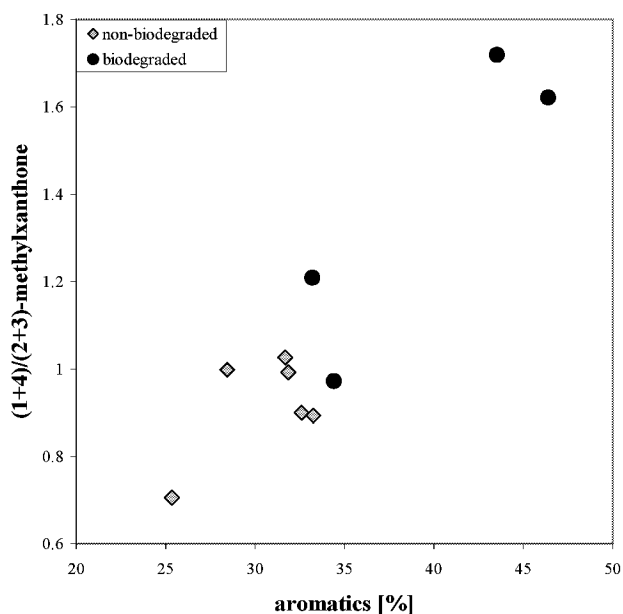


Fig. 5.4.20: Plot illustrating the influence of biodegradation on the distribution of the methylxanthenes in oils from the Heidrun Field.

the oils from well 6507/7-2 for which methylxanthone concentrations were not quantifiable. It is remarkable that the strongly biodegraded oils from well 6507/8-4 are characterised by high values for this ratio.

These results may indicate an effect of partitioning processes, as described above, since biodegraded oils must have been exposed to water. As the non-shielded isomers have a higher affinity to water, they are more bioavailable than the shielded isomers. However, preferential biodegradation of particular methylxanthones could also influence the distribution of the methylxanthones, as illustrated in Figure 5.4.21. Many aerobic bacteria prefer initial dioxygenolytic attack at positions 3 and 4 or 1 and 9a of xanthone, as described by Tomasek and Crawford (1986) and Wilkes (1993).

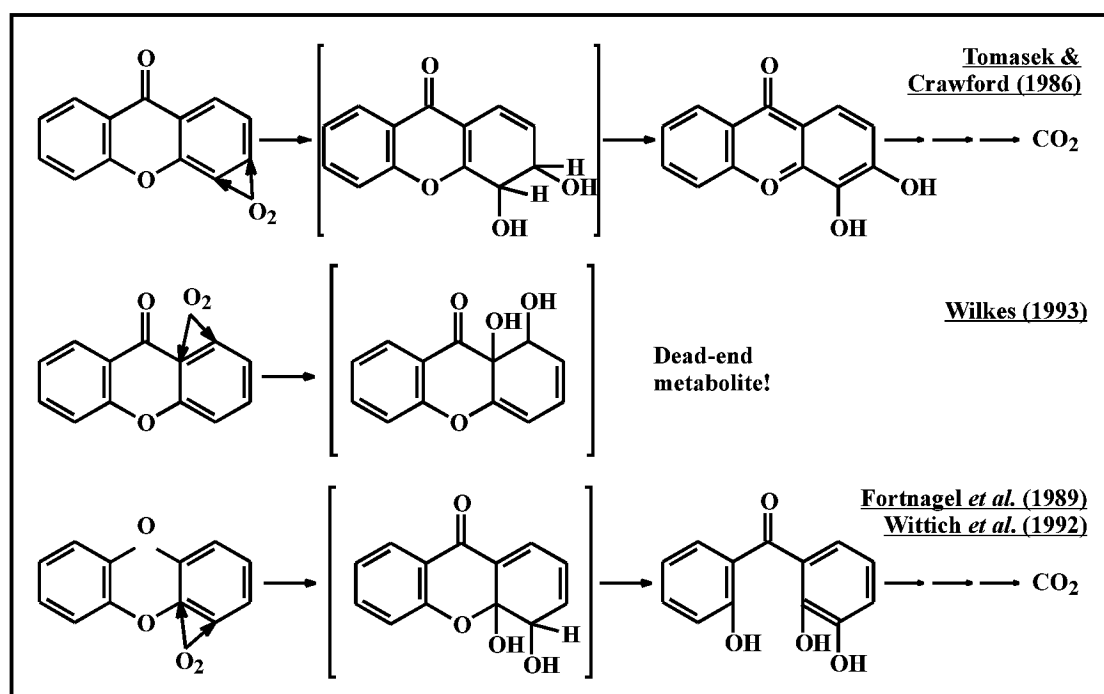


Fig. 5.4.21: Different initial reactions proposed for the catabolism of xanthone by aerobic bacteria described by Tomasek & Crawford (1986) and Wilkes (1993), and for dibenzo-*p*-dioxin (Fortnagel et al., 1989; Wittich et al., 1992).

Regioselective dioxygenation of biaryl ether structures is known to prompt cleavage of ether bonds which corresponds to an initial oxygenation in positions 4 and 4a for xanthenes (Fortnagel et al., 1989; Wittich et al., 1992). These proposed xanthone catabolic pathways of aerobic bacterial degradation indicate that methyl groups in positions 1 and 4 might provide a steric shielding against enzymatic attack of the

oxygen functionalities. Initial dioxygenation in positions 2 and 3 are not known, which supports the assumption that the (1+4)/(2+3)-methylxanthone ratio should increase with increasing biodegradation. Possible mechanisms of anaerobic xanthone metabolism have not yet been described, and the possible fate of xanthonenes during crude oil biodegradation in anoxic reservoirs therefore remains an open question.

In summary, two different mechanisms may influence the distribution of methylxanthonenes and both produce the same effects: 1. water washing, which causes preferential removal of 2- and 3-methylxanthone from the oil, and 2. biodegradation, which may result in a preferential degradation of 2- and 3-methylxanthone due to steric shielding of 1- and 4-methylxanthone.

5.4.7 Possible origins of xanthonenes

It is suggested that xanthonenes may originate via several possible mechanisms including the diagenetic transformation of biogenic xanthonenes; pseudo Friedel-Crafts reactions in carrier systems (geosynthesis); and the oxidation of xanthenes either in sub-surface environments or on exposure to air during sample storage and analysis. The relevance of these possibilities is briefly discussed in the light of the current observations on the presence or absence of xanthonenes in different petroleum systems. A

studied areas	source rock type	SR	oil
offshore Norway	clastic	low	yes
Posidonia Shale, Germany	marl	no	n.a.
Sonda de Campeche, Mexico	carbonate	no	no
Ghareb, Jordan	marl	no	no
Western Desert, Egypt	clastic	yes	yes
Gulf of Suez, Egypt	carbonate	n.a.	no
Carboniferous coals, North England	coals	yes	n.a.
Moscow Basin, Russia	coals	no	n.a.

Tab. 5.4.1: Occurrence of xanthonenes in oils and source rocks from different study areas; (n.a. = information not available).

qualitative overview is given in Table 5.4.1; detailed data for study areas other than the North Sea will be published elsewhere.

Xanthonenes could not be detected in either source rocks or crude oils from the Sonda de Campeche, Mexico. As described by Santamaria et al. (1998), this petroleum system comprises brecciated carbonate reservoirs (Paleocene) fed from local generative carbonate source rocks (Tithonian) via faults. Xanthonenes could not be detected in similar carbonate petroleum systems of the Gulf of Suez, Egypt (M. M. Y. Bakr and H. Wilkes, unpublished results). In this context, it is noteworthy that recovered rock extracts and expelled oils from hydrous pyrolysis experiments using an immature limestone from the Ghareb Formation also do not contain xanthonenes. The common features of these observations are a lack of potential precursors (terrestrial plants) and the occurrence of migration pathways where the capacity for water-rock-oil interactions are small because migration distances are short and permeability is ostensibly high.

In contrast to the carbonate systems described above, the potential source rocks of the Jurassic Khatatba Formation (Western Desert, Egypt) contain a significant contribution of terrestrial organic matter. Xanthonenes are abundant in both the source rocks and the (presumed) related crude oils (M. M. Y. Bakr and H. Wilkes, unpublished results). The database for humic coals from England (Westphalian, Northumberland Basin) and Russia (Visé, Moscow Basin) supports the correlation between terrestrial organic matter and the occurrence of xanthonenes, but only in the rank range $R_o = 0.5 - 1.0\%$; outside this range xanthonenes are absent (A. Armstroff, H. Wilkes, B. Horsfield, unpublished results). This may indicate that xanthonenes are released or generated during coalification at maturities between 0.5 and 1.0% vitrinite reflectance and destroyed at higher temperatures and pressures which could explain why xanthonenes could not be detected in the very immature and very mature coaly samples from the Åre Formation, offshore Norway. The results for the Posidonia Shale (L. Jurassic, Lower Saxony Basin, Germany) indicate that xanthonenes are absent over a similarly wide maturity range ($R_o = 0.48 - 1.45\%$) from organic-matter-rich clastic source rocks in which the organic matter is derived primarily from algal precursors. The observations therefore support the assumption that xanthonenes may be generated as diagenetic products from functionalised biogenic xanthonenes which lose their functional groups. As described above, highly substituted xanthonenes occur in many different terrestrial plants.

The current database for Norwegian petroleum systems points to the occurrence of high concentrations of xanthenes in crude oils and essentially on their absence in source rocks. If this preliminary finding could be substantiated through the analysis of an expanded (statistically relevant) sample set of source rocks, then the formation of xanthenes after petroleum expulsion, rather than being directly inherited from terrestrial precursors, has to be given serious consideration. It is speculated that the xanthenes might originate by geosynthesis from suitable aromatic precursors in carrier systems. As described above for the preparative synthesis of alkylated xanthenes, these compounds can be synthesized at high temperatures ($T = 180\text{--}200^\circ\text{C}$) and in the presence of catalysts from benzoic acid derivatives and phenols, compounds which occur widely in sedimentary organic matter. Formation water, which is more available in carrier rocks than in source rocks exerts a beneficial influence on the conditions for xanthone generation (e.g. lower pH for intramolecular Friedel-Crafts acylation). The mechanism for generating xanthenes in subsurface environments would then have the following essential steps:

1. Generation and expulsion of precursor benzoic acids and phenols in the oil phase;
2. Partition of the precursors into the aqueous phase in the carrier system;
3. Reaction of precursors in the aqueous phase, especially at clay mineral surfaces, to form xanthenes;
4. Partition back into the oil phase.

Xanthenes therefore show great promise as indicators of the degree of organic-inorganic interaction in carrier systems.

Following the work of Bennett and Larter (2000) on fluorenes/fluorenones, it was considered whether xanthenes may simply result from the oxidation of xanthenes. Window-sill experiments (oil contained in a clear glass vial exposed to the sun and air over a period of six months) showed that significant changes in the concentration of xanthone and its derivatives, or in the isomer distribution of alkylated xanthenes, did not occur. Furthermore, the results of screening analysis on the oils from offshore Norway showed that xanthenes are either absent or present in very low amounts, whereas alkylxanthenes are generally absent. These observations suggest either a fast and complete oxidation of xanthenes in petroleum systems or that xanthenes are not the precursors of xanthenes in crude oils.

5.4.8 Conclusions

This is the first description of xanthenes in crude oils. Xanthone was identified by comparison with an authentic standard, on the basis of the mass spectrum and relative retention times on two GC columns of different polarity. The elution order of the four methylxanthenes was established for the first time as 1-4-2-3 on a BPX-5 column. This elution order reflects the steric shielding of the polar keto- and ether-functions by the methyl substituents. The retention times of two dimethylxanthenes (2,4- and 3,4-dimethylisomers) were also determined.

A maturity dependence of the relative abundances of xanthone, the sum of the methylxanthenes and the sum of the C₂-xanthenes was observed for the oils from the Tampen Spur and, more tentatively, for the oils from Haltenbanken. However, an influence of facies variation on the relative distribution of the three xanthone groups was also determined for the oils from Haltenbanken. Focusing on the methylxanthone distribution, only an increase of the 4/(4+2)-methylxanthone ratio with increasing maturity was observed for the oils from the Tampen Spur. A facies dependence of the 4/(4+1)-methylxanthone ratio was observed for oils from the Haltenbanken area.

The results of the study show that partitioning processes are an important control on the distribution of the methylxanthenes. Molecular dynamics calculations substantiate the observed enhanced preservation of the shielded isomers (1- and, to a lesser extent, 4-methylxanthone) in the oil phase in comparison to the non-shielded isomers (2- and 3-methylxanthone). It is suggested that the (1+4)/(2+3)-methylxanthone ratio might be useful as an indicator of secondary migration and biodegradation. As the non-shielded isomers have a higher affinity for the water phase, they are more bioavailable than the shielded isomers. In addition, proposed xanthone dioxygenation mechanisms in aerobic bacteria suggest that the 1- and 4-methylxanthenes are probably less susceptible to microbial degradation than 2- and 3-methyl isomers, again reflecting the shielding effect of the methyl substituents on the oxygen functionalities.

The origin of xanthenes in crude oils and source rocks is not known; they could be diagenetic products, formed by oxidation of xanthenes in the reservoir or they may originate by geosynthesis from aromatic precursors.

6. Summary

The overall aim of this research project was to provide new insights into the geochemical significance of NSO compounds in crude oils from the Norwegian Shelf. The study involved the analysis of oils from all of Norway's petroleum systems. In addition, samples of the two main potential source rocks from the Haltenbanken area were analysed for facies and maturity correlations. The effect of primary migration on NSO compound distribution was investigated by the analysis of expelled oils and corresponding recovered bitumens obtained by hydrous pyrolysis of an immature source rock from Ghareb, Jordan.

The analytical programme focussed initially on the hydrocarbons, and the data were used in conjunction with information from the sponsors and published literature to place the samples within subsets relating to facies, maturity, migration and biodegradation. The results from the analysis of quantitatively significant compound classes of the low-polar NSO compound fractions were interpreted within the frameworks. Three compound classes - carbazoles, fluorenones and xanthenes - were investigated in detail in an attempt to determine their behaviour in response to geochemical processes.

Whereas carbazoles and fluorenones have previously been reported as constituents in crude oils, this is the first description of xanthenes in fossil fuels. The elution order of the four methylxanthenes was established for the first time as 1-4-2-3 (using a BPX-5 column) which reflects the shielding effect on the polar groups, the keto- and ether-function by the alkyl substituents. The retention times of two dimethylxanthenes (2,4- and 3,4-dimethylisomers) were also determined.

In quantitative terms, carbazoles, fluorenones and xanthenes were detected in similar abundance in most of the crude oils. Higher concentrations of carbazoles and fluorenones were found in the source rock extracts than in the crude oils, whereas the amounts of xanthenes were below the detection limit in the source rock extracts. This may indicate generation of xanthenes during migration or within the reservoir. Results from hydrous pyrolysis experiments revealed high concentrations of carbazoles in the recovered rock extracts and minor amounts in the expelled oils. Whereas abundances of

xanthenes are below the detection limit in both the extracts and expelled oils significant concentrations of fluorenones were detected only in the extracts.

Investigations of the effect of source facies on the distribution of carbazoles and fluorenones in the two different potential source rocks from the Haltenbanken area revealed that the source rocks are characterised by significantly different distributions of both compound classes independent of maturity. The differentiation is seen in the relative abundance of the compound groups, in several homologue group and isomer ratios of alkylated carbazoles and fluorenones as well as in the distributions of benzocarbazoles and benzofluorenones. Correlations between source rock extracts and the probable corresponding crude were successful only for the carbazoles but showed that other factors such as expulsion or partitioning processes play an important role in controlling the compound distributions.

The maturity dependence of the distribution of carbazoles and fluorenones in source rock extracts was clearly demonstrated by the variation in their absolute concentrations. The amounts of these compounds increased systematically with increasing maturity, both for the natural source rock and the artificially matured rock. An influence of maturity was also observed for some ratios of alkylated carbazoles and fluorenones as well as for the distribution of the benzoisomers, e.g. the ratio of $a/(a+c)$ -benzocarbazole. For the oils, however, only a slight maturity dependence on the distribution of carbazoles, fluorenones and xanthenes was observed in a few settings, and it is suggested that other processes control the composition of these compound classes in these samples.

Whereas facies and maturity clearly control the distributions of carbazoles and fluorenones in source rocks, partitioning processes are thought to be the main control on the composition of these polar compounds in oils. The results of this study indicate different scenarios for the three compound classes for the crude oils.

Due to their moderate polarity (dipole moment of carbazole: 1.39 D), only part of the carbazoles generated within the source rocks is liberated during primary migration. The effects of expulsion on compound distributions are demonstrated by hydrous pyrolysis experiments. Shielded carbazoles (carbazoles with alkyl groups in positions 1 and 8 on the ring structure) were significantly enriched relative to non-shielded carbazoles in the expelled oils in comparison to the recovered rock extracts. This implies stronger

interactions of the more polar non-shielded compounds with organic matter and mineral phases in the rock matrix and therefore stronger retention relative to the shielded isomers during expulsion. These partition/sorption effects continue during secondary migration, as revealed by the study of two sample sequences from the Haltenbanken and Tampen Spur area. With increasing (estimated) migration distance (i.e. increasing contact with mineral/organic matter in the carrier bed rock matrix), the relative abundance of non-shielded carbazole isomers decreased in comparison to shielded isomers, indicating the protective effect of alkyl groups adjacent to the polar function.

Although high concentrations of fluorenones are observed in source rock extracts, it is suggested that they are more strongly retained than the carbazoles during expulsion due to their high polarity (dipole moment of fluorenone: 2.91 D). In the hydrous pyrolysis experiments, fluorenones could be quantified only in the recovered rock extracts; the concentrations of these compounds in the expelled oils were below the detection limit. It is possible that fluorenes which were liberated from the source rock could be oxidised to the corresponding ketones due to the activation of the methylene bridge by two adjacent benzene rings. Also, oil-water and/or oil-mineral matter interactions may lead to oxidation of the fluorenes in the expelled oils during migration to the reservoir. Analysis of oils from a migration suite from Haltenbanken showed that the concentration of the shielded 1-methylfluorenone decreased with increasing secondary migration distance compared to the non-shielded isomers. This may reflect the reduced susceptibility to oxidation of the isomer with a methyl group adjacent to the methylene function due to steric hindrance. The reduced susceptibility to oxidation might result in a relative decrease of 1-methylfluorenone with increasing degree of interaction with the carrier bed matrix during migration. Indications that fluorenones are the oxidation products of fluorenes were obtained from two observations: A comparison of the methylfluorenone distribution with the methylfluorene distribution of the crude oils revealed similarities between these compound groups which may indicate that the ketones are oxidation products of the fluorenes. This was supported by window-sill experiments in which an oil contained in a clear glass vial was exposed to sun and air for a period of about six months. The concentrations of the fluorenones were two orders of magnitude higher after exposure compared with the initial oil concentrations. These results indicate that artificial oxidation during storage and sample handling can be an important factor controlling the abundance of fluorenones.

Xanthenes occurred in amounts similar to the carbazoles and fluorenones in oils whereas they were not detected in source rock extracts. This may indicate that xanthenes originate by geosynthesis from suitable aromatic precursors within carrier systems. Xanthenes can be synthesized (at $T = 180\text{--}200^\circ\text{C}$ and in the presence of catalysts) from benzoic acid derivatives and phenols, compounds which occur widely in sedimentary organic matter. Formation water, which is more available in carrier rocks than in source rocks, contributes to more favourable conditions for xanthone generation (e.g. lower pH for intramolecular Friedel-Crafts acylation). It is speculated that the mechanism for generating xanthenes in subsurface environments would involve the following essential steps: 1. generation and expulsion of precursor benzoic acids and phenols in the oil phase; 2. partition of the precursors into the aqueous phase in the carrier system; 3. reaction of the precursors in the aqueous phase, especially at clay mineral surfaces, to form xanthenes; 4. partition of xanthenes back into the oil phase. Xanthenes, therefore, show great promise as indicators of the degree of organic-inorganic interactions in carrier systems. This assumption is supported by field observations of an increase in the concentration of the xanthenes in oils with increasing migration distance. The ratio of the shielded methylxanthenes to the non-shielded isomers $(1+4)/(2+3)$ increases with increasing migration distance in the same way as revealed for the carbazoles, indicating partitioning effects on these high polar compounds (dipole moment of xanthone: 3.11 D). Molecular dynamics calculations of the partitioning behaviour of methylxanthenes support this assumption.

Biodegradation within the reservoir can also influence the distribution of the carbazoles, fluorenones and xanthenes in oils. As non-shielded isomers have a higher affinity for the water phase these compounds are more bioavailable than shielded isomers. In addition, proposed dioxygenation pathways of aerobic bacteria suggest that the non-shielded isomers of carbazoles and xanthenes are probably preferentially biodegraded in comparison to the shielded isomers, reflecting steric hindrance by the alkyl groups around the nitrogen and oxygen functionalities, respectively. In this respect, an increase in abundance of the shielded isomers relative to the non-shielded isomers for carbazoles and xanthenes is demonstrated by a biodegradation sequence from the Gullfaks field. In contrast, the concentration of 1-methylfluorenone decreases with increasing degree of biodegradation compared to its non-shielded isomers. As biological degradation of fluorene results in fluorenone production as a partly dead-end

product, steric hindrance of the methyl group adjacent to the methylene bridge of the fluorene structure might result in the relative decrease of this isomer. However, aerobic degradation is unlikely in this deep reservoir. Although little is known about anaerobic degradation mechanisms, it is possible that the initial steps of anaerobic degradation could be similar to those of aerobic degradation.

The parallel investigation of crude oils and source rocks in natural systems and hydrous pyrolysis experiments showed that the polar compound constituents of fossil fuels provide important information for petroleum exploration and production.

7. Zusammenfassung

Ziel des Forschungsprojekts war es, neue Erkenntnisse über die geochemische Signifikanz von Stickstoff-, Schwefel- und Sauerstoffverbindungen (NSO-Verbindungen) in Erdölen des norwegischen Schelfgebietes zu gewinnen. Zu diesem Zweck wurden Erdölproben aus allen Regionen im *offshore*-Bereich Norwegens untersucht. Zusätzlich wurden Proben von zwei potentiellen Erdölmuttergesteinen aus dem Gebiet Haltenbanken zur Untersuchung von Fazies- und Reifekorrelationen herangezogen. Auswirkungen primärer Erdölmigration auf die Zusammensetzung polarer Verbindungen wurde mittels generierter Erdöle und Restextrakten einer künstlichen Reifesequenz, die aus wässrigen Pyrolyseexperimenten eines unreifen Erdölmuttergesteins von Ghareb, Jordan, erhalten wurden, untersucht.

Alle Proben wurden mit organisch-geochemischen Methoden analysiert. Die Kohlenwasserstoffgeochemie bildete den ersten Teil der Untersuchungen. Unter Einbeziehung des Kenntnisstandes der Sponsoren und der veröffentlichten Literatur konnten die Erdöle bezüglich Fazies, Reife, Migration und Biodegradation klassifiziert werden. Basierend auf dieser Klassifizierung wurden die Analysenergebnisse quantitativ bedeutsamer Verbindungsgruppen der niedrig-polaren NSO-Verbindungen Fraktionen interpretiert. Für die drei Verbindungsgruppen, Carbazole, Fluorenone und Xanthone, wurde das Verhalten hinsichtlich geochemischer Prozesse detailliert untersucht.

Während Carbazole und Fluorenone als Bestandteile von Erdölen bekannt sind, wurde im Rahmen dieser Arbeit zum ersten Mal das Vorkommen von Xanthonen in Erdölen beschrieben. Die Elutionsreihenfolge 1-4-2-3 der vier Methylxanthone wurde erstmalig mittels einer BPX-5 Säule etabliert, was den abschirmenden Effekt der Alkylsubstituenten zu den polaren Gruppen, der Keto- und Etherfunktion, widerspiegelt. Die Retentionszeit von zwei Dimethylxanthonen (2,4- und 3,4-Dimethylxanthon) konnte ebenso bestimmt werden.

In den meisten Erdölproben war die Größenordnung der detektierten Menge an Carbazolen, Fluorenonen und Xanthonen gleich. Verglichen mit den Erdölen wurden in den Erdölmuttergesteinen höhere Konzentrationen von Carbazolen und Fluorenonen

gefunden, während die Menge an Xanthonen in den Erdölmuttergesteinen unterhalb der Nachweisgrenze lag. Dies kann als Hinweis für die Bildung von Xanthonen während der Migration oder in der Erdöllagerstätte gewertet werden.

Ähnliche Ergebnisse wurden bei den künstlichen wässrigen Pyrolyseexperimenten erhalten. In den Restextrakten sind hohe Konzentrationen an Carbazolen vorhanden und geringere Mengen in den generierten Erdölen. Xanthone konnten weder in den generierten Erdölen noch aus den Restextrakten erhalten werden, während signifikante Mengen an Fluorenonen nur in den Extrakten vorhanden sind.

Die Untersuchung des Einflusses der Fazies auf die Verteilung der Carbazole und Fluorenone in den beiden potentiellen Erdölmuttergesteinen zeigt, dass die zwei Erdölmuttergesteine anhand der Verteilung der Verbindungsgruppen unabhängig von Reifeinflüssen unterscheidbar sind. Diese fazielle Unterscheidung schließt die relativen Konzentrationen der Verbindungsgruppen, mehrere Verhältnisse der alkylierten Carbazole und Fluorenone und auch die Verteilung von Benzocarbazolen und Benzofluorenonen ein. Korrelationen mit den wahrscheinlich korrespondierenden Erdölen ergeben nur anhand der Carbazole Hinweise auf ihren Ursprung, zeigen aber auch, dass andere Faktoren wie Expulsion oder Partitionierungsprozesse eine wichtige Rolle in der Kontrolle der Verbindungsverteilung spielen.

Die Reifeabhängigkeit der Carbazol- und Fluorenonverteilung konnte ideal anhand der absoluten Konzentrationen demonstriert werden. Die Konzentrationen dieser Verbindungen steigen systematisch mit zunehmender Reife, was anhand der natürlichen Erdölmuttergesteine und der Reifungsexperimente demonstriert werden konnte. Einen Einfluss der Reife auf einige Verhältnisse alkylierter Carbazole und Fluorenone und auf die Verteilung der Benzoisomeren, wie z.B. das Verhältnis von $a/(a+c)$ -Benzocarbazol, konnte ebenso anhand der Extraktanalysen gezeigt werden. Da nur eine geringfügige Abhängigkeit der Reife auf die Verteilung der Carbazole, Fluorenone und Xanthone für die Erdöle in wenigen Fällen beobachtet werden konnte, wird vermutet, dass andere Prozesse die Zusammensetzung dieser Verbindungsgruppen kontrollieren.

Während Fazies und Reife eindeutig die Verteilung dieser Verbindungsgruppen in den Erdölmuttergesteinen kontrollieren, haben Partitionierungsprozesse einen bedeutenden Einfluss auf die Zusammensetzung dieser polaren Verbindungen in den

Erdölen. Die Ergebnisse dieser Studie weisen auf verschiedene Szenarien für diese drei Verbindungsgruppen hin:

Nur ein Teil der generierten Carbazole verlässt das Erdölmuttergestein während primärer Migration aufgrund der moderaten Polarität (Dipolmoment: 1,39 D). Die Expulsionseffekte konnten eindrucksvoll anhand der wässrigen Pyrolyseexperimente gezeigt werden. Abgeschirmte Carbazole (Carbazole mit Alkylgruppen in Position 1 und 8 der Ringstruktur) sind verglichen mit den Gesteinsextrakten gegenüber den nicht abgeschirmten Carbazolen eindeutig in den Ölen angereichert. Dies deutet auf stärkere Wechselwirkungen der polarerer Verbindungen mit dem organischen Material und den Mineralphasen hin, wodurch diese Verbindungen stärker zurückgehalten werden als die abgeschirmten Isomere während der Expulsion. Diese Auswirkungen der primären Migration werden verstärkt durch sekundäre Migration, wie anhand zweier Probensequenzen aus den Gebieten Haltenbanken und Tampen Spur mit abgeschätzten Migrationsdistanzen gezeigt werden konnte. Mit zunehmender Migrationsdistanz verringert sich die Konzentration der nicht abgeschirmten Carbazole relativ zu denen der abgeschirmten Isomere, was auf einen schützenden Effekt der Isomere mit Alkylgruppen nahe der polaren Funktion hinweist.

Hohe Konzentrationen an Fluorenonen wurden nur in den Erdölmuttergesteinsextrakten erhalten, was darauf hindeutet, dass die Fluorenone während der Expulsion aufgrund ihrer höheren Polarität (Dipolmoment 2,91 D) stärker zurückgehalten werden als Carbazole. Dies konnte anhand der wässrigen Pyrolyseexperimente demonstriert werden. Während hohe Konzentrationen an Fluorenone in den Gesteinsextrakten quantifiziert werden konnten, liegen die Konzentrationen dieser Verbindungen in den Ölen unterhalb der Nachweisgrenze. Dennoch können Fluorene, die während der Expulsion aus den Erdölmuttergesteinen migrieren, aufgrund der durch die beiden benachbarten Benzolringe aktivierten Methylenbrücke leicht zu den korrespondierenden Ketonen oxidiert werden. Öl-Wasser und/oder Öl-Mineral Wechselwirkungen können zur Oxidation der Fluorene im Erdöl während der Migration zur Erdöllagerstätte führen. Wie anhand einer Probensequenz aus dem Haltenbanken-Gebiet gezeigt werden konnte, verringert sich die Konzentration des geschützten 1-Methylfluorenons mit zunehmender sekundären Migrationsdistanz im Vergleich zu seinen Isomeren. Dies weist auf eine reduzierte Reaktivität des 1-Methylfluorens für die Oxidation durch die Methylgruppe in Nachbarschaft zur

Methylenbrücke aufgrund sterischer Hinderung hin. Die reduzierte Reaktivität zur Oxidation führt zur relativen Abnahme von 1-Methylfluorennon im Vergleich zu seinen Isomeren bei zunehmenden Wechselwirkungen.

Hinweise darauf, dass Fluorenone die Oxidationsprodukte der Fluorene sind, wurden aus den zwei folgenden Beobachtungen erhalten: Ein Vergleich der Methylfluorennonverteilung mit der Verteilung der Methylfluorene der Erdöle offenbart Ähnlichkeiten dieser zwei Verbindungsgruppen. Diese Beobachtung wurde unterstützt durch ‚Fensterbank‘-Experimente, in denen ein Erdöl in ein Weißglas gefüllt wurde und der Sonne und Luft über sechs Monate ausgesetzt wurde. Die Konzentration der Fluorenone war nach dem Experiment um zwei Größenordnungen höher als zu Beginn des Experiments. Diese Ergebnisse zeigen, dass künstliche Oxidation während Lagerung und Probenbehandlung ein wichtiger Faktor sein kann und die Menge der Fluorenone kontrollieren kann. Dies kann insbesondere Bedeutsam für Erdöle sein, die gewöhnlich geringe Mengen an Fluorenonen enthalten. Dennoch sollte der Effekt auf die Verteilung innerhalb der Verbindungsgruppe klein sein.

Obwohl die Konzentrationen der Xanthone in den Erdölmuttergesteinen nur sehr gering sind oder unterhalb der Nachweisgrenze liegen, wurden ähnliche Konzentrationen wie die der anderen beiden Verbindungsgruppen in den Erdölen detektiert. Dies läßt vermuten, dass Xanthone während der sekundären Migration aus aromatischen Vorläufern geosynthetisiert werden. Xanthone können bei erhöhten Temperaturen ($T = 180-200^{\circ}\text{C}$) und der Präsenz von Katalysatoren aus Benzoessäurederivaten und Phenolen, also aus Verbindungen, die gewöhnlich in sedimentärem organischem Material vorkommen, synthetisiert werden. Formationswasser, die mehr in Trägergesteinen als in Erdölmuttergesteinen verfügbar sind, üben einen vorteilhaften Einfluss auf die Bedingungen der Xanthongenerierung aus (z.B. niedriger pH für die intramolekulare Friedel-Crafts Acylierung). Es wird vermutet, dass die Mechanismen zur Bildung der Xanthone in sedimentärer Umgebung folgende essentielle Schritte beinhalten: 1. Bildung und Expulsion der Vorläufer Benzoessäuren und Phenolen in der Erdölphase; 2. Wanderung der Vorläufer in die wässrige Phase des Trägergesteins; 3. Reaktion der Vorläufer in der wässrigen Phase insbesondere bei Tonmineralschichten zur Bildung der Xanthone; 4. Wanderung der Xanthone zurück in die Erdölphase. Xanthone sind daher vielversprechend als Indikatoren für organisch-anorganische Wechselwirkungen im Trägergestein. Diese Vermutung wird dadurch

unterstützt, dass die Konzentrationen der Xanثone mit zunehmender Migrationsdistanz zunehmen. Das Verhältnis der geschützten Methylxanثone zu den nicht geschützten Isomeren $(1+4)/(2+3)$ steigt mit zunehmender Migrationsdistanz, wie es bei den Carbazolen beobachtet wurde. Dies deutet auf einen Partitionierungseffekt dieser hochpolaren Verbindungen hin (Dipolmoment: 3.11 D). Berechnungen der molekularen Dynamik bezüglich des Partitionierungsverhaltens der Methylxanثone unterstützen diese Annahme.

Biodegradation kann gleichfalls die Verteilung dieser Erdölbestandteile in der Erdöllagerstätte verändern. Da die nicht geschützten Isomere eine höhere Affinität zu der Wasserphase haben, stehen diese Verbindungen den Bakterien mehr zur Verfügung als die geschützten Isomere. Zusätzlich zeigen vorgeschlagene dioxygenolytische Abbauewege aerober Bakterien, dass nicht geschützte Isomere der Carbazole und Xanثone wahrscheinlich bevorzugt biodegradiert werden im Vergleich zu geschützten Isomeren. Dies ist das Resultat sterischer Hinderung von Alkylgruppen in der Nähe der Stickstoff- beziehungsweise Sauerstofffunktionen. Eine relative Zunahme der geschützten Isomere zu nicht geschützten Isomeren konnte anhand einer Biodegradationssequenz der Erdöllagerstätte Gullfaks für Carbazole und Xanثone demonstriert werden. Im Gegensatz dazu nimmt die Konzentration des 1-Methylfluorenons mit zunehmendem Grad der Biodegradation im Vergleich zu seinen Isomeren ab. Die Ursache für die relative Abnahme des 1-Methylfluorenons kann das Resultat des biologischen Abbaus von Fluorenen sein, da der biologische Abbau von Fluorenen über die Produktion von Fluorenonen führt. Durch die Methylgruppe des 1-Methylfluorens ist eine Oxidation zum korrespondierenden Keton sterisch gehindert. Dennoch ist ein aerober Abbau in dieser tiefen Erdöllagerstätte eher unwahrscheinlich. Obwohl der anaerobe Abbaumechanismus bisher nicht bekannt ist, könnten die initialen Umwandlungsschritte der anaeroben Degradation denen der aeroben Degradation ähnlich sein.

Durch die parallele Untersuchung von Erdölen und Erdölmuttergesteinen in natürlichen Systemen und anhand künstlicher wässriger Pyrolyseexperimente konnte gezeigt werden, dass polare Verbindungen als Bestandteil fossilen organischen Materials wichtige Informationen für die Exploration und Produktion von Erdöl liefern.

8. References

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9. Appendix

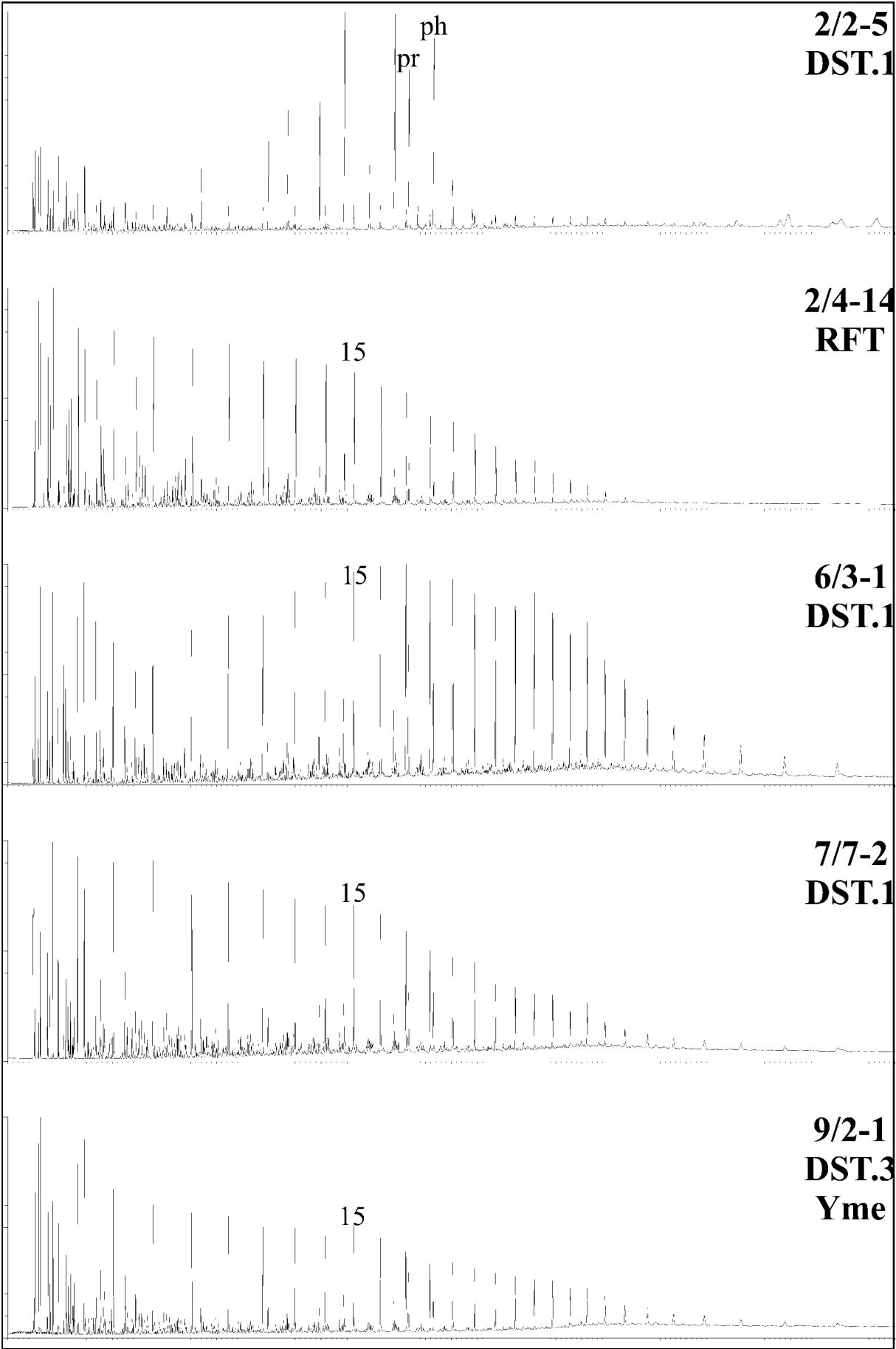
Appendix 1: Fraction amounts of oils and extracts

[mg/g oil]	saturates	aromatics	low polars	medium polars	high polars	bases	acids
2/2-5	411.5	142.2	89.1	17.6	14.1	8.0	3.1
2/4-14	300.8	39.7	9.1	5.0	0.6	1.7	0.6
6/3-1	420.4	174.9	71.0	11.5	4.8	6.7	0.1
7/7-2	242.9	167.2	79.4	24.9	9.5	3.4	4.7
9/2-1	417.5	163.4	52.3	9.4	6.1	7.8	1.9
15/12-5	310.9	133.2	60.2	10.9	17.6	6.6	5.2
15/12-6	405.5	166.0	65.3	10.8	27.6	8.4	1.3
25/5-1	380.6	147.0	50.0	8.1	7.4	8.1	3.5
25/11-T-21A	274.2	251.5	139.7	25.0	7.0	21.2	10.1
30/9-1 oil leg[mg/gTOC]	354.9	143.5	145.0	78.3	62.8	33.8	23.8
30/9-1 tar mat[mg/gTOC]	375.7	182.1	202.8	76.0	36.1	34.0	14.8
30/9-10	371.6	189.4	71.8	19.1	9.2	5.0	2.0
NSO-1Std oil	359.4	161.5	78.6	14.0	5.1	11.3	1.4
31/2-G-3H	177.9	193.0	78.3	7.8	4.0	12.1	1.3
35/3-4	102.0	62.6	3.5	6.3	3.5	0.3	0.3
35/11-4	455.4	118.7	33.5	9.5	4.8	3.2	0.2
6201/11-1	289.6	112.8	39.9	6.1	2.4	2.7	1.6
33/9-12	390.8	172.9	53.1	7.6	3.4	9.9	2.5
33/9-14	400.3	162.8	63.2	16.3	4.9	7.5	1.4
34/4-6	403.0	138.0	65.3	1.7	2.5	2.5	0.7
34/7-4	285.0	142.7	58.7	12.9	57.0	10.8	1.7
34/7-6	362.3	142.7	57.6	10.1	7.3	11.9	2.6
34/7-8	334.9	167.8	84.7	15.8	2.9	11.0	5.4
34/7-10	309.8	153.8	73.8	22.7	12.7	13.6	40.2
34/7-13 DST.1	389.0	177.7	70.9	6.2	3.7	6.7	1.8
34/7-13 DST.1.1	412.3	166.9	66.7	10.4	6.5	5.4	1.3
34/7-14	407.5	172.1	61.7	9.5	4.9	6.8	1.6
34/7-16 DST.2	370.1	175.8	72.0	6.5	4.5	10.3	3.0
34/7-16 DST.3	353.2	157.0	61.1	7.9	4.2	5.5	2.1
34/7-18	427.5	260.1	98.7	7.6	3.8	10.2	2.2
34/7-21	379.2	164.5	70.9	10.1	4.4	8.9	2.5
34/7-22	377.7	177.1	72.2	4.5	2.2	11.5	1.2
34/7-23A	358.6	172.5	74.0	6.8	4.1	10.5	1.1
34/7-26A	401.8	192.0	86.9	6.5	4.8	11.3	2.4
34/8-8R	464.9	155.4	47.2	10.0	6.3	7.1	0.2
34/10-1	259.2	199.2	67.9	13.2	9.2	8.9	1.7
34/10-3 DST2	221.1	235.9	91.3	12.8	5.6	18.8	3.6
34/10-3 DST3	299.0	231.7	92.7	8.4	6.0	12.6	2.6
34/10-7 DST2	399.4	141.0	57.6	6.4	1.4	8.9	1.2
34/10-8 DST1	356.4	219.7	91.8	10.4	5.2	11.6	2.8
34/10-9 DST3	360.6	205.7	81.5	9.1	3.2	11.7	2.5
34/10-14 DST1	306.1	209.0	94.0	9.2	4.2	9.0	2.9
34/10-A-1H DST1	331.4	218.9	93.8	9.0	6.3	9.2	4.1
34/10-17	462.1	153.2	69.5	10.5	5.7	8.5	8.8
34/10-30	570.8	57.5	41.6	13.0	2.0	4.0	1.1
34/10-32R	619.4	158.0	44.6	9.5	4.7	5.0	0.6
34/10-34	280.6	182.7	83.0	15.4	32.2	2.1	31.2
34/10-35	335.8	153.0	9.1	6.1	1.0	0.2	0.3

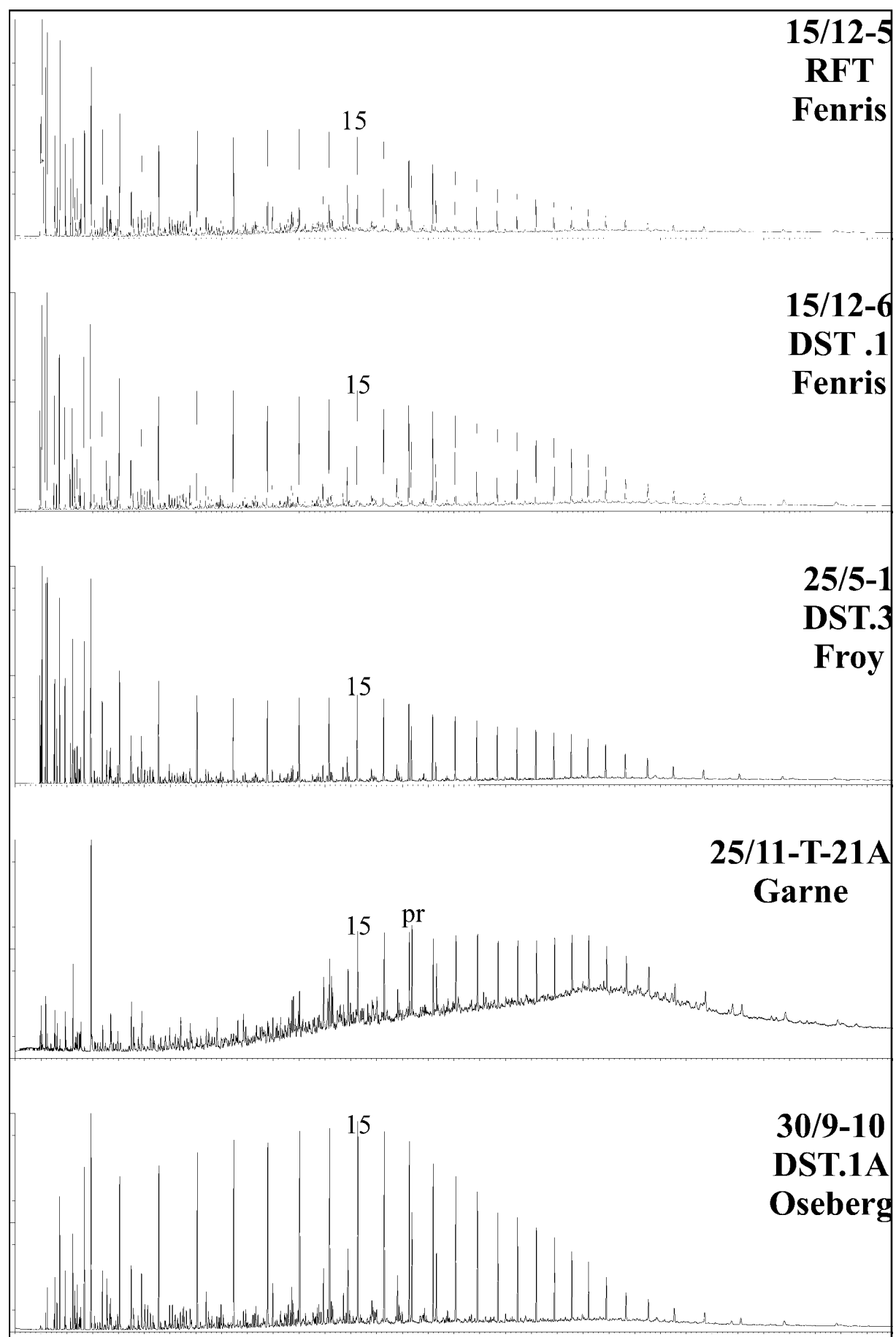
Appendix 1: Fraction amounts of oils and extracts

[mg/g oil or extract]	saturates	aromatics	low polars	medium polars	high polars	bases	acids
6406/11-1S	366.6	78.4	14.2	3.2	0.3	1.9	3.2
6406/3-2	396.9	154.4	36.2	5.5	2.1	3.4	2.3
6407/7-4	567.5	147.5	46.4	6.3	3.0	2.8	1.7
6407/9-1	377.1	151.5	45.7	8.4	17.1	4.5	1.3
6506/11-2	457.0	85.0	69.5	4.6	7.2	2.0	1.5
6506/12-3	532.2	103.8	21.1	0.6	0.9	0.5	7.2
6507/3-1	405.2	103.1	6.5	1.7	0.7	0.8	1.3
6507/7-2 DST.2	381.5	276.8	99.3	8.1	3.3	9.0	20.3
6507/7-2 DST.3	371.3	282.5	98.6	6.4	9.9	16.1	16.5
6507/7-2 DST.4R	407.0	228.0	73.8	8.3	2.8	6.8	10.7
6507/7-3	371.7	155.8	65.4	10.2	3.4	6.1	1.0
6507/7-5 DST.1	418.8	243.3	72.6	6.8	2.1	7.5	9.5
6507/7-5 DST.2	415.7	200.9	60.0	4.8	2.9	11.4	8.4
6507/7-6 DST.1	388.7	291.1	102.9	20.1	7.2	9.0	20.6
6507/7-6 DST.2	267.7	161.7	56.1	6.1	3.5	3.3	10.5
6507/7-8 DST.1	377.2	240.6	83.9	7.7	2.8	6.2	17.1
6507/7-8 DST.2	389.3	251.4	82.6	6.3	2.6	6.0	15.6
6507/8-4 DST.2	150.7	243.9	91.5	9.3	5.0	7.5	14.8
6507/8-4 DST.3	433.3	286.6	114.6	9.4	4.0	8.2	3.3
6507/8-4 DST.4	154.1	121.6	2.8	0.0	0.2	0.7	0.1
6507/11-3 DST.1	478.3	198.0	35.1	2.8	1.4	2.0	0.1
6507/11-3 DST.2	267.9	81.7	7.7	1.4	0.0	2.1	0.5
6507/11-3 DST.3	166.2	47.8	1.8	0.6	0.0	0.4	0.3
7120/1-2	129.4	119.2	45.8	4.4	2.3	3.8	2.1
7121/5-1	564.3	197.0	67.5	5.4	3.2	5.7	3.8
7124/3-1	315.6	145.7	49.9	6.9	1.3	3.2	1.0
source rocks							
Åre 5647.15 6406/2-1R	85.8	174.7	143.7	91.2	44.0	12.4	2.3
Åre 5647.60 6406/2-1R	24.2	281.8	225.4	40.3	51.5	81.3	8.1
Spekk 3744 6406/12-2	211.6	219.5	157.0	44.0	162.3	8.5	1.5
Spekk 3744 6406/12-3	194.9	192.4	120.5	32.9	292.8	14.2	2.4
Åre 1406.40 6507/3-2	110.5	32.2	187.5	162.0	587.7	51.7	130.2
Åre 1406.50 6507/3-3	26.9	13.6	71.2	66.0	231.2	80.3	78.3
Spekk 1623.30 6407/9-3	140.5	52.3	143.4	52.4	277.6	28.6	49.9
Spekk 1627.50 6407/9-3	32.7	7.6	16.8	8.5	32.5	4.7	4.0
Spekk 1675 6407/9-3	65.8	16.2	29.2	29.8	159.9	8.0	29.9
Ghareb (hydrous pyrolysis)							
oil 310°C	86.6	210.3	67.4	30.0	29.2	8.9	2.0
oil 330°C	118.5	275.7	100.7	41.3	46.7	22.2	3.1
oil 345°C	107.8	249.3	86.0	39.5	57.5	21.1	2.6
oil 355°C	85.7	178.9	77.3	35.2	12.0	13.6	0.9
oil 360°C	89.1	218.1	46.8	33.8	22.5	16.0	0.1
oil 365°C	97.0	225.7	42.9	36.4	32.7	18.0	4.3
bitumen 310°C	73.9	346.1	167.1	92.2	181.9	91.8	15.5
bitumen 330°C	68.7	343.3	153.8	85.3	133.5	30.8	3.5
bitumen 345°C	57.7	335.2	178.6	167.7	166.9	91.9	13.7
bitumen 355°C	71.7	381.7	113.4	101.0	155.1	51.7	6.7
bitumen 360°C	42.6	286.8	110.9	107.5	113.1	55.8	13.5
bitumen 365°C	38.1	277.2	94.6	132.9	124.8	56.2	6.2

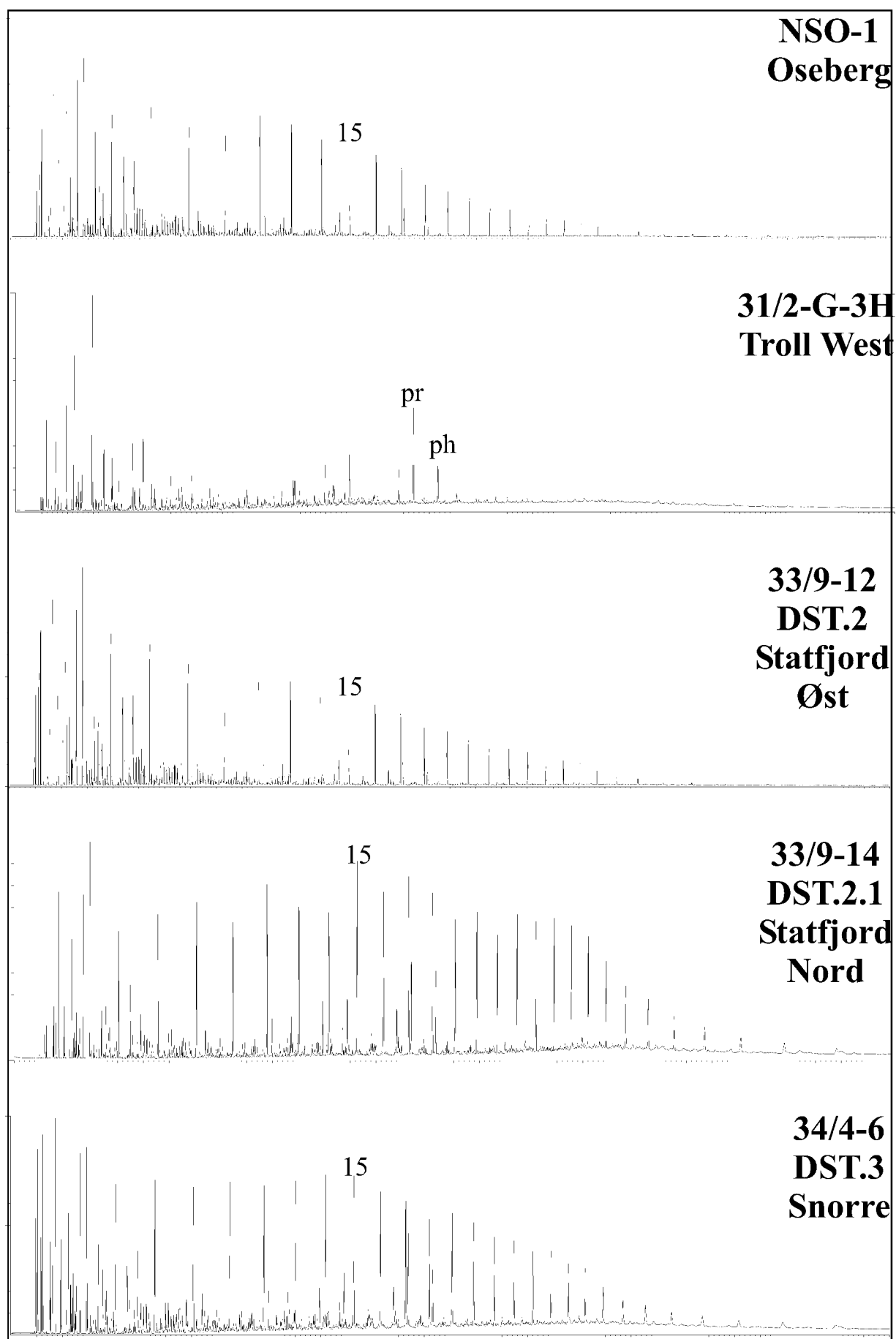
Appendix 2: Whole oil chromatograms



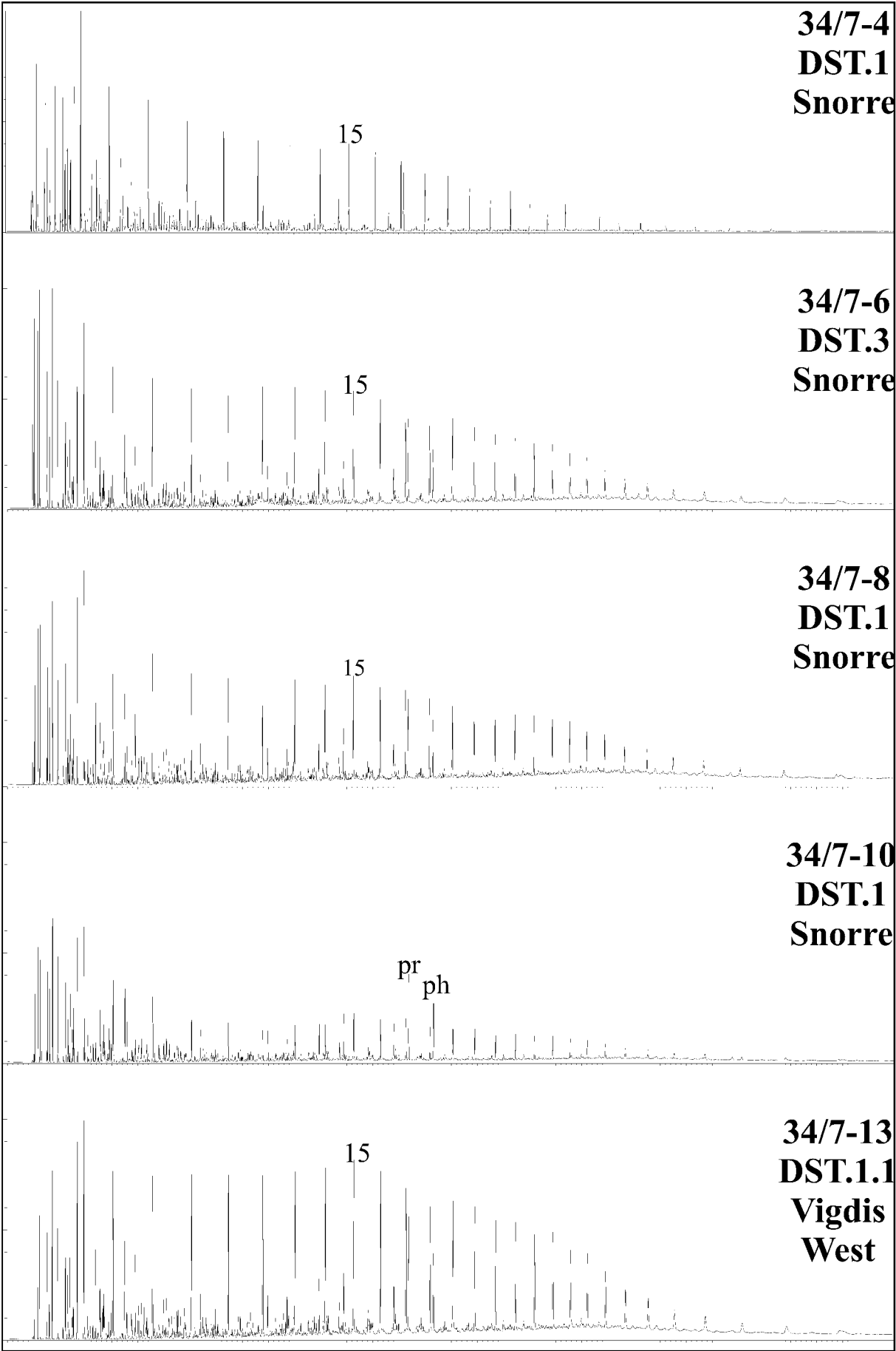
Appendix 2: Whole oil chromatograms



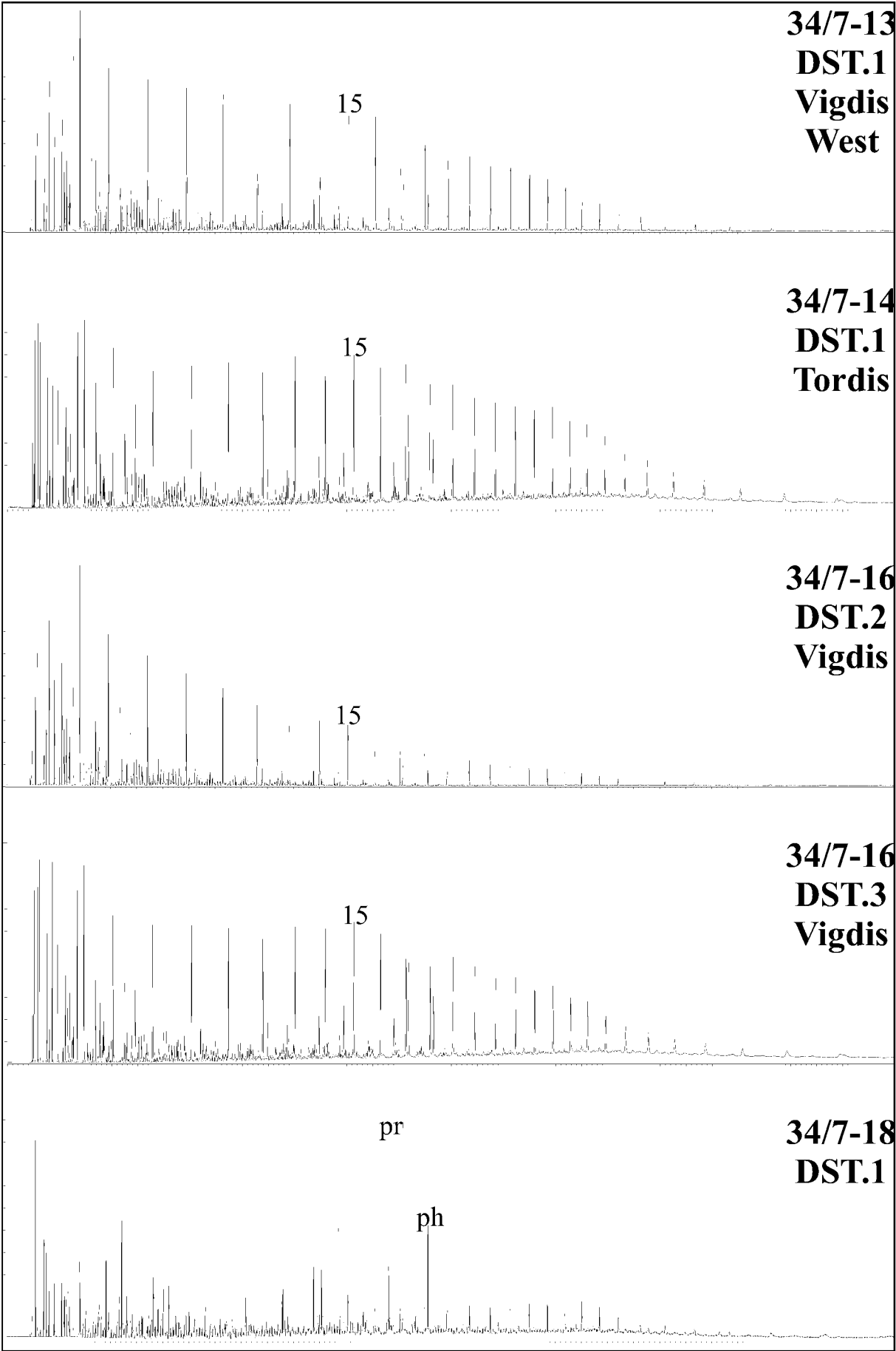
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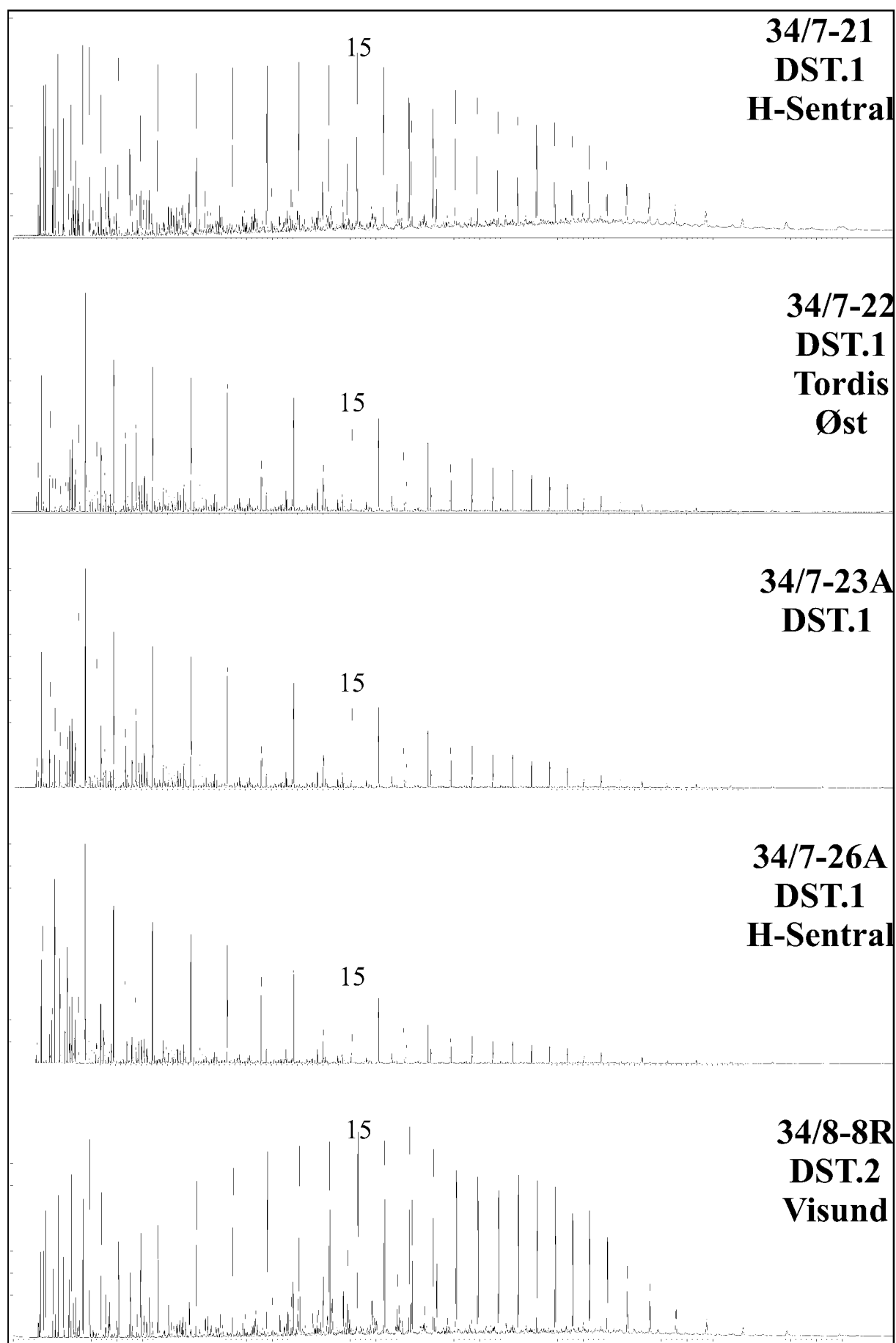
Appendix 2: Whole oil chromatograms



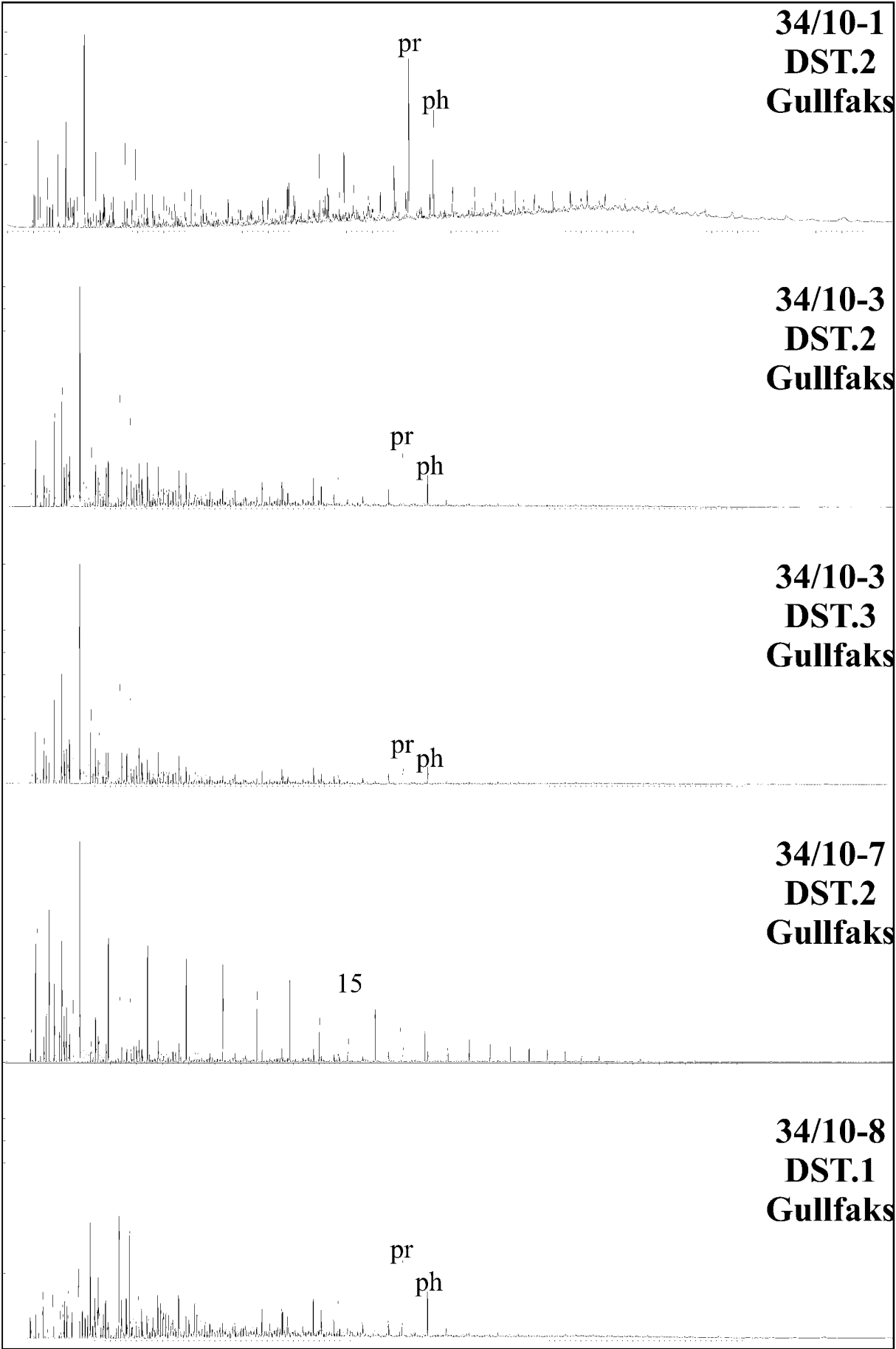
Appendix 2: Whole oil chromatograms



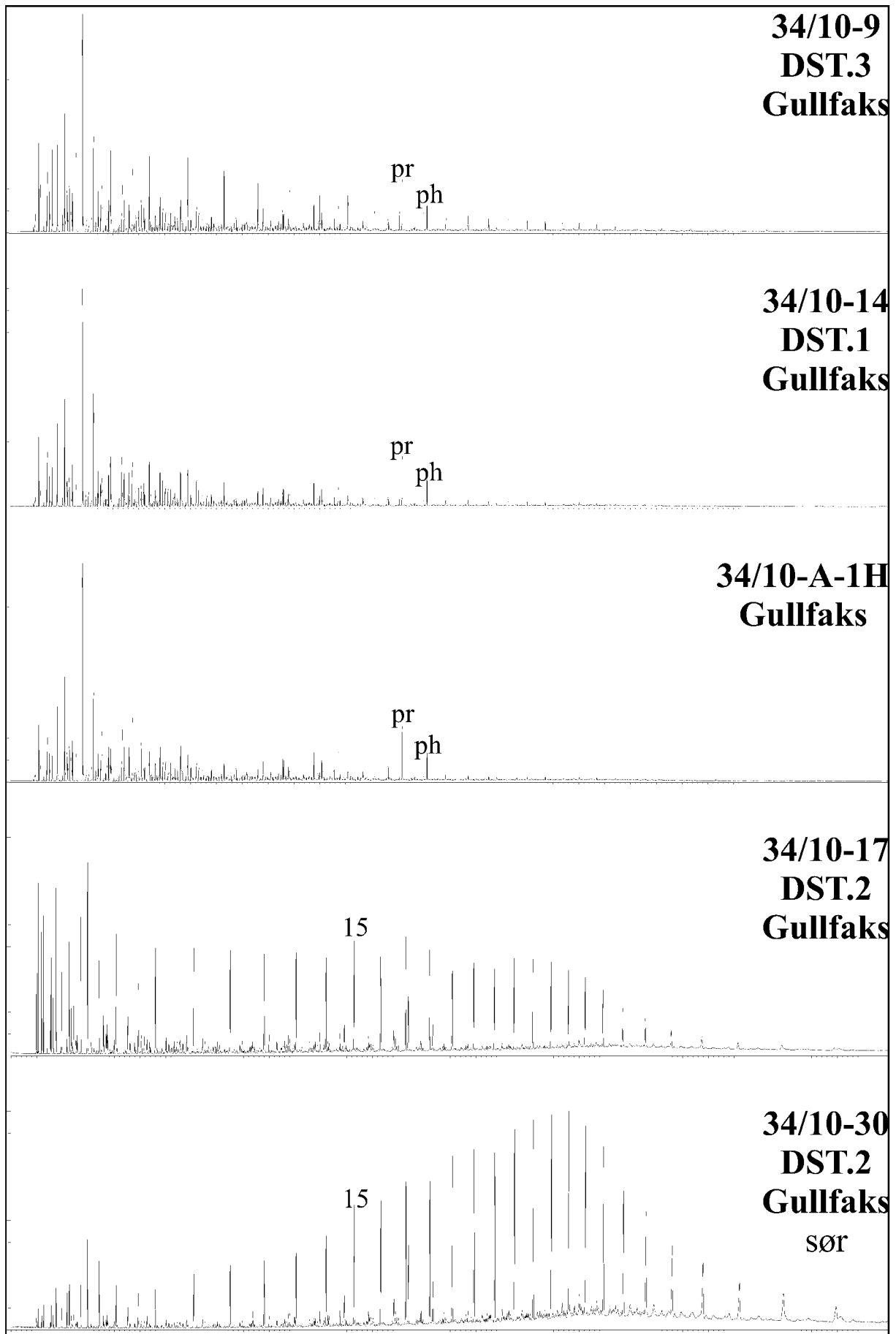
Appendix 2: Whole oil chromatograms



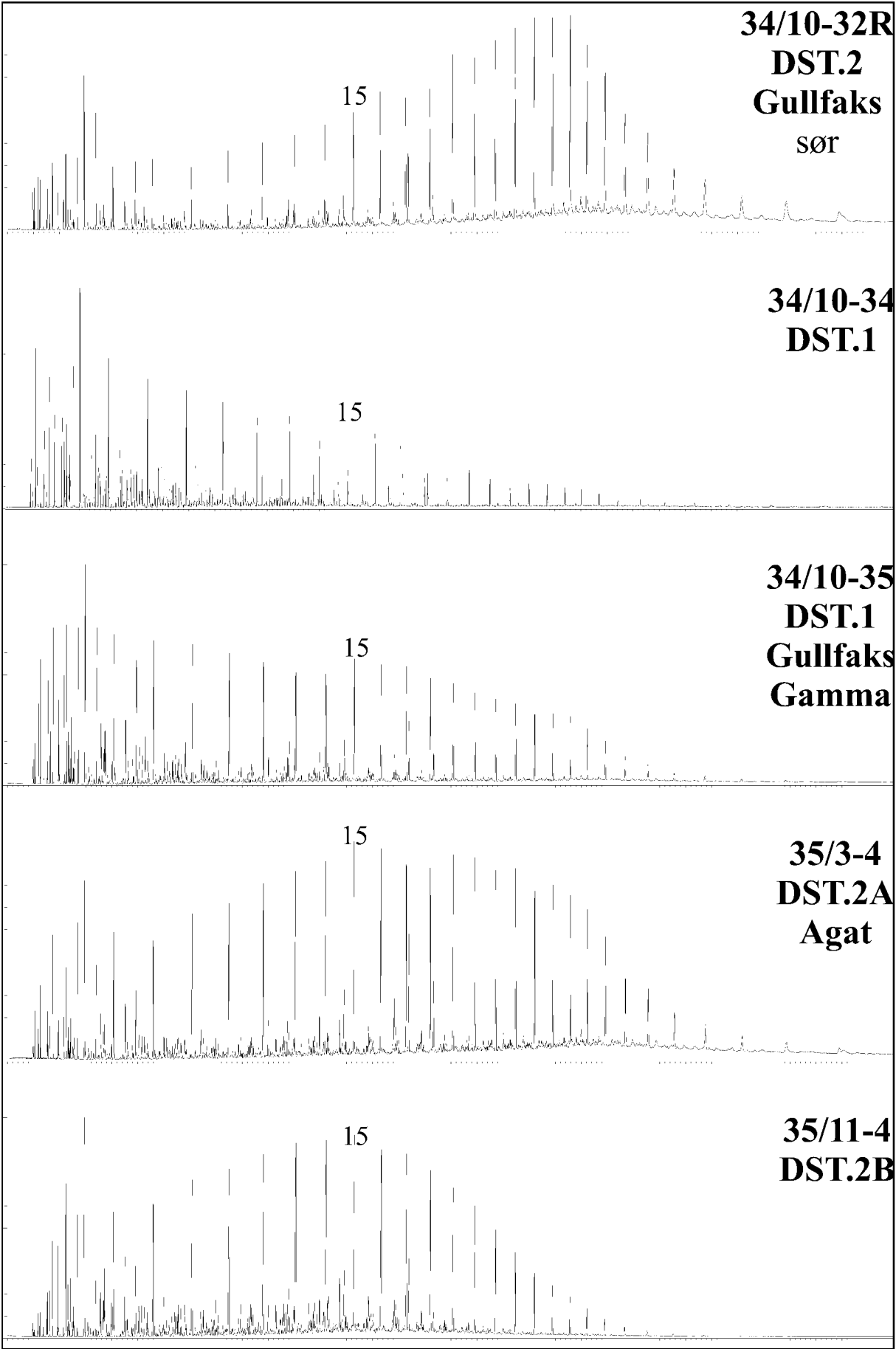
Appendix 2: Whole oil chromatograms



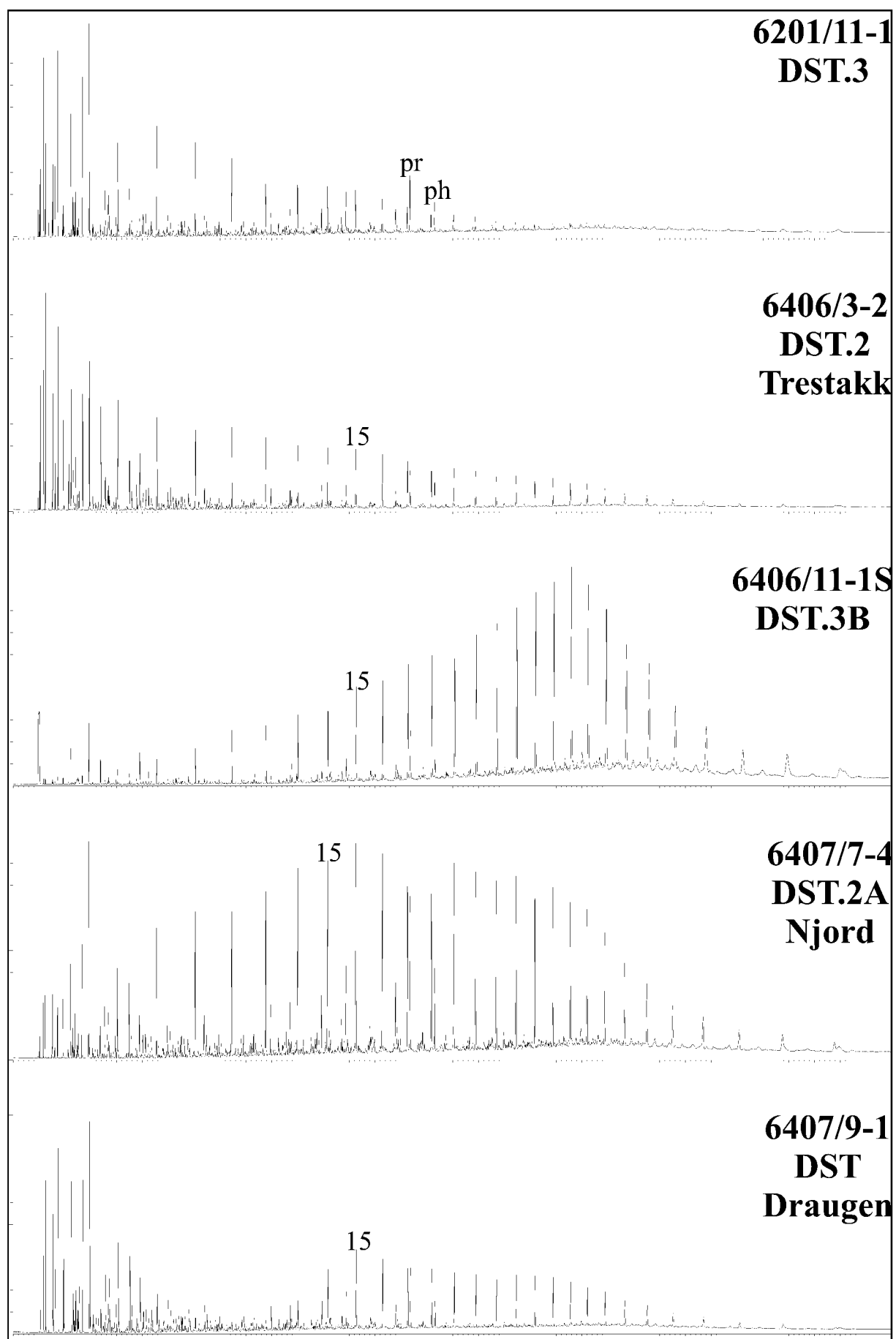
Appendix 2: Whole oil chromatograms



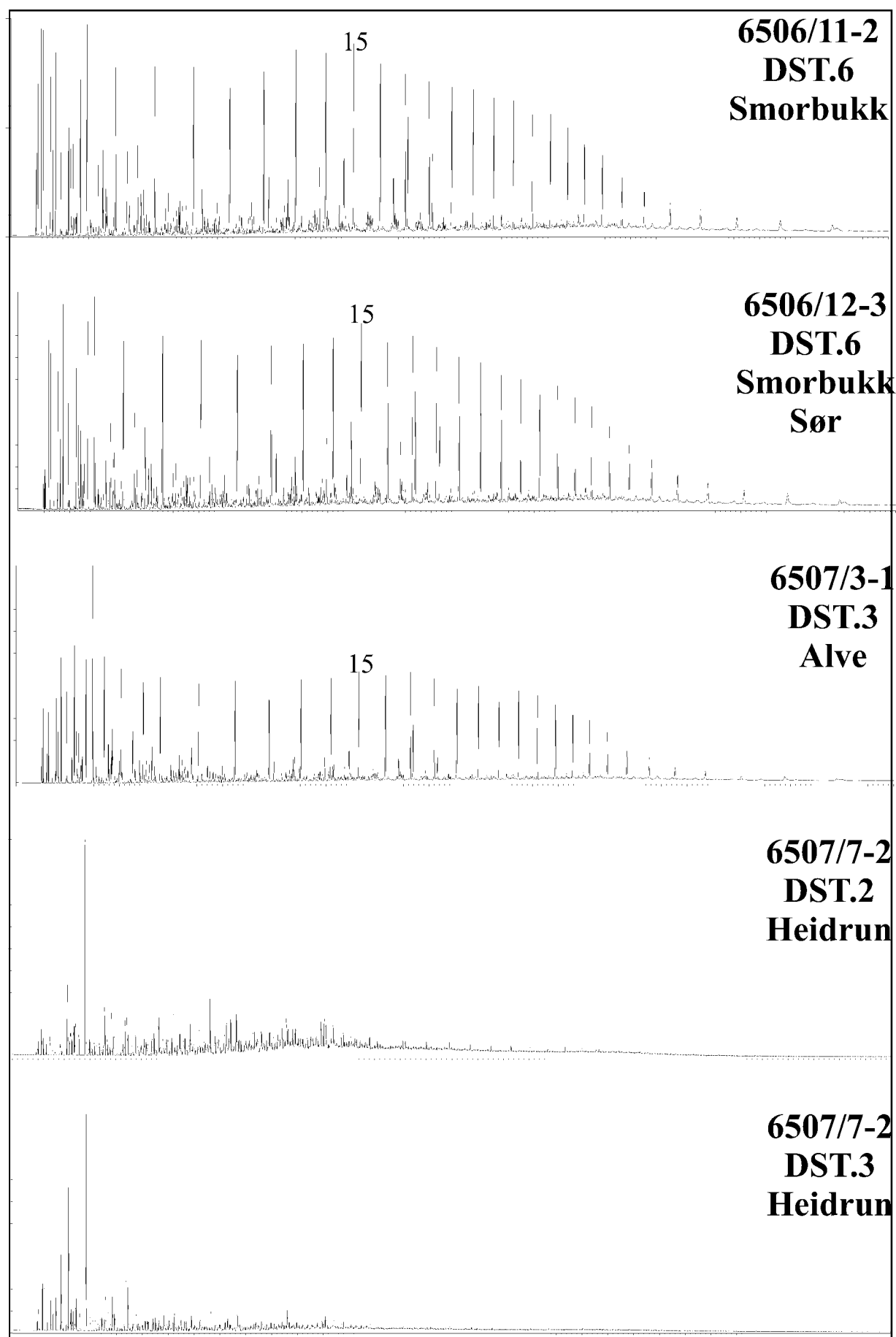
Appendix 2: Whole oil chromatograms



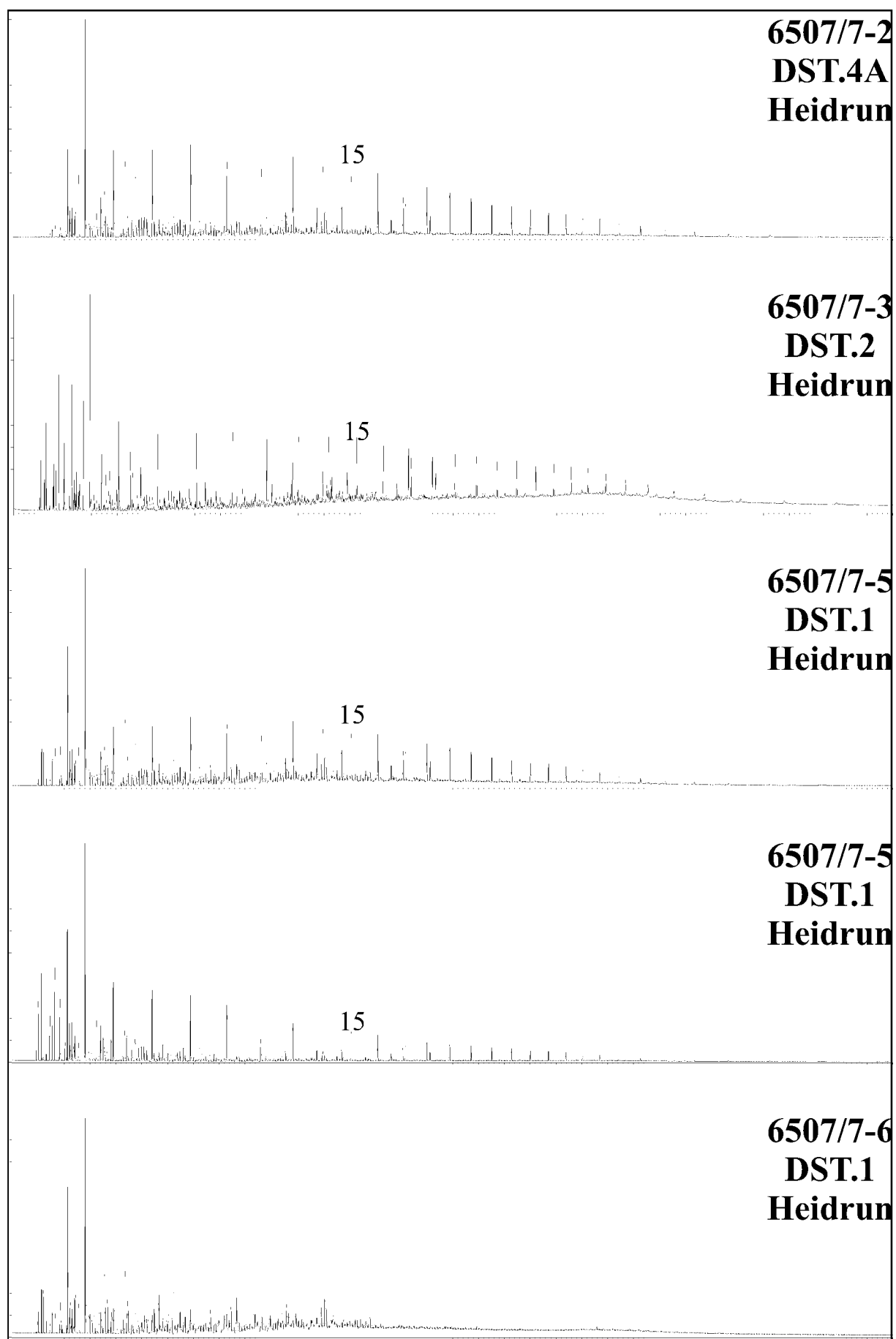
Appendix 2: Whole oil chromatograms



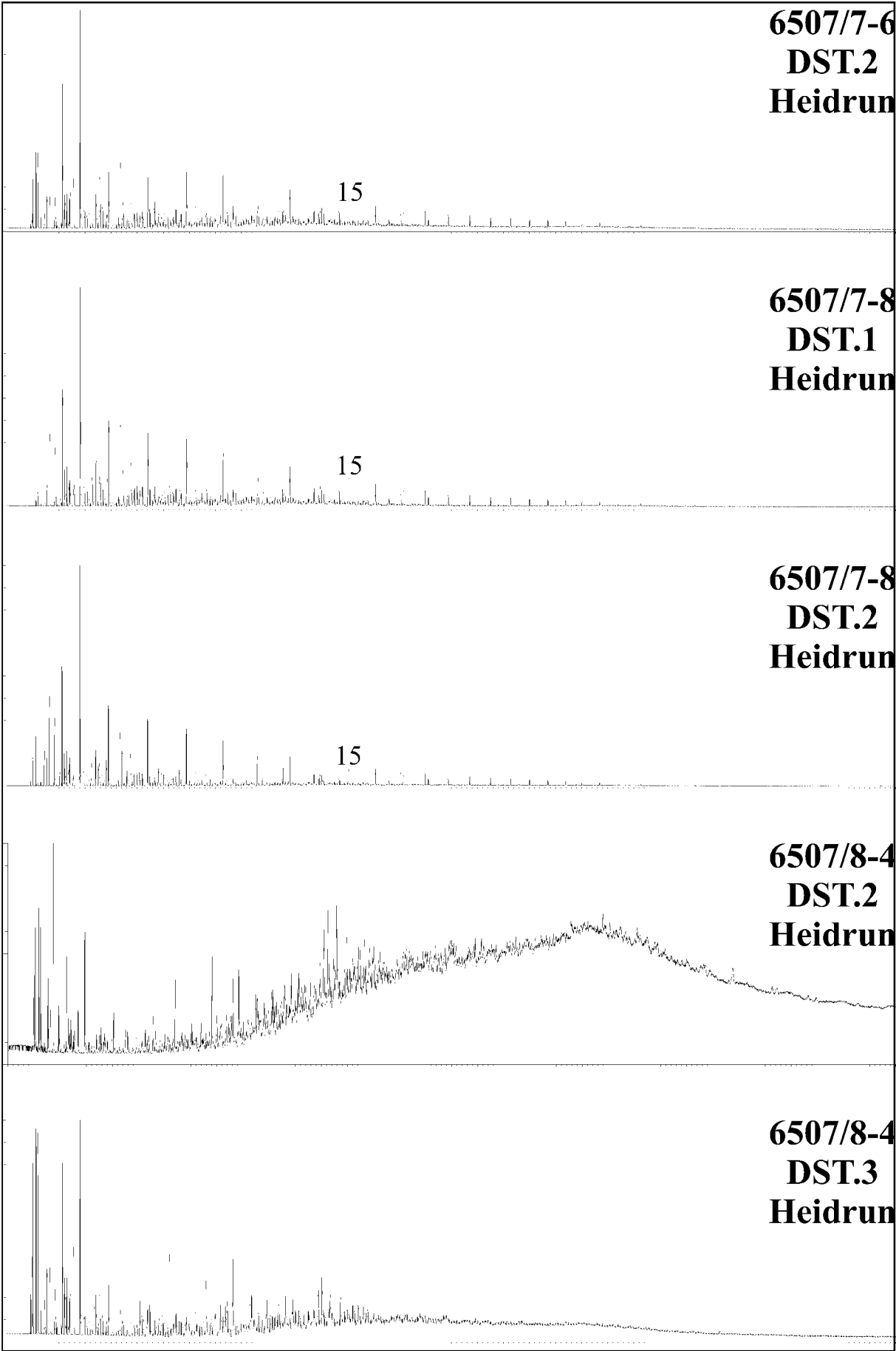
Appendix 2: Whole oil chromatograms



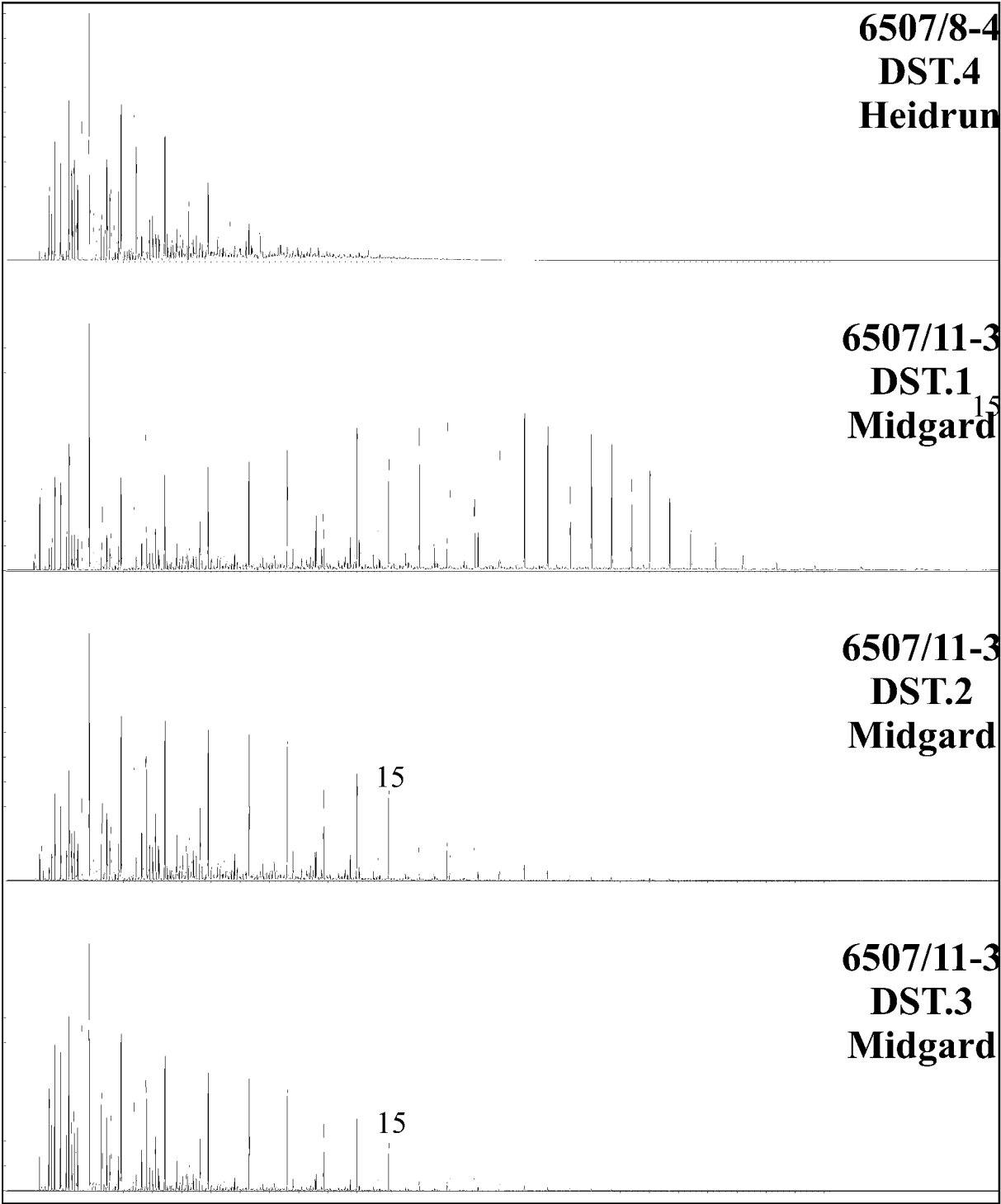
Appendix 2: Whole oil chromatograms



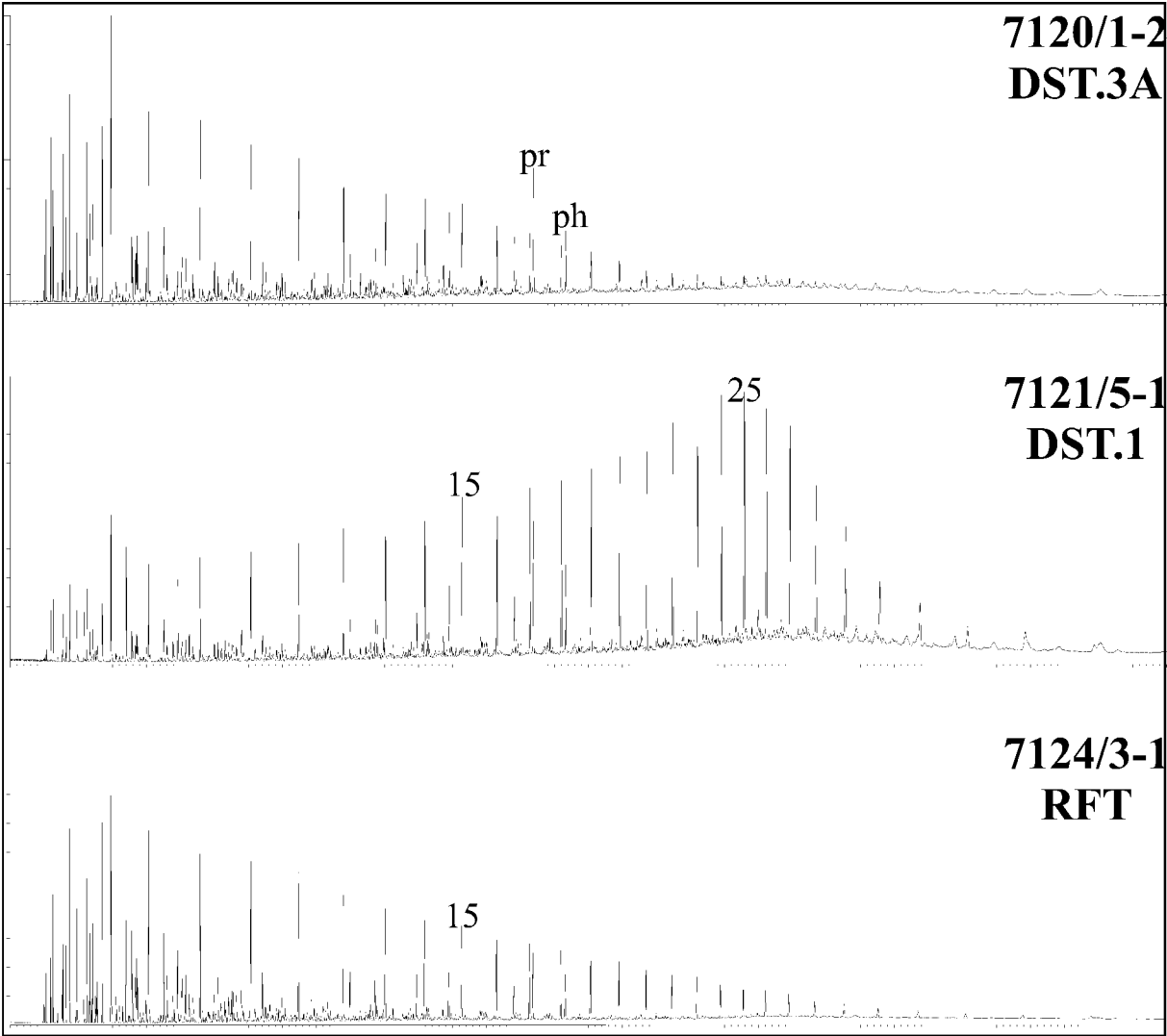
Appendix 2: Whole oil chromatograms



Appendix 2: Whole oil chromatograms



Appendix 2: Whole oil chromatograms



Appendix 3a: Maturity and facies parameter

[mg/g oil]	CPI [24-32]	A) pr/ n-C ₁₇	B) ph/ n-C ₁₈	A/B	pr/ph	C ₁₇ / (C ₁₇ +C ₂₇)	[%] less than C ₁₅ H ₃₂	API gravity
2/2-5	1.04	6.00	9.42	0.64	0.72	0.77	11.6	31.7
2/4-14	1.08	0.40	0.33	1.22	1.44	0.89	33.2	48.5
6/3-1	1.02	0.56	0.47	1.19	1.32	0.75	15.3	33.5
7/7-2	0.90	0.59	0.66	0.90	0.98	0.78	20.0	20.8
9/2-1	1.06	0.72	0.56	1.29	1.54	0.77	17.8	36.3
15/12-5	1.02	0.68	0.56	1.23	1.42	0.74	18.1	27.4
15/12-6	1.03	0.66	0.55	1.21	1.41	0.75	17.1	34.9
25/5-1	1.06	0.72	0.35	2.05	2.45	0.72	23.8	40.3
25/11-T-21A	1.04	1.08	0.72	1.50	1.70	0.73	-	18.7
30/9-1 oil leg[mg/gTOC]	1.02	0.63	0.47	1.34	1.59	0.79	-	-
30/9-1 tar mat[mg/gTOC]	1.02	0.71	0.56	1.26	1.48	0.85	11.6	30.7
30/9-10	1.03	0.59	0.49	1.22	0.74	0.65	-	-
NSO-1Stdoil	1.02	0.6	0.46	1.31	0.99	0.69	-	-
31/2-G-3H	-	14.15	-	-	2.08	1.00	-	28.6
35/3-4	1.10	0.34	0.14	2.41	2.87	0.92	31.6	50.4
35/11-4	1.04	0.59	0.36	1.64	1.88	0.75	17.6	36.9
6201/11-1	1.06	2.20	1.47	1.50	1.85	0.88	21.6	37.8
33/9-12	1.03	0.68	0.54	1.28	1.47	0.78	18.9	35.9
33/9-14	1.00	0.65	0.53	1.23	1.40	0.74	12.5	37.5
34/4-6	1.01	0.67	0.51	1.32	1.53	0.79	22.4	40.8
34/7-4	1.00	0.98	0.77	1.27	1.44	0.76	23.4	38.4
34/7-6	1.01	0.82	0.63	1.30	1.47	0.76	22.6	37.4
34/7-8	1.02	0.98	0.80	1.23	1.42	0.77	16.3	33.1
34/7-10	1.01	1.91	1.72	1.11	1.30	0.78	20.2	34.2
34/7-13 DST.1	1.00	0.70	0.56	1.26	1.46	0.76	14.1	34.5
34/7-13 DST.1.1	1.02	0.74	0.58	1.27	1.45	0.73	19.0	35.5
34/7-14	1.02	0.72	0.57	1.27	1.45	0.75	17.7	35.5
34/7-16 DST.2	1.01	0.77	0.61	1.26	1.44	0.76	18.9	36.4
34/7-16 DST.3	1.01	0.81	0.65	1.26	1.43	0.74	-	-
34/7-18	0.98	2.70	2.48	1.09	1.42	0.67	5.0	27.6
34/7-21	1.02	0.72	0.56	1.29	1.48	0.78	16.7	34.8
34/7-22	1.01	0.73	0.57	1.28	1.47	0.75	19.7	35.9
34/7-23A	1.01	0.71	0.55	1.29	1.46	0.75	19.2	35.6
34/7-26A	1.09	0.83	0.68	1.22	1.39	0.74	-	-
34/8-8R	1.02	0.66	0.41	1.60	1.75	0.78	15.3	34.4
34/10-1	1.02	4.50	3.47	1.30	1.45	0.79	15.1	28.6
34/10-3 DST2	0.99	9.65	5.18	1.86	1.49	0.74	13.0	28.4
34/10-3 DST3	0.97	9.51	5.25	1.81	1.42	0.73	13.4	28.8
34/10-7 DST2	1.04	0.85	0.60	1.41	1.67	0.79	20.7	37.2
34/10-8 DST1	1.52	5.56	5.37	1.03	1.46	0.89	13.5	28.6
34/10-9 DST3	1.04	1.67	1.33	1.25	1.50	0.78	15.6	31.1
34/10-14 DST1	1.21	3.59	3.36	1.07	1.44	0.80	13.4	28.9
34/10-A-1H DST1	1.12	4.17	3.72	1.12	1.44	0.80	13.2	30.9
34/10-17	1.04	0.61	0.35	1.75	1.95	0.72	19.6	36.1
34/10-30	1.04	0.58	0.32	1.78	1.85	0.63	8.9	31.7
34/10-32R	1.06	0.55	0.24	2.25	2.19	0.58	10.3	31.5
34/10-34	1.01	1.02	0.82	1.24	1.44	0.77	14.3	31.7
34/10-35	1.08	0.55	0.33	1.66	1.90	0.77	42.4	43.5

Appendix 3a: Maturity and facies parameter

[mg/g oil or extract]	CPI [24-32]	A) pr/ n-C ₁₇	B) ph/ n-C ₁₈	A/B	pr/ph	C ₁₇ / (C ₁₇ +C ₂₇)	[%] less than C ₁₅ H ₃₂	API gravity
6406/11-1S	1.11	0.44	0.23	1.97	1.77	0.33	13.2	17.3
6406/3-2	0.99	0.80	0.73	1.08	1.21	0.75	22.3	38.3
6407/7-4	1.03	0.77	0.46	1.67	1.90	0.77	10.4	35.2
6407/9-1	1.04	0.94	0.54	1.73	2.00	0.75	20.7	35.9
6506/11-2	1.00	0.68	0.52	1.30	1.49	0.80	21.2	43.1
6506/12-3	1.02	0.70	0.49	1.43	1.61	0.77	22.3	43.1
6507/3-1	1.11	0.60	0.27	2.19	2.26	0.74	27.1	42.4
6507/7-2 DST.2	1.05	1.34	0.79	1.70	1.88	0.73	-	-
6507/7-2 DST.3	-	1.41	1.20	1.18	1.38	0.78	-	-
6507/7-2 DST.4R	1.03	0.80	0.60	1.32	1.44	0.69	-	-
6507/7-3	1.00	0.70	0.57	1.23	1.38	0.74	11.6	29.1
6507/7-5 DST.1	1.03	0.96	0.70	1.36	1.48	0.75	-	-
6507/7-5 DST.2	1.02	0.81	0.61	1.33	1.43	0.75	-	-
6507/7-6 DST.1	-	2.07	1.81	1.14	1.88	-	-	-
6507/7-6 DST.2	1.02	0.90	0.53	1.70	1.85	0.78	-	-
6507/7-8 DST.1	1.04	0.94	0.72	1.31	1.50	0.78	-	-
6507/7-8 DST.2	1.02	0.93	0.71	1.31	1.46	0.77	-	-
6507/8-4 DST.2	-	-	-	-	-	-	2.7	23.8
6507/8-4 DST.3	-	-	-	-	-	-	-	-
6507/8-4 DST.4	-	-	-	-	-	-	-	-
6507/11-3 DST.1	1.09	0.67	0.39	1.73	1.79	0.67	-	-
6507/11-3 DST.2	1.11	0.77	0.44	1.74	2.28	0.96	-	-
6507/11-3 DST.3	-	0.76	0.44	1.74	2.31	0.96	-	-
7120/1-2	1.05	1.95	1.32	1.48	1.78	0.89	20.5	37.3
7121/5-1	1.11	0.81	0.59	1.37	1.45	0.56	0.6	30.4
7124/3-1	1.05	0.92	0.78	1.18	1.38	0.81	23.6	40.2
source rocks							OEP1	MDR'
Åre 5647.15 6406/2-1R	1.02	0.89	0.69	1.28	1.45	0.71	0.96	0.96
Åre 5647.60 6406/2-1R	1.05	0.45	0.45	1.00	0.79	0.42	0.96	0.95
Spekk 3744 6406/12-2	1.92	0.64	0.28	2.28	2.00	0.07	2.19	
Spekk 3744 6406/12-3	1.96	1.07	0.41	2.60	3.32	0.06	1.96	
Åre 1406.40 6507/3-2	0.91	1.05	0.98	1.08	1.13	0.72	0.90	0.82
Åre 1406.50 6507/3-3	0.91	0.98	1.00	0.98	0.99	0.71	0.90	0.82
Spekk 1623.30 6407/9-3	-	1.49	1.25	1.19	2.19	-	1.26	0.54
Spekk 1627.50 6407/9-3	1.42	1.48	1.38	1.07	1.14	0.87	1.12	0.49
Spekk 1675 6407/9-3	2.02	1.39	1.03	1.36	2.69	0.94	1.31	0.69

Appendix 3b: Maturity and facies parameters

	25NH/ (25NH+H)	C ₃₅ HHI	C ₃₄ S/ (C ₃₄ S+C ₃₅ S)	GI	DNH/ (DNH+H)	DNH/ (DNH+Tm)	25NH/ (25NH+30NH)	25NH/ (25NH+DNH)	Ts/(Ts+Tm)	22S/(S+R)	$\alpha\beta/(\alpha\beta+\beta\alpha)$
2/2-5	0.01	5.9	0.54	25.1	0.11	0.41	0.02	0.09	0.44	0.58	0.95
2/4-14	-	-	-	-	-	-	-	-	0.57	0.60	-
6/3-1	0.01	7.1	0.52	1.8	0.06	0.28	0.02	0.12	0.66	0.58	0.95
7/7-2	0.01	13.4	0.42	3.6	0.37	0.72	0.01	0.01	0.55	0.60	0.96
9/2-1	0.01	5.9	0.61	1.6	0.00	0.03	0.02	0.74	0.70	0.65	0.95
15/12-5	0.01	6.8	0.52	1.8	0.05	0.26	0.02	0.15	0.62	0.66	0.95
15/12-6	0.01	7.0	0.52	1.9	0.06	0.26	0.02	0.13	0.62	0.63	0.95
25/5-1	0.01	6.0	0.53	1.3	0.15	0.50	0.02	0.04	0.63	0.62	0.95
25/11-T-21A	0.33	7.3	0.58	3.1	0.32	0.58	0.44	0.51	0.61	0.59	0.95
NSO-1	0.15	7.8	0.52	3.1	0.28	0.65	0.27	0.31	0.63	0.63	0.95
30/9-10	0.15	9.0	0.52	2.8	0.28	0.71	0.29	0.31	0.60	0.59	0.95
30/9-1[OL]	0.15	7.5	0.56	2.6	0.28	0.66	0.26	0.30	0.61	0.58	0.95
30/9-1[TM]	0.12	6.5	0.57	2.2	0.24	0.66	0.21	0.30	0.62	0.58	0.97
31/2-C-3H	0.15	8.1	0.53	3.1	0.28	0.63	0.26	0.31	0.62	0.57	0.95
35/3-4	-	-	-	-	-	-	-	-	-	-	-
35/11-4	0.05	7.2	0.49	-	0.18	0.62	0.11	0.19	0.77	0.63	0.95
6201/11-1	0.25	6.4	0.53	2.2	0.12	0.37	0.40	0.71	0.73	0.62	0.94
33/9-12	0.04	7.8	0.50	2.6	0.30	0.71	0.08	0.09	0.66	0.60	0.95
33/9-14	0.04	8.8	0.48	1.5	0.20	0.64	0.10	0.15	0.67	0.63	0.96
34/4-6	0.03	10.4	0.50	2.1	0.30	0.83	0.07	0.06	0.72	0.60	0.96
34/7-4	0.03	8.6	0.50	2.1	0.33	0.78	0.05	0.05	0.64	0.62	0.95
34/7-6	0.03	7.6	0.52	2.3	0.34	0.77	0.05	0.06	0.66	0.57	0.95
34/7-8	0.03	7.4	0.54	1.8	0.29	0.73	0.07	0.07	0.61	0.61	0.96
34/7-10	0.02	9.1	0.57	1.6	0.29	0.78	0.04	0.05	0.54	0.61	0.96
34/7-13 DST.1.1	0.04	9.1	0.48	1.6	0.18	0.56	0.09	0.16	0.64	0.60	0.96
34/7-13 DST.1	0.04	9.6	0.45	1.6	0.20	0.57	0.10	0.14	0.64	0.61	0.96
34/7-14	0.04	7.0	0.53	2.3	0.27	0.68	0.09	0.11	0.63	0.61	0.95
34/7-16 DST.3	0.04	7.8	0.50	2.2	0.32	0.73	0.08	0.08	0.64	0.62	0.96
34/7-16 DST.2	0.03	8.9	0.52	1.9	0.28	0.66	0.05	0.08	0.62	0.63	0.96
34/7-18	0.03	5.6	0.56	1.9	0.26	0.72	0.06	0.08	0.66	0.54	0.97

Appendix 3b: Maturity and facies parameters

	25NH/ (25NH+H)	C ₃₅ HHI	C ₃₄ S/ (C ₃₄ S+C ₃₅ S)	GI	DNH/ (DNH+H)	DNH/ (DNH+Tm)	25NH/ (25NH+30NH)	25NH/ (25NH+DNH)	Ts/(Ts+Tm)	22S/(S+R)	$\alpha\beta/(\alpha\beta+\beta\alpha)$
34/7-21	0.04	7.3	0.54	2.2	0.27	0.65	0.09	0.11	0.64	0.59	0.95
34/7-22	0.03	6.9	0.52	2.0	0.25	0.66	0.07	0.09	0.64	0.59	0.96
34/7-23A	0.03	6.5	0.52	2.4	0.27	0.68	0.08	0.08	0.65	0.64	0.97
34/7-26A	0.04	7.7	0.51	2.3	0.26	0.64	0.09	0.11	0.63	0.66	0.96
34/8-8R	0.03	8.5	0.54	2.0	0.13	0.55	0.09	0.17	0.78	0.60	0.95
34/10-1	0.04	7.4	0.53	2.3	0.25	0.69	0.08	0.12	0.64	0.60	0.95
34/10-3 DST2	0.04	7.93	0.53	2.66	0.26	0.66	0.10	0.12	0.65	0.58	0.95
34/10-3 DST3	0.04	7.59	0.53	2.00	0.25	0.66	0.08	0.12	0.65	0.59	0.96
34/10-7	0.02	7.43	0.53	1.53	0.18	0.61	0.06	0.10	0.76	0.60	0.96
34/10-8	0.04	6.97	0.52	2.37	0.25	0.67	0.09	0.11	0.65	0.60	0.96
34/10-9	0.04	6.15	0.54	1.86	0.24	0.38	0.08	0.11	0.66	0.60	0.96
34/10-14	0.04	6.77	0.53	2.20	0.24	0.37	0.09	0.12	0.66	0.59	0.96
34/10-A-1H	0.03	5.17	0.53	1.86	0.24	0.36	0.07	0.09	0.66	0.62	0.97
34/10-17	0.01	8.0	0.53	0.0	0.10	0.42	0.03	0.11	0.70	0.55	0.94
34/10-30	0.03	6.4	0.54	1.8	0.14	0.56	0.05	0.15	0.70	0.60	0.95
34/10-32R	0.01	5.5	0.61	1.6	0.13	0.44	0.03	0.08	0.62	0.62	0.95
34/10-34	0.03	9.6	0.54	2.1	0.20	0.79	0.08	0.12	0.64	0.59	0.96
34/10-35	-	-	-	-	-	-	-	-	-	0.63	-
6406/11-1S	0.39	6.33	0.60	1.04	0.15	0.63	0.55	0.78	0.59	0.59	0.94
6406/3-2	0.02	11.15	0.50	2.01	0.13	0.65	0.05	0.12	0.73	0.59	0.95
6407/7-4	0.02	9.59	0.55	1.85	0.20	0.71	0.08	0.09	0.74	0.60	0.95
6407/9-1	0.14	9.15	0.55	1.69	0.20	0.78	0.31	0.40	0.68	0.61	0.94
6506/11-2	0.05	10.43	0.50	2.02	0.20	0.70	0.12	0.17	0.82	0.59	0.94
6506/12-3	0.08	8.77	0.54	2.35	0.22	0.72	0.16	0.22	0.75	0.57	0.92
6507/3-1	0.15	5.46	0.62	1.45	0.15	0.56	0.26	0.50	0.67	0.62	0.96
6507/7-2 DST.2	0.21	7.96	0.52	2.31	0.19	0.42	0.36	0.53	0.75	0.57	0.96
6507/7-2 DST.3	0.23	9.00	0.50	2.43	0.16	0.42	0.41	0.61	0.73	0.60	0.96
6507/7-2 DST.4R	0.25	8.52	0.49	2.95	0.18	0.42	0.39	0.61	0.74	0.59	0.95
6507/7-3	0.01	9.84	0.51	1.51	0.20	0.65	0.04	0.06	0.67	0.61	0.96
6507/7-5 DST.1	0.22	7.50	0.49	2.71	0.22	0.44	0.37	0.49	0.75	0.56	0.95

Appendix 3b: Maturity and facies parameters

	25NH/ (25NH+H)	C ₃₅ HHI	C ₃₄ S/ (C ₃₄ S+C ₃₅ S)	GI	DNH/ (DNH+H)	DNH/ (DNH+Tm)	25NH/ (25NH+30NH)	25NH/ (25NH+DNH)	Ts(Ts+Tm)	22S/(S+R)	$\alpha\beta/(\alpha\beta+\beta\alpha)$
6507/7-5 DST.2	0.19	7.58	0.50	1.85	0.18	0.44	0.35	0.52	0.75	0.59	0.95
6507/7-6 DST.1	0.26	8.60	0.50	3.12	0.24	0.43	0.38	0.53	0.75	0.57	0.95
6507/7-6 DST.2	0.21	7.36	0.52	-	0.24	0.43	0.36	0.45	0.74	0.58	0.94
6507/7-8 DST.1	0.19	7.49	0.55	2.08	0.22	0.42	0.32	0.46	0.74	0.60	0.96
6507/7-8 DST.2	0.18	6.81	0.56	2.14	0.24	0.45	0.32	0.41	0.74	0.59	0.95
6507/8-4 DST.2	0.13	10.34	0.49	1.14	0.14	0.59	0.28	0.47	0.75	0.59	0.95
6507/8-4 DST.3	0.11	5.83	0.54	1.94	0.16	0.40	0.19	0.39	0.76	0.59	0.95
6507/8-4 DST.4	-	-	-	-	-	-	-	-	-	-	-
6507/11-3 DST.1	-	5.47	0.60	-	0.15	0.68	-	-	0.75	0.57	0.96
6507/11-3 DST.2	0.07	5.53	0.50	3.24	0.07	0.29	0.09	0.50	0.59	0.56	0.94
6507/11-3 DST.3	-	-	-	-	-	-	-	-	0.73	-	-
7120/1-2	0.23	6.87	0.60	1.89	0.09	0.50	0.38	0.74	0.77	0.58	0.95
7121/5-1	0.06	7.28	0.61	2.09	0.08	0.41	0.12	0.41	0.57	0.61	0.95
7124/3-1	0.01	8.57	0.58	1.61	0.07	0.37	0.02	0.10	0.55	0.60	0.96

Appendix 3c: Maturity and facies parameters

	DNH/ (DNH+25NH)	C ₂₉ Ts/30NH	DH/30NH	DH/(DH+30NM)	%C ₂₉ hopanes	%C ₂₈ hopanes	%C ₂₇ hopanes	DH/(DH+M)	reg. steranes/ hopanes	diasteranes(DS)/ (DS+steranes)
2/2-5	0.91	0.34	0.06	0.46	0.64	0.10	0.26	0.36	1.32	0.40
2/4-14	-	0.52	-	-	0.55	-	0.45	-	-	-
6/3-1	0.88	0.40	0.13	0.62	0.61	0.04	0.35	0.59	0.67	0.69
7/7-2	0.99	0.50	0.14	0.64	0.44	0.30	0.27	0.64	1.07	0.69
9/2-1	0.26	0.49	0.16	0.68	0.69	0.00	0.31	0.60	0.61	0.67
15/12-5	0.85	0.46	0.13	0.64	0.61	0.05	0.34	0.57	0.68	0.66
15/12-6	0.87	0.47	0.13	0.61	0.60	0.05	0.35	0.55	0.72	0.66
25/5-1	0.96	0.90	0.47	0.79	0.53	0.13	0.35	0.75	0.59	0.76
25/11-T-21A	0.49	0.61	0.23	0.66	0.45	0.19	0.36	0.75	1.01	0.69
NSO-1	0.69	0.33	0.14	0.59	0.42	0.24	0.34	0.57	0.63	0.73
30/9-10	0.69	0.41	0.16	0.61	0.46	0.27	0.28	0.57	0.56	0.73
30/9-1[OL]	0.70	0.40	0.16	0.61	0.44	0.24	0.32	0.60	0.65	0.72
30/9-1[TM]	0.70	0.11	0.10	0.57	0.44	0.23	0.32	0.61	0.52	0.73
31/2-G-3H	0.69	0.42	0.22	0.66	0.44	0.22	0.34	0.66	0.77	0.70
35/3-4	-	-	-	-	-	-	-	-	-	-
35/11-4	0.81	0.70	0.54	0.81	0.48	0.14	0.38	0.81	0.77	0.77
6201/11-1	0.29	0.73	0.46	0.76	0.48	0.07	0.45	0.79	0.79	0.77
33/9-12	0.91	0.54	0.14	0.59	0.49	0.23	0.28	0.62	1.26	0.60
33/9-14	0.85	0.63	0.25	0.74	0.51	0.19	0.31	0.69	0.68	0.72
34/4-6	0.94	0.51	0.25	0.73	0.48	0.30	0.22	0.70	0.83	0.66
34/7-4	0.95	0.32	0.15	0.69	0.45	0.31	0.24	0.62	0.95	0.59
34/7-6	0.94	0.39	0.14	0.65	0.45	0.29	0.26	0.59	1.06	0.60
34/7-8	0.93	0.54	0.11	0.75	0.46	0.27	0.26	0.54	1.12	0.55
34/7-10	0.95	0.29	0.07	0.53	0.52	0.30	0.18	0.48	0.88	0.51
34/7-13 DST.1.1	0.84	0.50	0.19	0.67	0.48	0.17	0.36	0.67	0.80	0.70
34/7-13 DST.1	0.86	0.74	0.24	0.69	0.47	0.17	0.36	0.69	0.93	0.71
34/7-14	0.89	0.50	0.15	0.57	0.46	0.24	0.30	0.56	1.27	0.58
34/7-16 DST.3	0.92	0.47	0.15	0.65	0.44	0.28	0.28	0.63	1.08	0.63
34/7-16 DST.2	0.92	0.27	0.11	0.58	0.45	0.23	0.32	0.57	1.11	0.61
34/7-18	0.92	0.33	0.12	0.60	0.46	0.25	0.29	0.63	1.18	0.59

Appendix 3c: Maturity and facies parameters

	DNH/ (DNH+25NH)	C ₂₉ Is/30NH	DH/30NH	DH/(DH+30NM)	%C ₂₉ hopanes	%C ₂₈ hopanes	%C ₂₇ hopanes	DI/(DH+M)	reg. steranes/ hopanes	diasteranes(DS)/ (DS+steranes)
34/7-21	0.89	0.51	0.16	0.59	0.46	0.22	0.32	0.62	1.51	0.59
34/7-22	0.91	0.45	0.15	0.64	0.46	0.22	0.32	0.62	1.29	0.59
34/7-23A	0.92	0.72	0.17	0.58	0.44	0.24	0.32	0.65	1.32	0.58
34/7-26A	0.89	0.46	0.16	0.55	0.45	0.22	0.33	0.63	1.42	0.58
34/8-8R	0.83	0.97	0.59	0.79	0.49	0.11	0.40	0.78	0.85	0.76
34/10-1	0.88	0.42	0.13	0.68	0.50	0.22	0.28	0.56	1.07	0.58
34/10-3 DST2	0.88	0.57	0.16	0.60	0.46	0.22	0.32	0.60	1.21	0.59
34/10-3 DST3	0.88	0.44	0.14	0.60	0.48	0.21	0.31	0.59	1.21	0.60
34/10-7	0.90	0.60	0.31	0.71	0.47	0.14	0.38	0.76	0.91	0.72
34/10-8	0.89	0.53	0.16	0.62	0.47	0.22	0.31	0.61	1.24	0.60
34/10-9	0.89	0.59	0.16	0.64	0.47	0.20	0.33	0.62	1.15	0.61
34/10-14	0.88	0.49	0.15	0.59	0.46	0.20	0.34	0.61	1.33	0.59
34/10-A-1H	0.91	0.44	0.15	0.61	0.44	0.23	0.32	0.62	1.19	0.60
34/10-17	0.89	0.58	0.43	0.71	0.52	0.09	0.39	0.73	0.57	0.77
34/10-30	0.85	0.37	0.21	0.77	0.56	0.12	0.32	0.68	0.99	0.66
34/10-32R	0.92	0.93	0.29	0.67	0.54	0.10	0.35	0.67	1.05	0.60
34/10-34	0.88	0.37	0.14	0.57	0.57	0.25	0.18	0.56	0.88	0.55
34/10-35	-	1.98	2.92	-	0.40	-	0.60	1.00	6.02	0.76
6406/11-1S	0.22	0.38	0.24	0.67	0.65	0.15	0.20	0.66	0.82	0.65
6406/3-2	0.88	1.16	0.48	0.83	0.63	0.12	0.25	0.77	0.67	0.78
6407/7-4	0.91	1.32	0.64	0.73	0.52	0.19	0.30	0.76	0.19	0.75
6407/9-1	0.60	0.51	0.33	0.70	0.56	0.23	0.21	0.67	0.81	0.80
6506/11-2	0.83	1.39	0.98	0.80	0.55	0.13	0.32	0.86	1.15	0.84
6506/12-3	0.78	0.96	0.66	0.73	0.57	0.17	0.26	0.76	0.87	0.84
6507/3-1	0.50	0.49	0.33	0.75	0.57	0.12	0.30	0.78	1.08	0.74
6507/7-2 DST.2	0.47	0.75	0.48	0.75	0.44	0.11	0.45	0.83	0.90	0.83
6507/7-2 DST.3	0.39	0.73	0.47	0.75	0.42	0.10	0.49	0.83	0.92	0.84
6507/7-2 DST.4R	0.39	0.76	0.48	0.77	0.43	0.10	0.47	0.83	0.99	0.83
6507/7-3	0.94	0.64	0.22	0.72	0.51	0.19	0.30	0.67	0.67	0.72
6507/7-5 DST.1	0.51	0.85	0.46	0.74	0.40	0.12	0.48	0.81	1.06	0.82

Appendix 3c: Maturity and facies parameters

	DNH/ (DNH+25NH)	C ₂₉ Is/30NH	DIH/30NH	DIH/(DIH+30NH)	%C ₂₉ hopanes	%C ₂₈ hopanes	%C ₂₇ hopanes	DIH/(DIH+M)	reg. steranes/ hopanes	diasteranes(DS)/ (DS+steranes)
6507/7-5 DST.2	0.48	0.91	0.44	0.74	0.43	0.10	0.46	0.79	0.91	0.83
6507/7-6 DST.1	0.47	0.73	0.38	0.73	0.39	0.11	0.49	0.81	1.09	0.83
6507/7-6 DST.2	0.55	0.77	0.49	0.75	0.38	0.13	0.49	0.80	1.04	0.81
6507/7-8 DST.1	0.54	0.78	0.43	0.77	0.42	0.12	0.46	0.85	1.19	0.82
6507/7-8 DST.2	0.59	0.96	0.48	0.79	0.42	0.14	0.44	0.81	1.14	0.81
6507/8-4 DST.2	0.53	0.65	0.37	0.75	0.52	0.13	0.35	0.75	0.58	0.78
6507/8-4 DST.3	0.61	0.60	0.28	0.73	0.47	0.10	0.42	0.75	0.76	0.80
6507/8-4 DST.4	-	0.59	0.32	0.71	0.56	-	0.44	-	0.59	0.94
6507/11-3 DST.1	-	0.88	0.53	0.81	0.48	0.08	0.44	0.87	0.73	0.83
6507/11-3 DST.2	0.50	0.33	0.08	0.38	0.58	0.04	0.38	0.50	0.05	0.81
6507/11-3 DST.3	-	0.88	0.51	-	0.42	-	0.58	-	1.14	0.90
7120/1-2	0.26	0.56	0.45	0.78	0.59	0.08	0.33	0.79	0.65	0.76
7121/5-1	0.59	0.88	0.21	0.62	0.70	0.07	0.23	0.64	0.54	0.66
7124/3-1	0.90	0.52	0.15	0.63	0.67	0.07	0.26	0.61	0.40	0.70

Appendix 3d: Maturity and facies parameters

	%C ₂₉ - ββ-steranes	%C ₂₈ - ββ-steranes	%C ₂₇ - ββ-steranes	ββ/(ββ+αα)	20S/(S+R)
2/2-5	0.44	0.30	0.26	0.70	0.49
2/4-14	-	-	-	-	-
6/3-1	0.40	0.30	0.29	0.75	0.42
7/7-2	0.37	0.32	0.32	0.76	0.48
9/2-1	0.40	0.30	0.30	0.74	0.46
15/12-5	0.41	0.32	0.28	0.75	0.43
15/12-6	0.41	0.29	0.29	0.76	0.42
25/5-1	0.46	0.25	0.29	0.77	0.46
25/11-T-21A	0.43	0.29	0.28	0.77	0.44
NSO-1	0.43	0.29	0.28	0.75	0.47
30/9-10	0.47	0.28	0.25	0.75	0.46
30/9-1[OL]	0.44	0.28	0.28	0.74	0.45
30/9-1[TM]	0.41	0.32	0.27	0.75	0.46
31/2-G-3H	0.42	0.31	0.27	0.72	0.46
35/3-4	-	-	-	-	-
35/11-4	0.43	0.28	0.28	0.76	0.44
6201/11-1	0.43	0.30	0.27	0.77	0.52
33/9-12	0.42	0.30	0.29	0.73	0.42
33/9-14	0.41	0.30	0.29	0.74	0.42
34/4-6	0.40	0.31	0.28	0.74	0.47
34/7-4	0.40	0.30	0.29	0.73	0.44
34/7-6	0.41	0.32	0.27	0.73	0.48
34/7-8	0.41	0.30	0.29	0.73	0.44
34/7-10	0.41	0.29	0.30	0.71	0.43
34/7-13 DST.1.1	0.40	0.30	0.30	0.73	0.41
34/7-13 DST.1	0.41	0.32	0.27	0.74	0.48
34/7-14	0.41	0.31	0.28	0.74	0.45
34/7-16 DST.3	0.40	0.30	0.29	0.74	0.44
34/7-16 DST.2	0.38	0.34	0.28	0.74	0.49
34/7-18	0.41	0.30	0.29	0.74	0.41

	%C ₂₉ - ββ-steranes	%C ₂₈ - ββ-steranes	%C ₂₇ - ββ-steranes	ββ/(ββ+αα)	20S/(S+R)
34/7-21	0.42	0.30	0.28	0.72	0.43
34/7-22	0.44	0.28	0.28	0.74	0.45
34/7-23A	0.41	0.30	0.29	0.72	0.42
34/7-26A	0.43	0.29	0.28	0.71	0.38
34/8-8R	0.41	0.32	0.27	0.76	0.46
34/10-1	0.41	0.31	0.28	0.73	0.44
34/10-3 DST.2	0.42	0.30	0.28	0.72	0.42
34/10-3 DST.3	0.44	0.26	0.30	0.74	0.43
34/10-7	0.39	0.28	0.33	0.77	0.44
34/10-8	0.40	0.32	0.28	0.73	0.45
34/10-9	0.44	0.27	0.29	0.73	0.39
34/10-14	0.41	0.32	0.27	0.75	0.46
34/10-A-1H	0.41	0.30	0.29	0.74	0.45
34/10-17	0.44	0.30	0.27	0.77	0.40
34/10-30	0.44	0.30	0.26	0.78	0.44
34/10-32R	0.46	0.27	0.27	0.75	0.47
34/10-34	0.47	0.27	0.26	0.74	0.43
34/10-35	0.39	0.34	0.27	0.78	0.52
6406/11-1S	0.56	0.24	0.20	0.76	0.44
6406/3-2	0.43	0.29	0.29	0.79	0.45
6407/7-4	0.43	0.29	0.28	0.78	0.50
6407/9-1	0.44	0.28	0.29	0.78	0.45
6506/11-2	0.42	0.31	0.27	0.67	0.60
6506/12-3	0.43	0.29	0.28	0.75	0.42
6507/3-1	0.48	0.27	0.26	0.78	0.48
6507/7-2 DST.2	0.39	0.32	0.29	0.81	0.53
6507/7-2 DST.3	0.37	0.34	0.29	0.80	0.54
6507/7-2 DST.4R	0.40	0.30	0.30	0.81	0.52
6507/7-3	0.40	0.31	0.29	0.73	0.40
6507/7-5 DST.1	0.38	0.33	0.28	0.79	0.50

Appendix 3d: Maturity and facies parameters

	%C ₂₉ - ββ-steranes	%C ₂₈ - ββ-steranes	%C ₂₇ - ββ-steranes	ββ/(ββ+αα)	20S/(S+R)
6507/7-5 DST.2	0.38	0.30	0.31	0.79	0.52
6507/7-6 DST.1	0.39	0.30	0.31	0.79	0.55
6507/7-6 DST.2	0.39	0.32	0.29	0.79	0.47
6507/7-8 DST.1	0.39	0.33	0.29	0.81	0.49
6507/7-8 DST.2	0.37	0.31	0.32	0.80	0.54
6507/8-4 DST.2	0.41	0.31	0.29	0.78	0.49
6507/8-4 DST.3	0.37	0.32	0.32	0.79	0.47
6507/8-4 DST.4	-	-	-	-	-
6507/11-3 DST.1	0.44	0.29	0.27	0.77	0.48
6507/11-3 DST.2	0.63	0.00	0.37	0.78	0.46
6507/11-3 DST.3	0.50	-	0.50	0.78	0.29
7120/1-2	0.43	0.31	0.26	0.76	0.48
7121/5-1	0.52	0.23	0.26	0.75	0.46
7124/3-1	0.45	0.25	0.30	0.74	0.43

pr/ph : pristane/phytane

αβ/(αβ+βα) : 17α(H), 21β(H)-hopane/(17α(H), 21β(H)-hopane + 17β(H), 21α(H)-hopane)

22S/(S+R) : C32 17α(H), 21β(H)-hopane 22(S)/((22(S) + 22(R))

Ts/(Ts+Tm) : 18α(H)-22,29,30-trisnorneohopane/
(18α(H)-22,29,30-trisnorneohopane + 17α(H)-22,29,30-trisnorhopane)

20S/(S+R) : (24-ethyl-5α(H),14α(H),17α(H),20(S)-cholestane +
24-ethyl-5α(H),14α(H),17α(H),20(R)-cholestane)

ββ/(ββ+αα) : (24-ethyl-5α(H),14β(H),17β(H),20(S+R)-cholestane +
24-ethyl-5α(H),14α(H),17α(H),20(S+R)-cholestane)

25NH : 17α(H), 21β(H)-25-norhopane (25-norhopane)

DNH : 17α(H), 21β(H)-28,30-bisnorhopane

C₃₅HHI : homohopane index
[C₃₅-homohopane(S+R)/C₃₁₋₃₅-homohopane(S+R)*100]

DH : 15α-methyl-17α(H)-27-norhopane (diahopane)

DH/30NH : 15α-methyl-17α(H)-27-norhopane/ 17α(H), 21β(H)-30-norhopane

DS : 14β-methyl-19-norcholestanes (diasteranes)

GI : gammacerane index [(gammacerane/hopane)*100]

H : 17α(H), 21β(H)-hopane (hopane)

M : 17β(H), 21α(H)-hopane (moretane)

30NH : 17α(H), 21β(H)-30-norhopane (norhopane)

30NM : 17β(H), 21α(H)-30-norhopane (normoretane; C₂₉βα)

C₂₉Ts : 18α(H)-norneohopane (norneohopane)

Appendix 4a: Concentration of carbazoles and benzocarbazoles

	C	1MC	3MC	2MC	4MC	1,8DMC	1E1C	1,3DMC	1,7DMC	1,6DMC	1,4DMC +4E1C	1,5DMC +3E1C	2,7DMC	1,2DMC	2,4DMC	2,5DMC	2,3DMC	3,4DMC	BC[a]	BC[b]	BC[c]
2/2-5	3.28	7.71	2.82	4.37	3.49	3.64	1.59	3.00	4.70	2.77	3.75	4.99	3.71	2.73	2.77	2.74	0.53	0.22	0.19	0.00	0.07
2/4-14	0.57	0.97	0.24	0.38	0.48	0.37	0.16	0.22	0.16	0.24	0.31	0.36	0.17	0.10	0.14	0.13	0.03	0.01	0.00	-	0.00
6/3-1	0.12	0.75	0.25	0.27	0.27	0.86	0.14	0.71	0.88	0.67	0.81	0.85	0.47	0.40	0.32	0.31	0.07	0.02	0.00	0.00	0.00
7/7-2	1.51	3.74	1.29	1.99	1.85	2.10	1.11	1.84	8.22	1.68	2.37	2.91	1.82	1.36	1.36	1.32	0.28	0.13	0.21	0.01	0.05
9/2-1	1.35	5.40	1.40	2.33	1.81	3.96	1.25	2.61	3.43	2.38	3.70	4.54	2.68	2.11	2.29	2.29	0.24	0.06	0.06	-	0.02
15/12-5	2.93	3.87	1.55	2.43	1.83	2.25	0.99	1.41	4.61	1.48	1.93	2.89	1.61	1.14	1.25	1.25	0.17	0.06	0.05	0.01	0.04
15/12-6	1.74	3.22	1.18	1.72	1.55	2.09	0.79	1.18	5.25	1.19	1.64	3.00	1.32	0.53	1.27	1.28	0.17	0.07	0.06	0.00	0.02
25/5-1	2.55	4.27	2.01	2.28	1.72	2.27	1.54	1.57	3.29	1.54	1.86	2.39	1.86	1.21	1.14	1.02	0.21	0.07	1.34	0.29	1.00
25/11-T-21A	0.04	0.08	0.04	0.04	0.07	0.10	0.03	0.04	0.19	0.07	0.07	0.12	0.06	0.02	0.04	0.04	0.00	0.00	0.03	-	0.02
NSO-1	7.35	18.15	8.05	8.96	7.42	19.89	4.70	13.56	7.11	13.16	14.13	21.50	12.04	5.18	8.06	8.34	1.66	0.62	4.82	0.87	3.29
30/9-10	1.43	5.01	1.35	1.95	1.66	2.88	0.90	2.56	1.04	2.61	2.42	3.31	1.93	1.25	1.12	1.01	0.17	0.00	0.20	-	0.19
30/9-1[OL]	0.61	1.66	0.51	0.56	0.48	1.14	0.30	0.60	2.53	0.82	0.62	1.19	0.49	0.42	0.27	0.34	0.05	0.01	0.56	0.07	0.50
30/9-1[TM]	0.22	0.69	0.19	0.20	0.19	0.67	0.22	0.22	1.36	0.44	0.34	0.56	0.25	0.15	0.08	0.14	0.01	0.00	0.10	0.00	0.06
31/2-G-3H	0.09	0.22	0.14	0.13	0.09	0.22	0.07	0.19	5.64	0.18	0.20	0.19	0.16	0.13	0.11	0.09	0.03	0.01	0.06	0.01	0.03
35/3-4	1.31	2.34	0.61	0.73	0.85	1.33	0.40	0.61	2.50	0.60	0.83	1.04	0.45	0.38	0.36	0.30	0.05	0.02	0.01	0.00	0.00
35/11-4	0.92	2.70	0.99	1.31	0.74	1.97	0.91	1.55	2.50	1.50	1.71	2.15	1.55	1.01	0.86	0.76	0.12	0.00	0.03	-	0.01
6201/11-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
33/9-12	0.31	1.07	0.52	0.51	0.40	1.87	0.30	1.41	5.61	1.38	1.37	1.21	1.09	0.46	0.59	0.54	0.15	0.05	0.02	-	0.01
33/9-14	1.68	3.62	1.48	1.60	1.38	2.74	1.22	2.00	5.41	1.89	2.27	2.80	1.83	1.26	1.08	1.01	0.26	0.10	0.20	0.00	0.07
34/4-6	0.72	2.35	0.53	1.12	1.52	2.67	0.61	1.08	6.13	1.03	1.97	2.89	1.41	0.45	1.45	1.23	0.20	0.07	0.05	-	0.05
34/7-4	0.45	1.77	0.30	0.67	0.88	2.10	0.40	0.86	5.32	0.88	1.34	2.10	0.98	0.66	0.86	0.78	0.12	0.05	0.09	0.00	0.04
34/7-6	0.36	1.37	0.28	0.65	0.81	1.59	0.33	0.63	2.59	0.64	1.14	1.76	0.92	0.62	0.84	0.76	0.10	0.03	0.51	0.00	0.41
34/7-8	0.25	0.67	0.07	0.23	0.43	0.91	0.07	0.17	2.91	0.20	0.43	0.86	0.25	0.10	0.29	0.33	0.02	0.01	0.01	0.00	0.01
34/7-10	0.39	0.62	0.08	0.17	0.52	0.82	0.10	0.15	1.23	0.17	0.37	0.84	0.26	0.08	0.27	0.27	0.02	0.02	0.06	0.00	0.05
34/7-13 DST.1.1	0.50	1.73	0.78	0.87	0.75	1.73	0.71	1.37	2.88	1.16	1.66	1.54	1.26	0.84	0.82	0.70	0.16	0.05	0.29	-	0.07
34/7-13 DST.1	5.58	14.89	7.76	8.30	7.25	14.85	6.50	12.17	2.53	9.90	13.03	15.94	10.45	7.38	7.59	6.73	1.73	0.55	5.06	0.51	3.15
34/7-14	0.12	0.58	0.30	0.29	0.17	1.12	0.17	0.77	1.80	0.75	0.75	0.64	0.58	0.53	0.37	0.34	0.09	0.02	0.04	0.00	0.01
34/7-16 DST.3	0.24	1.27	0.48	0.64	0.50	1.83	0.44	1.28	6.11	1.13	1.27	1.59	1.11	0.80	0.70	0.64	0.14	0.05	0.07	0.00	0.02
34/7-16 DST.2	0.18	0.86	0.34	0.43	0.34	1.38	0.34	0.92	5.33	0.81	0.96	1.16	0.82	0.32	0.51	0.52	0.11	0.05	0.13	0.01	0.06
34/7-18	0.36	0.66	0.35	0.31	0.28	1.50	0.27	1.15	4.30	1.02	1.03	0.90	0.87	0.67	0.47	0.39	0.11	0.04	0.15	0.04	0.12
34/7-21	0.23	0.78	0.35	0.36	0.30	1.44	0.26	1.06	3.60	0.96	1.01	0.90	0.79	0.61	0.42	0.34	0.11	0.04	0.01	0.00	0.01

Appendix 4a: Concentration of carbazoles and benzocarbazoles

	C	1MC	3MC	2MC	4MC	1,8DMC	1E1C	1,3DMC	1,7DMC	1,6DMC	1,4DMC +4E1C	1,5DMC +3E1C	2,7DMC	1,2DMC	2,4DMC	2,5DMC	2,3DMC	3,4DMC	BC[a]	BC[b]	BC[c]
34/7-22	0.00	0.72	0.08	0.23	0.22	1.46	0.26	1.08	6.27	1.04	0.91	0.94	0.81	0.03	0.35	0.44	0.10	0.01	0.07	0.01	0.02
34/7-23A	0.26	0.97	0.36	0.42	0.26	1.53	0.25	1.11	3.94	1.07	1.11	1.09	0.83	0.60	0.44	0.42	0.12	0.03	0.05	0.00	0.01
34/7-26A	0.07	0.54	0.11	0.20	0.14	0.59	0.18	0.54	1.57	0.45	0.59	0.36	0.42	0.02	0.15	0.19	0.04	0.02	0.00	-	0.00
34/8-8R	1.75	3.96	1.59	1.95	1.80	2.85	0.97	1.12	1.06	1.43	1.06	1.18	0.34	0.90	0.59	1.18	0.57	0.28	0.08	1.24	0.19
34/10-1	0.18	0.75	0.43	0.23	0.15	1.20	0.17	0.69	0.53	0.63	0.55	0.66	0.02	0.52	0.16	0.58	0.20	0.02	0.02	0.18	0.00
34/10-3 DST2	0.06	0.28	0.18	0.14	0.10	0.57	0.12	0.79	1.30	0.60	0.45	0.34	0.41	0.15	0.23	0.16	0.08	0.02	0.07	0.01	0.06
34/10-3 DST3	0.10	0.53	0.26	0.24	0.17	0.94	0.20	1.04	7.15	0.88	0.73	0.58	0.66	0.58	0.35	0.30	0.11	0.03	0.11	0.02	0.08
34/10-7	0.09	0.30	0.14	0.17	0.14	0.47	0.11	0.36	3.42	0.30	0.40	0.37	0.34	0.22	0.23	0.20	0.05	0.02	0.09	0.01	0.09
34/10-8	0.04	0.21	0.13	0.10	0.07	0.36	0.08	0.42	1.62	0.39	0.31	0.25	0.28	0.19	0.14	0.12	0.05	0.02	0.04	0.00	0.03
34/10-9	0.14	0.56	0.32	0.30	0.23	0.82	0.23	1.00	7.02	0.79	0.68	0.62	0.69	0.53	0.38	0.30	0.11	0.04	0.13	0.02	0.09
34/10-14	0.11	0.37	0.26	0.18	0.14	0.62	0.14	0.56	10.42	0.67	0.40	0.49	0.48	0.45	0.25	0.22	0.08	0.03	0.07	0.01	0.04
34/10-A-1H	0.20	0.67	0.45	0.36	0.25	1.00	0.25	1.08	14.51	1.06	0.68	0.80	0.83	0.74	0.39	0.39	0.13	0.05	0.07	0.01	0.03
34/10-17	0.37	0.60	0.56	0.38	0.25	0.38	0.16	0.55	1.55	0.51	0.44	0.36	0.46	0.35	0.22	0.18	0.08	0.02	0.01	0.00	0.01
34/10-30	0.02	0.43	0.04	0.07	0.12	0.53	0.06	0.31	0.24	0.27	0.38	0.53	0.15	0.08	0.10	0.10	0.00	0.00	0.00	-	0.00
34/10-32R	2.92	3.58	2.43	2.29	1.53	1.45	0.96	1.59	5.70	1.52	1.47	1.70	1.58	1.16	1.02	0.77	0.27	0.08	0.23	0.04	0.11
34/10-34	0.21	0.33	0.43	0.17	0.40	0.17	0.06	0.33	0.13	0.21	0.23	0.19	0.64	0.15	0.34	0.19	0.09	0.05	0.03	0.01	0.03
34/10-35	2.46	6.34	1.40	2.24	2.59	2.16	0.68	1.39	1.23	1.24	1.73	2.97	1.27	0.98	0.93	0.84	0.08	0.04	0.06	-	0.01
6406/11-1S	1.43	1.51	0.62	0.65	0.65	0.37	0.40	0.38	0.93	0.33	0.44	0.52	0.36	0.21	0.21	0.18	0.03	0.01	0.11	0.00	0.03
6406/3-2	5.91	11.85	3.06	5.53	5.85	6.27	2.55	4.77	9.59	4.69	6.05	7.10	4.26	3.35	3.17	2.92	0.69	0.39	4.77	0.21	2.25
6407/7-4	1.23	2.01	1.58	1.31	0.76	1.09	0.54	1.43	6.16	1.30	1.30	1.03	1.33	0.99	0.64	0.51	0.25	0.07	0.02	0.00	0.02
6407/9-1	0.05	0.22	0.09	0.10	0.08	0.47	0.10	0.44	0.52	0.34	0.33	0.27	0.32	0.20	0.19	0.13	0.02	0.01	0.01	-	0.00
6506/11-2	2.66	2.47	1.73	1.69	1.21	0.76	0.88	1.01	3.69	0.90	1.16	0.95	1.18	0.76	0.69	0.45	0.19	0.05	0.03	0.00	0.01
6506/12-3	1.08	1.50	1.00	0.91	0.64	0.61	0.48	0.80	0.87	0.75	0.80	0.80	0.78	0.48	0.41	0.33	0.10	0.04	0.09	0.00	0.02
6507/3-1	1.41	2.59	1.12	1.37	0.89	1.31	0.71	1.24	6.68	1.05	1.25	1.30	1.04	0.82	0.51	0.56	0.16	0.06	0.06	0.01	0.01
6507/7-2 DST.2	1.27	6.18	2.71	2.50	1.51	8.80	3.00	9.19	2.00	6.12	6.48	6.63	5.08	3.47	2.97	2.11	0.74	0.31	1.24	0.18	0.80
6507/7-2 DST.3	4.70	23.27	10.09	9.29	5.47	29.16	10.83	24.46	0.84	18.91	18.45	22.63	12.73	8.71	9.13	5.94	1.50	0.68	0.12	-	0.06
6507/7-2 DST.4R	9.15	49.71	19.23	20.22	14.18	45.49	15.96	36.10	2.11	29.55	31.41	36.35	22.61	16.76	15.14	11.85	2.25	1.06	0.06	-	0.05
6507/7-3	1.58	3.41	1.41	1.59	1.39	2.50	1.22	1.96	2.37	1.71	2.30	2.61	1.77	1.23	1.17	1.00	0.24	0.09	0.03	0.00	0.01
6507/7-5 DST.1	5.42	29.05	11.57	10.94	7.41	31.42	11.22	26.70	1.32	22.90	22.40	23.47	16.65	11.88	9.70	6.87	1.92	0.42	0.05	0.04	0.03
6507/7-5 DST.2	7.71	36.45	13.03	12.46	9.22	31.57	11.98	25.63	1.93	23.05	21.55	25.33	17.19	11.75	10.10	7.18	1.84	0.80	0.08	-	0.00
6507/7-6 DST.1	1.84	14.87	6.16	4.94	2.81	22.53	7.81	22.25	0.78	16.60	14.44	15.59	11.93	7.22	5.90	4.04	1.11	0.30	0.04	0.03	0.03

Appendix 4a: Concentration of carbazoles and benzocarbazoles

	C	1MC	3MC	2MC	4MC	1,8DMC	1E1C	1,3DMC	1,7DMC	1,6DMC	1,4DMC +4E1C	1,5DMC +3E1C	2,7DMC	1,2DMC	2,4DMC	2,5DMC	2,3DMC	3,4DMC	BC[a]	BC[b]	BC[c]
6507/7-6 DST.2	2.31	14.89	6.14	5.33	2.85	19.47	7.31	18.86	1.33	13.61	14.20	12.25	8.38	5.66	4.72	3.57	1.05	0.29	0.08	-	0.01
6507/7-8 DST.1	22.92	68.67	33.91	30.04	20.09	61.95	25.37	51.95	3.56	41.69	46.66	49.24	34.88	21.49	19.47	14.61	3.97	1.36	0.80	0.04	0.38
6507/7-8 DST.2	28.37	82.31	40.38	33.40	28.21	71.70	28.70	62.33	3.46	51.11	54.78	58.21	39.26	26.38	24.11	15.92	5.02	1.61	0.85	-	0.51
6507/8-4 DST.2	0.04	0.23	0.14	0.07	0.06	0.27	0.08	0.57	0.32	0.34	0.26	0.20	0.25	0.23	0.10	0.07	0.03	0.01	0.00	-	0.00
6507/8-4 DST.3	0.50	2.82	1.47	1.09	1.02	3.03	1.13	5.17	1.04	4.35	3.37	2.86	3.43	2.35	1.72	1.09	0.39	0.18	0.90	0.08	0.41
6507/8-4 DST.4	0.03	0.19	0.15	0.12	0.10	0.32	0.07	0.46	0.11	0.32	0.21	0.23	0.28	0.33	0.12	0.08	0.01	0.02	0.01	-	0.01
6507/11-3 DST.1	7.03	23.26	11.45	10.25	6.82	29.69	9.49	24.22	0.84	21.19	23.27	20.28	17.91	11.58	8.40	5.77	0.97	0.00	0.00	-	0.03
6507/11-3 DST.2	2.26	6.54	2.09	3.08	2.06	8.13	2.06	4.86	0.37	5.07	4.08	5.00	3.49	1.68	1.69	1.31	0.17	0.02	0.00	-	0.00
6507/11-3 DST.3	0.26	0.67	0.42	0.29	0.20	0.90	0.28	0.64	0.21	0.62	0.53	0.51	0.53	0.46	0.20	0.11	0.07	0.01	0.00	-	0.00
7120/1-2	0.07	0.29	0.09	0.13	0.12	0.21	0.06	0.17	1.26	0.18	0.16	0.23	0.14	0.13	0.10	0.10	0.01	0.01	0.02	0.00	0.01
7121/5-1	1.84	7.04	3.23	3.53	2.33	6.89	1.91	6.12	15.47	5.63	4.80	5.22	4.66	3.46	2.36	2.24	0.83	0.24	0.19	0.01	0.06
7124/3-1	0.23	0.58	0.41	0.25	0.14	0.83	0.28	0.76	1.93	0.78	0.41	0.34	0.51	0.17	0.18	0.15	0.08	0.01	0.00	-	0.00
Are 5647.15	63.53	28.77	9.24	21.80	18.65	2.07	1.26	1.80	0.46	1.77	2.82	4.24	3.19	1.44	3.37	2.80	0.43	0.13	143.82	19.80	83.89
Are 5647.60	218.68	64.77	25.29	52.61	47.81	2.38	1.80	3.45	0.27	2.93	3.69	8.86	5.69	1.66	5.77	6.18	0.43	0.32	447.88	61.97	346.93
Spekk 3744	10.59	26.38	5.18	9.14	8.40	8.37	4.27	6.18	4.96	7.28	8.38	12.16	5.70	1.87	3.49	3.63	0.70	0.25	12.37	0.40	9.74
Spekk 3744	5.22	14.99	2.80	5.13	3.98	6.03	2.96	4.17	6.97	4.68	5.48	7.73	3.44	1.19	1.78	1.68	0.41	0.11	8.57	0.22	6.52
Are 1406.40	0.19	0.13	0.06	0.09	0.10	0.08	0.04	0.04	0.01	0.01	0.03	0.10	0.06	0.00	0.07	0.02	0.00	0.01	0.21	0.14	0.22
Are 1406.50	0.12	0.08	0.07	0.06	0.13	0.04	0.02	0.03	0.02	0.03	0.03	0.11	0.10	0.04	0.09	0.07	0.02	0.00	0.33	0.17	0.34
Spekk 1623.30	1.14	2.27	0.52	0.67	1.25	0.61	0.83	0.74	0.93	0.44	1.21	1.06	0.81	0.03	0.46	0.39	0.11	0.11	2.44	0.11	2.69
Spekk 1627.50	0.56	0.92	0.20	0.30	0.42	0.17	0.20	0.25	0.20	0.17	0.30	0.34	0.29	0.04	0.16	0.11	0.01	0.05	0.49	0.02	0.33
Spekk 1675	0.38	0.99	0.13	0.12	0.51	0.29	0.29	0.22	0.06	0.15	0.47	0.37	0.17	0.02	0.18	0.12	0.02	0.04	0.52	-	1.23
Ghareb oil 310°C	3.97	5.88	2.67	3.57	6.07	1.47	1.54	1.39	1.80	1.61	2.02	5.24	2.66	1.06	2.49	1.93	0.70	1.03	0.39	0.13	0.35
Ghareb oil 330°C	5.44	9.79	1.93	1.98	2.87	0.67	0.54	2.07	2.55	2.08	4.05	8.96	13.86	3.82	5.33	7.26	3.06	3.82	1.42	0.58	1.45
Ghareb oil 345°C	5.24	14.37	10.09	7.57	14.01	4.66	2.98	5.31	5.74	4.44	7.83	12.01	14.68	5.52	10.08	11.01	4.67	4.19	2.06	0.98	2.28
Ghareb oil 355°C	18.34	24.77	19.79	17.54	32.70	9.53	7.28	9.70	11.65	10.54	12.38	21.16	42.72	5.76	10.77	25.12	7.29	8.76	3.32	2.04	3.54
Ghareb oil 360°C	22.02	29.75	27.58	19.62	41.97	8.29	7.38	11.08	12.97	11.51	13.43	26.85	58.34	11.39	17.67	30.55	9.35	5.81	4.62	2.80	4.98
Ghareb oil 365°C	25.38	35.82	24.42	23.42	43.12	10.21	9.38	14.18	16.97	14.68	19.06	30.84	31.07	19.81	17.59	23.51	8.79	7.72	5.52	3.26	5.19
Ghareb bit. 310°C	27.30	33.04	19.66	21.75	36.25	6.72	6.91	8.53	12.66	12.43	9.57	32.04	24.68	7.54	13.57	21.44	6.97	5.58	4.12	1.98	4.74
Ghareb bit. 330°C	16.89	21.19	12.29	13.64	24.15	4.29	4.60	6.73	7.49	6.14	9.18	18.59	15.52	3.95	9.36	10.86	4.19	4.30	2.42	0.91	2.67
Ghareb bit. 345°C	22.10	26.39	14.08	16.88	29.11	4.53	5.45	7.37	8.53	7.84	9.75	23.60	14.66	3.69	11.29	11.70	4.48	5.11	3.11	1.41	3.13
Ghareb bit. 355°C	115.91	143.45	79.84	91.04	155.63	32.25	29.52	40.99	53.44	45.78	67.69	121.66	97.57	28.11	53.51	65.34	25.97	23.29	14.90	8.06	14.60
Ghareb bit. 360°C	79.21	102.43	59.58	61.77	113.14	34.74	26.31	34.29	40.91	32.55	39.51	79.63	68.13	22.96	44.24	53.68	19.90	18.09	15.44	9.18	14.93
Ghareb bit. 365°C	116.83	176.50	103.38	102.81	186.56	56.39	42.67	48.26	64.77	57.23	70.21	121.06	121.63	41.31	58.99	60.79	23.77	20.95	16.60	9.42	15.67

Appendix 4b: Carbazole and benzocarbazole ratios

	1/(1+2) MC	1/(1+3) MC	1/(1+4) MC	2/(2+3) MC	2/(2+4) MC	3/(3+4) MC	1MC/ (1+C)	4MC/ (4+C)	(3+2)/ (3+2+C)	1,8/C	1,8/ (1,8+C)	1,8/ (1,8+2,5)	1,8/ (1,8+2,4)	1,8/(1,8+ 2+3)	1,8/ (3+2)	1,8DMC/ 4MC	1,8/ (1,8+1E6)	1,8/1,3 DMC	1,8/2,5 DMC	1,8/2,4 DMC	1,3/2,4 DMC
2/2-5	0.64	0.73	0.69	0.61	0.56	0.45	0.70	0.52	0.69	1.11	0.53	0.57	0.57	0.34	0.51	1.04	0.70	1.21	1.33	1.32	1.08
2/4-14	0.72	0.80	0.67	0.61	0.44	0.34	0.63	0.46	0.52	0.65	0.39	0.73	0.72	0.37	0.60	0.77	0.70	1.64	2.73	2.61	1.59
6/3-1	0.74	0.75	0.74	0.52	0.50	0.48	0.86	0.69	0.81	7.07	0.88	0.73	0.73	0.62	1.65	3.17	0.86	1.21	2.77	2.70	2.23
7/7-2	0.65	0.74	0.67	0.61	0.52	0.41	0.71	0.55	0.68	1.38	0.58	0.61	0.61	0.39	0.64	1.14	0.65	1.14	1.58	1.54	1.35
9/2-1	0.66	0.76	0.67	0.61	0.51	0.40	0.77	0.62	0.73	2.81	0.74	0.63	0.49	0.51	1.03	1.75	0.78	2.19	1.71	0.95	0.43
15/12-5	0.61	0.71	0.68	0.61	0.57	0.46	0.57	0.38	0.58	0.77	0.43	0.64	0.64	0.36	0.56	1.23	0.69	1.59	1.80	1.80	1.13
15/12-6	0.65	0.73	0.67	0.59	0.52	0.43	0.65	0.47	0.63	1.20	0.55	0.62	0.62	0.42	0.72	1.34	0.72	1.77	1.63	1.65	0.93
25/5-1	0.65	0.68	0.71	0.53	0.57	0.54	0.63	0.40	0.63	0.89	0.47	0.69	0.67	0.35	0.53	1.32	0.60	1.45	2.22	1.99	1.37
25/11-T-21A	0.68	0.69	0.56	0.52	0.37	0.36	0.67	0.62	0.65	2.54	0.72	0.73	0.71	0.58	1.35	1.56	0.81	2.56	2.76	2.46	0.96
NSO-1	0.67	0.69	0.71	0.53	0.55	0.52	0.71	0.50	0.70	2.71	0.73	0.70	0.71	0.54	1.17	2.68	0.81	1.47	2.39	2.47	1.68
30/9-10	0.72	0.79	0.75	0.59	0.54	0.45	0.78	0.54	0.70	2.01	0.67	0.74	0.72	0.47	0.88	1.74	0.76	1.13	2.86	2.58	2.29
30/9-1[OL]	0.75	0.76	0.77	0.52	0.54	0.51	0.73	0.44	0.64	1.87	0.65	0.77	0.81	0.51	1.06	2.35	0.79	1.89	3.36	4.21	2.23
30/9-1[TM]	0.78	0.78	0.79	0.51	0.52	0.51	0.76	0.46	0.64	3.05	0.75	0.83	0.89	0.63	1.69	3.55	0.75	3.09	4.73	8.25	2.67
31/2-G-3H	0.63	0.62	0.71	0.48	0.59	0.61	0.70	0.49	0.74	2.37	0.70	0.70	0.67	0.45	0.82	2.45	0.75	1.13	2.39	2.05	1.82
35/3-4	0.76	0.79	0.73	0.54	0.46	0.42	0.64	0.39	0.51	1.02	0.50	0.82	0.79	0.50	0.99	1.57	0.77	2.19	4.49	3.68	1.68
35/11-4	0.67	0.73	0.78	0.57	0.64	0.57	0.75	0.45	0.71	2.14	0.68	0.72	0.70	0.46	0.86	2.66	0.68	1.27	2.58	2.30	1.81
6201/11-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
33/9-12	0.68	0.67	0.73	0.49	0.56	0.57	0.78	0.57	0.77	6.08	0.86	0.77	0.76	0.64	1.81	4.68	0.86	1.32	3.44	3.19	2.41
33/9-14	0.69	0.71	0.72	0.52	0.54	0.52	0.68	0.45	0.65	1.63	0.62	0.73	0.72	0.47	0.89	1.99	0.69	1.37	2.71	2.53	1.85
34/4-6	0.68	0.82	0.61	0.68	0.42	0.26	0.76	0.68	0.69	3.69	0.79	0.69	0.65	0.62	1.62	1.76	0.81	2.47	2.18	1.84	0.74
34/7-4	0.73	0.85	0.67	0.69	0.43	0.26	0.80	0.66	0.68	4.64	0.82	0.73	0.71	0.68	2.16	2.38	0.84	2.44	2.70	2.45	1.00
34/7-6	0.68	0.83	0.63	0.70	0.45	0.26	0.79	0.69	0.72	4.40	0.81	0.68	0.65	0.63	1.69	1.95	0.83	2.51	2.09	1.88	0.75
34/7-8	0.75	0.91	0.61	0.77	0.35	0.14	0.73	0.63	0.54	3.62	0.78	0.74	0.76	0.76	3.09	2.13	0.93	5.40	2.79	3.10	0.57
34/7-10	0.79	0.89	0.54	0.69	0.25	0.13	0.62	0.57	0.39	2.13	0.68	0.75	0.75	0.77	3.35	1.59	0.89	5.37	3.05	3.06	0.57
34/7-13 DST.1.1	0.67	0.69	0.70	0.53	0.54	0.51	0.77	0.60	0.77	3.44	0.77	0.71	0.68	0.51	1.05	2.31	0.71	1.26	2.49	2.11	1.67
34/7-13 DST.1	0.64	0.66	0.67	0.52	0.53	0.52	0.73	0.56	0.74	2.66	0.73	0.69	0.66	0.48	0.92	2.05	0.70	1.22	2.21	1.96	1.60
34/7-14	0.67	0.66	0.77	0.49	0.62	0.63	0.83	0.60	0.83	9.54	0.91	0.77	0.75	0.66	1.91	6.41	0.87	1.45	3.29	3.01	2.08
34/7-16 DST.3	0.67	0.72	0.72	0.57	0.56	0.49	0.84	0.67	0.82	7.56	0.88	0.74	0.72	0.62	1.64	3.64	0.81	1.43	2.87	2.61	1.83
34/7-16 DST.2	0.67	0.72	0.72	0.56	0.55	0.49	0.83	0.66	0.81	7.82	0.89	0.73	0.73	0.65	1.82	4.03	0.80	1.50	2.64	2.69	1.79
34/7-18	0.69	0.65	0.70	0.46	0.52	0.55	0.65	0.44	0.65	4.20	0.81	0.79	0.76	0.70	2.28	5.28	0.85	1.30	3.84	3.21	2.47
34/7-21	0.68	0.69	0.72	0.51	0.55	0.54	0.77	0.56	0.75	6.17	0.86	0.81	0.77	0.67	2.03	4.80	0.85	1.36	4.28	3.42	2.52

Appendix 4b: Carbazole and benzocarbazole ratios

	1/(1+2) MC	1/(1+3) MC	1/(1+4) MC	2/(2+3) MC	2/(2+4) MC	3/(3+4) MC	1MC/ (1+C)	4MC/ (4+C)	(3+2)/ (3+2+C)	1,8/C	1,8/ (1,8+C)	1,8/ (1,8+2,5) (1,8+2,4)	1,8/(1,8+ 2+3)	1,8/ (3+2)	1,8DMC/ 4MC	1,8/ (1,8+1E6)	1,8/1,3 DMC	1,8/2,5 DMC	1,8/2,4 DMC	1,3/2,4 DMC
34/7-22	0.66	0.66	0.58	0.50	0.42	0.42	0.70	0.62	0.70	4.16	0.81	0.76	0.70	0.64	1.75	2.54	1.68	3.14	2.35	1.40
34/7-23A	0.70	0.73	0.79	0.54	0.62	0.58	0.79	0.50	0.75	5.81	0.85	0.78	0.78	0.66	1.95	5.82	1.38	3.60	3.45	2.50
34/7-26A	0.66	0.65	0.64	0.49	0.48	0.49	0.54	0.40	0.56	0.89	0.47	0.67	0.66	0.41	0.70	1.33	0.89	2.00	1.96	2.20
34/8-8R	0.67	0.71	0.69	0.55	0.52	0.47	0.69	0.51	0.67	1.62	0.62	0.83	0.71	0.45	0.80	1.58	2.55	5.04	2.42	0.95
34/10-1	0.76	0.64	0.83	0.35	0.60	0.74	0.81	0.46	0.79	6.73	0.87	0.86	0.68	0.64	1.80	7.89	1.75	5.90	2.08	1.19
34/10-3 DST2	0.66	0.61	0.74	0.44	0.59	0.65	0.83	0.64	0.85	10.02	0.91	0.78	0.72	0.64	1.75	5.74	0.72	3.49	2.52	3.49
34/10-3 DST3	0.69	0.67	0.76	0.48	0.59	0.61	0.84	0.63	0.83	9.48	0.90	0.76	0.73	0.65	1.89	5.66	0.82	3.13	2.69	3.00
34/10-7	0.63	0.68	0.67	0.55	0.55	0.49	0.76	0.60	0.77	5.05	0.83	0.71	0.67	0.60	1.52	3.32	1.31	2.42	2.05	1.56
34/10-8	0.67	0.63	0.74	0.45	0.58	0.63	0.84	0.65	0.85	8.92	0.90	0.74	0.72	0.61	1.58	4.81	0.86	2.92	2.59	3.01
34/10-9	0.65	0.63	0.71	0.48	0.57	0.59	0.80	0.62	0.82	5.92	0.86	0.73	0.68	0.57	1.32	3.62	0.81	2.73	2.14	2.63
34/10-14	0.67	0.58	0.72	0.41	0.56	0.65	0.78	0.57	0.81	5.84	0.85	0.74	0.71	0.58	1.39	4.41	1.12	2.82	2.47	2.21
34/10-A-1H	0.65	0.60	0.73	0.44	0.59	0.64	0.77	0.55	0.80	4.95	0.83	0.72	0.72	0.55	1.24	4.00	0.93	2.55	2.57	2.77
34/10-17	0.61	0.52	0.70	0.41	0.60	0.69	0.62	0.41	0.72	1.03	0.51	0.68	0.63	0.29	0.40	1.49	0.69	2.11	1.69	2.47
34/10-30	0.83	0.78	0.71	0.42	0.33	0.41	0.90	0.78	0.81	8.67	0.90	0.64	0.43	0.67	2.04	2.44	0.93	1.78	0.77	0.83
34/10-32R	0.61	0.60	0.70	0.48	0.60	0.61	0.55	0.34	0.62	0.50	0.33	0.65	0.59	0.24	0.31	0.95	0.91	1.89	1.43	1.56
34/10-34	0.66	0.43	0.45	0.28	0.30	0.52	0.62	0.66	0.75	0.81	0.45	0.47	0.33	0.21	0.27	0.42	0.51	0.90	0.49	0.96
34/10-35	0.74	0.82	0.71	0.61	0.46	0.35	0.72	0.51	0.60	0.88	0.47	0.72	0.70	0.37	0.59	0.83	1.55	2.56	2.33	1.50
6406/11-1S	0.70	0.71	0.70	0.51	0.50	0.49	0.51	0.31	0.47	0.26	0.21	0.67	0.64	0.23	0.29	0.57	0.97	2.01	1.80	1.84
6406/3-2	0.68	0.79	0.67	0.64	0.49	0.34	0.67	0.50	0.59	1.06	0.51	0.68	0.66	0.42	0.73	1.07	1.32	2.15	1.98	1.50
6407/7-4	0.61	0.56	0.73	0.45	0.63	0.67	0.62	0.38	0.70	0.89	0.47	0.68	0.63	0.27	0.38	1.43	0.77	2.16	1.72	2.24
6407/9-1	0.70	0.72	0.74	0.52	0.54	0.52	0.82	0.63	0.79	9.89	0.91	0.78	0.71	0.72	2.57	5.84	1.07	3.63	2.49	2.33
6506/11-2	0.59	0.59	0.67	0.49	0.58	0.59	0.48	0.31	0.56	0.28	0.22	0.63	0.52	0.18	0.22	0.63	0.75	1.69	1.09	1.46
6506/12-3	0.62	0.60	0.70	0.48	0.59	0.61	0.58	0.37	0.64	0.56	0.36	0.65	0.60	0.24	0.32	0.95	0.76	1.84	1.47	1.94
6507/3-1	0.65	0.70	0.74	0.55	0.61	0.56	0.65	0.39	0.64	0.93	0.48	0.70	0.72	0.34	0.53	1.48	1.06	2.36	2.58	2.43
6507/7-2 DST.2	0.71	0.70	0.80	0.48	0.62	0.64	0.83	0.54	0.80	6.93	0.87	0.81	0.75	0.63	1.69	5.83	0.96	4.18	2.96	3.09
6507/7-2 DST.3	0.71	0.70	0.81	0.48	0.63	0.65	0.83	0.54	0.80	6.21	0.86	0.83	0.76	0.60	1.50	5.33	1.19	4.91	3.19	2.68
6507/7-2 DST.4R	0.71	0.72	0.78	0.51	0.59	0.58	0.84	0.61	0.81	4.97	0.83	0.79	0.75	0.54	1.15	3.21	1.26	3.84	3.01	2.38
6507/7-3	0.68	0.71	0.71	0.53	0.53	0.50	0.68	0.47	0.65	1.58	0.61	0.71	0.68	0.45	0.83	1.80	1.27	2.51	2.13	1.67
6507/7-5 DST.1	0.73	0.72	0.80	0.49	0.60	0.61	0.84	0.58	0.81	5.79	0.85	0.82	0.76	0.58	1.40	4.24	1.18	4.57	3.24	2.75
6507/7-5 DST.2	0.75	0.74	0.80	0.49	0.57	0.59	0.83	0.54	0.77	4.10	0.80	0.81	0.76	0.55	1.24	3.42	1.23	4.40	3.12	2.54
6507/7-6 DST.1	0.75	0.71	0.84	0.45	0.64	0.69	0.89	0.60	0.86	12.27	0.92	0.85	0.79	0.67	2.03	8.02	1.01	5.57	3.82	3.77

Appendix 4b: Carbazole and benzocarbazole ratios

	1/(1+2) MC	1/(1+3) MC	1/(1+4) MC	2/(2+3) MC	2/(2+4) MC	3/(3+4) MC	1MC/ (1+C)	4MC/ (4+C)	(3+2)/ (3+2+C)	1,8/C	1,8/ (1,8+C)	1,8/ (1,8+2,5) (1,8+2,4)	1,8/(1,8+ 2+3)	1,8/ (3+2)	1,8DMC/ 4MC	1,8/ (1,8+1E6)	1,8/1,3 DMC	1,8/2,5 DMC	1,8/2,4 DMC	1,3/2,4 DMC
6507/7-6 DST.2	0.74	0.71	0.84	0.46	0.65	0.68	0.87	0.55	0.83	8.42	0.89	0.85	0.80	1.70	6.82	0.73	1.03	5.46	4.12	3.99
6507/7-8 DST.1	0.70	0.67	0.77	0.47	0.60	0.63	0.75	0.47	0.74	2.70	0.73	0.81	0.76	0.97	3.08	0.71	1.19	4.24	3.18	2.67
6507/7-8 DST.2	0.71	0.67	0.74	0.45	0.54	0.59	0.74	0.50	0.72	2.53	0.72	0.82	0.75	0.97	2.54	0.71	1.15	4.50	2.97	2.58
6507/8-4 DST.2	0.77	0.63	0.80	0.33	0.54	0.70	0.86	0.60	0.84	7.21	0.88	0.80	0.74	1.34	4.72	0.77	0.48	4.08	2.83	5.88
6507/8-4 DST.3	0.72	0.66	0.73	0.43	0.52	0.59	0.85	0.67	0.84	6.05	0.86	0.74	0.64	1.18	2.96	0.73	0.59	2.77	1.76	3.00
6507/8-4 DST.4	0.62	0.57	0.65	0.45	0.53	0.58	0.85	0.75	0.89	9.41	0.90	0.80	0.72	1.22	3.06	0.83	0.70	3.97	2.61	3.73
6507/11-3 DST.1	0.69	0.67	0.77	0.47	0.60	0.63	0.77	0.49	0.76	4.23	0.81	0.84	0.78	1.37	4.36	0.76	1.23	5.14	3.53	2.88
6507/11-3 DST.2	0.68	0.76	0.76	0.60	0.60	0.50	0.74	0.48	0.70	3.60	0.78	0.86	0.83	1.57	3.94	0.80	1.67	6.20	4.80	2.88
6507/11-3 DST.3	0.70	0.61	0.77	0.41	0.59	0.68	0.72	0.43	0.73	3.44	0.77	0.89	0.82	1.27	4.53	0.76	1.41	7.87	4.50	3.19
7120/1-2	0.69	0.76	0.71	0.59	0.52	0.43	0.81	0.64	0.76	3.14	0.76	0.68	0.69	0.97	1.77	0.78	1.25	2.11	2.20	1.76
7121/5-1	0.67	0.69	0.75	0.52	0.60	0.58	0.79	0.56	0.79	3.74	0.79	0.75	0.74	1.02	2.95	0.78	1.13	3.07	2.92	2.59
7124/3-1	0.70	0.59	0.81	0.38	0.64	0.75	0.71	0.37	0.74	3.55	0.78	0.85	0.83	1.26	5.98	0.75	1.10	5.61	4.73	4.32
Are 5647.15	0.57	0.76	0.61	0.70	0.54	0.33	0.31	0.23	0.33	0.03	0.03	0.43	0.38	0.07	0.11	0.62	1.15	0.74	0.61	0.53
Are 5647.60	0.55	0.72	0.58	0.68	0.52	0.35	0.23	0.18	0.26	0.01	0.01	0.28	0.29	0.03	0.05	0.57	0.69	0.39	0.41	0.60
Spekk 3744	0.74	0.84	0.76	0.64	0.52	0.38	0.71	0.44	0.57	0.79	0.44	0.70	0.71	0.37	1.00	0.66	1.35	2.31	2.40	1.77
Spekk 3744	0.75	0.84	0.79	0.65	0.56	0.41	0.74	0.43	0.60	1.15	0.54	0.78	0.77	0.76	1.51	0.67	1.45	3.59	3.39	2.34
Are 1406.40	0.61	0.71	0.57	0.60	0.46	0.36	0.42	0.35	0.43	0.44	0.31	0.79	0.53	0.37	0.81	0.65	2.04	3.70	1.11	0.54
Are 1406.50	0.57	0.52	0.39	0.44	0.32	0.37	0.41	0.52	0.53	0.37	0.27	0.38	0.32	0.32	0.35	0.73	1.63	0.60	0.46	0.28
Spekk 1623.30	0.77	0.81	0.64	0.56	0.35	0.29	0.67	0.52	0.51	0.53	0.35	0.61	0.57	0.34	0.48	0.42	0.82	1.55	1.33	1.63
Spekk 1627.50	0.76	0.82	0.69	0.60	0.42	0.32	0.62	0.42	0.47	0.30	0.23	0.60	0.52	0.25	0.34	0.40	0.68	1.47	1.08	1.59
Spekk 1675	0.89	0.88	0.66	0.48	0.19	0.20	0.72	0.57	0.39	0.77	0.43	0.71	0.61	1.19	0.58	0.50	1.36	2.45	1.59	1.17
Ghareb oil 310°C	0.62	0.69	0.49	0.57	0.37	0.31	0.60	0.60	0.61	0.37	0.27	0.43	0.37	0.24	0.24	0.49	1.06	0.76	0.59	0.56
Ghareb oil 330°C	0.83	0.84	0.77	0.51	0.41	0.40	0.64	0.35	0.42	0.12	0.11	0.08	0.11	0.17	0.23	0.55	0.32	0.09	0.13	0.39
Ghareb oil 345°C	0.65	0.59	0.51	0.43	0.35	0.42	0.73	0.73	0.77	0.89	0.47	0.30	0.32	0.26	0.33	0.61	0.88	0.42	0.46	0.53
Ghareb oil 355°C	0.59	0.56	0.43	0.47	0.35	0.38	0.57	0.64	0.67	0.52	0.34	0.27	0.47	0.20	0.29	0.57	0.98	0.38	0.88	0.90
Ghareb oil 360°C	0.60	0.52	0.41	0.42	0.32	0.40	0.57	0.66	0.68	0.38	0.27	0.21	0.32	0.15	0.18	0.20	0.53	0.27	0.47	0.63
Ghareb oil 365°C	0.60	0.59	0.45	0.49	0.35	0.36	0.59	0.63	0.65	0.40	0.29	0.30	0.37	0.18	0.21	0.24	0.52	0.43	0.58	0.81
Ghareb bit. 310°C	0.60	0.63	0.48	0.53	0.38	0.35	0.55	0.57	0.60	0.25	0.20	0.24	0.33	0.14	0.16	0.19	0.79	0.31	0.50	0.63
Ghareb bit. 330°C	0.61	0.63	0.47	0.53	0.36	0.34	0.56	0.59	0.61	0.25	0.20	0.28	0.31	0.14	0.17	0.18	0.64	0.40	0.46	0.72
Ghareb bit. 345°C	0.61	0.65	0.48	0.55	0.37	0.33	0.54	0.57	0.58	0.21	0.17	0.28	0.29	0.13	0.15	0.16	0.61	0.39	0.40	0.65
Ghareb bit. 355°C	0.61	0.64	0.48	0.53	0.37	0.34	0.55	0.57	0.60	0.28	0.22	0.33	0.38	0.16	0.19	0.21	0.79	0.49	0.60	0.77
Ghareb bit. 360°C	0.62	0.63	0.48	0.51	0.35	0.34	0.56	0.59	0.61	0.44	0.30	0.39	0.44	0.22	0.29	0.31	1.01	0.65	0.79	0.78
Ghareb bit. 365°C	0.63	0.63	0.49	0.50	0.36	0.36	0.60	0.61	0.64	0.48	0.33	0.48	0.49	0.21	0.27	0.30	1.17	0.93	0.96	0.82

Appendix 4c: Carbazole and benzocarbazole ratios

	(3+2)/ sumMC	1/ sumMC	BCa/c	BCa/ (a+e)	BC[b]/ sumBC	Sum MC	Sum C ₂ C	C/ sumMC	C/ sumC ₂ C	sumMC/ sumC ₂ C
2/2-5	0.39	0.42	2.74	0.73	0.01	18.38	37.14	0.18	0.09	0.50
2/4-14	0.30	0.47	-	-	-	2.07	2.39	0.28	0.24	0.86
6/3-1	0.34	0.49	0.66	0.40	0.26	1.55	6.52	0.08	0.02	0.24
7/7-2	0.37	0.42	4.11	0.80	0.03	8.87	26.50	0.17	0.06	0.33
9/2-1	0.36	0.43	1.78	0.64	0.07	4.74	14.72	0.13	0.04	0.32
15/12-5	0.41	0.40	1.29	0.56	0.07	9.68	21.03	0.30	0.14	0.46
15/12-6	0.38	0.42	3.10	0.76	0.04	7.68	19.76	0.23	0.09	0.39
25/5-1	0.42	0.42	1.35	0.57	0.11	10.29	19.98	0.25	0.13	0.52
25/11-T-21A	0.34	0.37	-	-	-	0.23	0.78	0.18	0.05	0.29
NSO-1	0.40	0.43	1.47	0.59	0.10	42.58	129.95	0.17	0.06	0.33
30/9-10	0.33	0.50	1.06	0.51	-	9.96	21.20	0.14	0.07	0.47
30/9-1[OL]	0.33	0.52	1.13	0.53	0.07	3.21	8.79	0.19	0.07	0.37
30/9-1[TM]	0.31	0.54	1.87	0.65	0.01	1.27	4.45	0.17	0.05	0.29
31/2-G-3H	0.46	0.38	-	-	-	0.57	7.22	0.16	0.01	0.08
35/3-4	0.30	0.52	5.11	0.84	0.05	4.54	8.86	0.29	0.15	0.51
35/11-4	0.40	0.47	2.33	0.70	-	5.73	16.59	0.16	0.06	0.35
620/11-1	-	-	-	-	-	-	-	-	-	-
33/9-12	0.41	0.43	2.22	0.69	-	2.50	16.02	0.12	0.02	0.16
33/9-14	0.38	0.45	3.03	0.75	0.00	8.08	23.85	0.21	0.07	0.34
34/4-6	0.30	0.43	1.11	0.53	-	5.52	21.20	0.13	0.03	0.26
34/7-4	0.27	0.49	2.06	0.67	0.00	3.62	16.45	0.12	0.03	0.22
34/7-6	0.30	0.44	1.23	0.55	0.00	3.12	11.93	0.12	0.03	0.26
34/7-8	0.21	0.48	1.15	0.53	0.04	1.39	6.54	0.18	0.04	0.21
34/7-10	0.18	0.45	1.20	0.55	0.00	1.38	4.61	0.28	0.08	0.30
34/7-13 DST.1.1	0.40	0.42	4.20	0.81	-	4.13	14.87	0.12	0.03	0.28
34/7-13 DST.1	0.42	0.39	1.60	0.62	0.06	38.20	109.35	0.15	0.05	0.35
34/7-14	0.44	0.43	2.85	0.74	0.05	1.34	7.92	0.09	0.01	0.17
34/7-16 DST.3	0.39	0.44	2.97	0.75	0.03	2.89	17.08	0.08	0.01	0.17
34/7-16 DST.2	0.39	0.44	2.25	0.69	0.05	1.97	13.23	0.09	0.01	0.15
34/7-18	0.41	0.41	1.31	0.57	0.13	1.61	12.71	0.22	0.03	0.13
34/7-21	0.40	0.44	1.46	0.59	0.18	1.79	11.53	0.13	0.02	0.16

	(3+2)/ sumMC	1/ sumMC	BCa/c	BCa/ (a+e)	BC[b]/ sumBC	Sum MC	Sum C ₂ C	C/ sumMC	C/ sumC ₂ C	sumMC/ sumC ₂ C
34/7-22	0.38	0.36	1.74	0.64	0.26	2.96	12.75	0.16	0.04	0.23
34/7-23A	0.39	0.48	3.83	0.79	0.07	2.02	12.55	0.13	0.02	0.16
34/7-26A	0.41	0.38	0.00	0.00	-	1.32	3.52	0.32	0.12	0.37
34/8-8R	0.38	0.43	1.97	0.66	0.09	9.30	13.26	0.19	0.13	0.70
34/10-1	0.42	0.48	1.29	0.56	-	1.57	5.91	0.11	0.03	0.27
34/10-3 DST.2	0.46	0.40	1.22	0.55	0.08	0.70	5.21	0.08	0.01	0.13
34/10-3 DST.3	0.42	0.45	1.44	0.59	0.08	1.19	13.55	0.08	0.01	0.09
34/10-7	0.42	0.39	1.01	0.50	0.07	0.75	6.49	0.13	0.01	0.12
34/10-8	0.44	0.41	1.37	0.58	0.04	0.51	4.23	0.08	0.01	0.12
34/10-9	0.44	0.40	1.48	0.60	0.07	1.40	13.21	0.10	0.01	0.11
34/10-14	0.47	0.39	1.72	0.63	0.07	0.96	14.80	0.11	0.01	0.06
34/10-A-1H	0.47	0.39	2.66	0.73	0.10	1.73	21.92	0.12	0.01	0.08
34/10-17	0.52	0.33	1.72	0.63	0.12	1.79	5.26	0.20	0.07	0.34
34/10-30	0.26	0.53	1.84	0.65	-	1.26	6.88	0.06	0.01	0.18
34/10-32R	0.48	0.36	2.16	0.68	0.11	9.82	19.26	0.30	0.15	0.51
34/10-34	0.45	0.25	0.87	0.47	0.08	1.33	2.78	0.15	0.07	0.48
34/10-35	0.29	0.50	5.53	0.85	-	12.57	15.53	0.20	0.16	0.81
6406/11-1S	0.37	0.44	3.31	0.77	0.03	3.44	4.40	0.42	0.33	0.78
6406/3-2	0.33	0.45	2.12	0.68	0.03	26.29	55.82	0.22	0.11	0.47
6407/7-4	0.51	0.36	1.15	0.53	0.04	5.67	16.64	0.22	0.07	0.34
6407/9-1	0.38	0.46	14.47	0.94	-	0.49	3.35	0.10	0.01	0.15
6506/11-2	0.48	0.35	2.89	0.74	0.12	7.09	12.67	0.37	0.21	0.56
6506/12-3	0.47	0.37	3.65	0.78	0.03	4.04	7.24	0.27	0.15	0.56
6507/3-1	0.42	0.43	5.42	0.84	0.13	5.97	16.69	0.24	0.08	0.36
6507/7-2 DST.2	0.40	0.48	1.56	0.61	0.08	12.89	56.89	0.10	0.02	0.23
6507/7-2 DST.3	0.40	0.48	-	-	-	48.12	163.98	0.10	0.03	0.29
6507/7-2 DST.4R	0.38	0.48	1.06	0.52	-	103.34	266.64	0.09	0.03	0.39
6507/7-3	0.38	0.44	3.33	0.77	0.04	7.80	20.18	0.20	0.08	0.39
6507/7-5 DST.1	0.38	0.49	-	-	-	58.96	186.87	0.09	0.03	0.32
6507/7-5 DST.2	0.36	0.51	-	-	-	71.16	189.90	0.11	0.04	0.37
6507/7-6 DST.1	0.39	0.52	-	-	-	28.78	130.53	0.06	0.01	0.22

Appendix 4c: Carbazole and benzocarbazole ratios

	(3+2)/ sumMC	1/ sumMC	BCa/c (a+c)	BCIb/ sumBC	sumMC	sumC ₂ C	C/ sumMC	C/ sumC ₂ C	sumMC/ sumC ₂ C
6507/7-6 DST.2	0.39	0.51	-	-	29.21	110.70	0.08	0.02	0.26
6507/7-8 DST.1	0.42	0.45	2.08	0.68	152.72	376.18	0.15	0.06	0.41
6507/7-8 DST.2	0.40	0.45	1.67	0.63	184.30	442.59	0.15	0.06	0.42
6507/8-4 DST.2	0.41	0.47	-	-	0.50	2.72	0.08	0.01	0.18
6507/8-4 DST.3	0.40	0.44	2.17	0.68	6.41	30.10	0.08	0.02	0.21
6507/8-4 DST.4	0.47	0.34	-	-	0.56	2.56	0.06	0.01	0.22
6507/11-3 DST.1	0.42	0.45	-	-	51.77	173.59	0.14	0.04	0.30
6507/11-3 DST.2	0.38	0.47	-	-	13.78	37.92	0.16	0.06	0.36
6507/11-3 DST.3	0.45	0.42	-	-	1.58	5.07	0.17	0.05	0.31
7120/1-2	0.35	0.46	3.57	0.78	0.63	2.76	0.11	0.02	0.23
7121/5-1	0.42	0.44	3.23	0.76	16.14	59.84	0.11	0.03	0.27
7124/3-1	0.48	0.42	-	-	1.38	6.45	0.17	0.04	0.21
Åre 5647.15	0.40	0.37	1.71	0.63	78.46	25.79	0.81	2.46	3.04
Åre 5647.60	0.41	0.34	1.29	0.56	190.49	43.43	1.15	5.04	4.39
Spekk 3744	0.29	0.54	1.27	0.56	0.02	67.24	0.22	0.16	0.73
Spekk 3744	0.29	0.56	1.31	0.57	0.01	26.91	0.19	0.11	0.58
Åre 1406.40	0.38	0.36	-	-	0.38	0.49	0.50	0.38	0.76
Åre 1406.50	0.40	0.24	0.95	0.49	0.20	0.34	0.35	0.20	0.56
Spekk 1623.30	0.25	0.48	0.91	0.48	0.02	4.72	0.24	0.15	0.61
Spekk 1627.50	0.27	0.50	1.47	0.60	0.03	1.83	0.31	0.25	0.81
Spekk 1675	0.14	0.57	0.42	0.30	-	1.74	0.22	0.16	0.72
Ghareb oil 310°C	0.34	0.32	-	-	18.18	24.95	0.22	0.16	0.73
Ghareb oil 330°C	0.24	0.59	0.98	0.49	0.17	16.57	0.33	0.09	0.29
Ghareb oil 345°C	0.38	0.31	0.90	0.47	0.18	46.04	0.11	0.06	0.49
Ghareb oil 355°C	0.39	0.26	0.94	0.48	0.23	94.81	0.19	0.10	0.52
Ghareb oil 360°C	0.40	0.25	0.93	0.48	0.23	118.92	0.19	0.10	0.53
Ghareb oil 365°C	0.38	0.28	1.06	0.52	0.23	126.78	0.20	0.11	0.57
Ghareb bit. 310°C	0.37	0.30	0.87	0.47	0.18	110.69	0.25	0.16	0.66
Ghareb bit. 330°C	0.36	0.30	0.91	0.48	0.15	71.26	0.24	0.16	0.68
Ghareb bit. 345°C	0.36	0.31	0.99	0.50	0.18	86.45	0.26	0.19	0.73
Ghareb bit. 355°C	0.36	0.31	1.02	0.51	0.21	469.96	0.25	0.17	0.69
Ghareb bit. 360°C	0.36	0.30	1.03	0.51	0.23	336.92	0.24	0.15	0.65
Ghareb bit. 365°C	0.36	0.31	1.06	0.51	0.23	569.25	0.21	0.15	0.72

C : carbazole

MC : methylcarbazole; number indicates position of methyl group (x)

DMC : dimethylcarbazole; number indicates position of methyl groups (x,y)

EtC : ethylcarbazole; number indicates position of ethyl group (x)

BC : benzocarbazole

C₂C : C₂-carbazoles

Appendix 5a: Concentration of fluorenones and benzofluorenones

	F	1MF	2MF	3MF	4MF	1EtF	1,8DMF	C ₂ F1	C ₂ F2	C ₂ F3	C ₂ F4	C ₂ F5	C ₂ F6	C ₂ F7	C ₂ F8	C ₂ F9	C ₂ F10	BF[a]	BF[b]	BF[c]
2/2-5	0.25	0.09	0.08	0.08	0.07	0.02	0.10	0.03	0.05	0.16	0.09	0.17	0.08	0.00	0.01	0.04	0.10	0.30	0.09	0.10
2/4-14	23.24	62.85	23.29	25.89	12.08	4.17	39.52	31.22	32.40	34.08	3.27	32.11	14.08	11.25	6.25	19.05	3.35	4.25	3.06	1.57
6/3-1	0.29	0.55	0.18	0.17	0.20	0.12	0.28	0.24	0.29	0.24	0.14	0.89	0.35	0.09	0.09	0.23	0.05	0.36	0.15	0.10
7/7-2	2.00	1.90	0.84	1.04	1.55	0.38	0.30	0.42	0.55	0.86	0.22	1.82	0.85	0.28	0.41	1.14	0.33	1.24	0.69	0.59
9/2-1	0.52	0.42	0.29	0.28	0.34	0.07	0.35	0.19	0.16	0.14	0.06	0.60	0.29	0.07	0.11	0.26	0.17	0.74	0.32	0.15
15/12-5	0.23	0.34	0.11	0.13	0.16	0.11	0.35	0.19	0.18	0.48	0.12	0.67	0.26	0.04	0.03	0.13	0.11	0.38	0.13	0.14
15/12-6	0.19	0.32	0.12	0.12	0.14	0.10	0.31	0.23	0.18	0.44	0.10	0.72	0.29	0.05	0.13	0.16	0.13	0.36	0.15	0.09
25/5-1	0.42	0.25	0.19	0.20	0.20	0.04	0.12	0.10	0.11	0.12	0.11	0.34	0.29	0.04	0.07	0.18	0.12	1.06	0.43	0.18
25/11-T-21A	0.06	0.09	0.04	0.02	0.02	0.01	0.04	0.02	0.02	0.05	0.02	0.08	0.03	0.01	0.01	0.01	0.01	-	-	-
NSO-1	3.51	4.56	2.93	3.22	2.62	1.59	2.11	2.48	3.29	3.13	1.33	6.11	5.72	1.38	1.58	3.86	1.62	10.52	3.26	2.32
30/9-10	4.63	6.36	3.30	4.02	3.69	1.14	1.59	2.12	2.73	3.82	0.40	6.50	3.66	1.47	1.58	4.36	0.97	3.52	2.49	1.09
30/9-1[OL]	45.25	100.69	33.51	32.03	20.47	16.79	26.71	27.84	27.61	31.64	6.39	41.84	23.67	10.42	7.77	19.80	5.88	18.80	4.73	3.91
30/9-1[TM]	54.14	119.42	38.87	41.77	25.42	22.33	36.47	33.78	36.27	44.51	7.85	55.06	30.44	13.10	9.55	27.12	8.26	23.54	5.67	4.96
31/2-G-3H	0.02	0.03	0.01	0.01	0.01	0.01	0.05	0.02	0.01	0.06	0.02	0.06	0.02	0.00	0.01	0.01	0.01	-	-	-
35/3-4	14.64	15.63	7.30	7.97	5.85	1.61	3.56	3.62	4.90	4.80	1.20	7.75	3.89	1.79	1.75	3.96	0.90	1.89	0.81	0.36
35/11-4	3.93	4.22	2.27	2.40	1.96	0.51	1.23	1.27	1.65	1.68	0.68	3.26	2.83	0.59	0.72	1.67	0.44	2.39	1.20	0.42
6201/11-1	0.11	1.30	0.08	0.10	0.09	0.10	0.64	0.38	0.57	0.64	0.07	1.59	0.33	0.04	0.04	0.13	0.03	0.26	0.06	0.03
33/9-12	0.25	0.27	0.28	0.19	0.18	0.09	0.26	0.14	0.12	0.35	0.10	0.52	0.19	0.06	0.12	0.20	0.14	0.13	0.06	0.06
33/9-14	3.48	3.13	2.13	2.52	2.72	0.62	0.82	0.99	1.31	1.59	0.53	2.97	1.90	0.71	0.83	2.22	0.56	2.84	2.62	1.29
34/4-6	0.26	0.39	0.19	0.19	0.19	0.05	0.39	0.27	0.18	0.64	0.17	0.92	0.29	0.06	0.10	0.22	0.20	0.34	0.16	0.11
34/7-4	0.56	0.87	0.39	0.42	0.41	0.15	0.36	0.34	0.34	0.63	0.26	1.08	0.48	0.14	0.25	0.43	0.19	0.84	0.09	0.12
34/7-6	0.25	0.48	0.18	0.21	0.20	0.08	0.19	0.20	0.22	0.37	0.08	0.68	0.23	0.07	0.11	0.26	0.09	0.55	0.16	0.03
34/7-8	0.33	0.39	0.22	0.21	0.20	0.06	0.10	0.14	0.15	0.17	0.37	0.09	0.56	0.44	0.08	0.07	0.00	0.23	0.12	0.14
34/7-10	1.39	7.19	1.10	1.41	1.48	1.43	1.97	1.96	2.59	3.13	0.43	6.71	1.85	0.54	0.78	1.94	0.34	2.54	0.52	0.51
34/7-13 DST.1.1	0.93	0.80	0.55	0.61	0.64	0.14	0.35	0.31	0.38	0.61	0.27	1.00	0.62	0.14	0.23	0.58	0.17	1.27	0.60	0.37
34/7-13 DST.1	1.76	0.82	0.94	0.94	1.01	0.28	0.53	0.48	0.37	0.70	0.28	1.19	0.85	0.36	0.37	1.07	0.83	-	-	-
34/7-14	0.28	0.33	0.20	0.21	0.21	0.03	0.25	0.18	0.15	0.37	0.11	0.56	0.31	0.05	0.08	0.23	0.05	0.38	0.14	0.19
34/7-16 DST.3	0.12	0.11	0.07	0.08	0.07	0.05	0.23	0.10	0.07	0.26	0.09	0.36	0.15	0.01	0.02	0.07	0.07	0.33	0.07	0.05
34/7-16 DST.2	0.08	0.07	0.05	0.07	0.06	0.02	0.06	0.03	0.05	0.04	0.02	0.11	0.07	0.03	0.03	0.08	0.11	-	-	-
34/7-18	0.11	0.09	0.09	0.07	0.07	0.03	0.09	0.05	0.03	0.04	0.04	0.12	0.07	0.02	0.04	0.08	0.08	-	-	-
34/7-21	0.46	0.66	0.33	0.39	0.38	0.10	0.51	0.29	0.33	0.63	0.16	1.00	0.43	0.10	0.13	0.36	0.16	0.46	0.24	0.20

Appendix 5a: Concentration of fluorenones and benzofluorenones

	F	1MF	2MF	3MF	4MF	1EtF	1,8DMF	C ₂ F1	C ₂ F2	C ₂ F3	C ₂ F4	C ₂ F5	C ₂ F6	C ₂ F7	C ₂ F8	C ₂ F9	C ₂ F10	BF[a]	BF[b]	BF[c]
34/7-22	0.13	0.15	0.10	0.11	0.10	0.06	0.12	0.06	0.07	0.07	0.03	0.22	0.11	0.03	0.04	0.11	0.10	-	-	-
34/7-23A	0.12	0.12	0.09	0.11	0.09	0.08	0.09	0.06	0.06	0.07	0.03	0.21	0.14	0.02	0.05	0.10	0.09	-	-	-
34/7-26A	0.06	0.06	0.06	0.05	0.04	0.03	0.08	0.04	0.03	0.03	0.04	0.12	0.08	0.00	0.02	0.04	0.06	-	-	-
34/8-8R	1.46	1.79	0.91	0.98	0.84	0.26	0.85	0.75	0.79	0.77	0.49	2.08	1.04	0.34	0.45	0.86	0.24	1.64	1.12	0.36
34/10-1	0.47	0.68	0.34	0.39	0.41	0.11	0.35	0.30	0.32	0.30	0.12	0.86	0.32	0.14	0.18	0.47	0.13	0.61	0.47	0.22
34/10-3 DST2	2.27	3.32	1.67	1.99	2.05	0.63	0.66	1.06	1.21	1.61	0.30	2.85	1.08	0.70	0.83	2.58	0.42	1.91	1.54	0.66
34/10-3 DST3	0.70	0.66	0.45	0.55	0.55	0.18	0.26	0.23	0.27	0.36	0.10	0.68	0.31	0.19	0.24	0.71	0.17	0.60	0.42	0.21
34/10-7	0.33	0.50	0.22	0.27	0.25	0.12	0.14	0.18	0.22	0.23	0.05	0.50	0.23	0.12	0.13	0.34	0.09	0.37	0.17	0.09
34/10-8	0.81	0.78	0.41	0.54	0.56	0.14	0.16	0.23	0.28	0.37	0.07	0.69	0.34	0.18	0.23	0.67	0.12	0.52	0.38	0.21
34/10-9	0.75	1.03	0.55	0.69	0.72	0.23	0.21	0.36	0.41	0.53	0.12	1.01	0.56	0.25	0.33	0.91	0.20	0.78	0.47	0.26
34/10-14	0.35	0.44	0.20	0.30	0.33	0.13	0.17	0.17	0.29	0.24	0.14	0.67	0.25	0.12	0.01	0.43	0.11	0.53	0.17	0.13
34/10-A-1H	0.15	0.15	0.10	0.16	0.11	0.07	0.11	0.07	0.10	0.10	0.06	0.27	0.11	0.03	0.04	0.15	0.09	0.08	0.01	0.03
34/10-17	2.84	3.78	2.27	2.55	1.75	0.61	1.53	1.56	2.09	2.11	0.69	3.33	2.23	0.87	0.87	1.95	0.44	1.66	1.46	0.60
34/10-30	2.66	11.38	2.84	3.04	2.17	1.18	3.91	3.60	4.93	5.17	0.99	8.34	3.30	1.33	1.44	3.11	0.55	2.10	0.90	0.59
34/10-32R	0.14	0.30	0.10	0.11	0.08	0.09	0.28	0.17	0.16	0.35	0.10	0.53	0.21	0.03	0.04	0.10	0.07	0.53	0.19	0.13
34/10-34	0.74	0.40	0.25	0.27	0.23	0.08	0.10	0.11	0.15	0.19	0.04	0.39	0.23	0.11	0.08	0.25	0.04	0.24	0.11	0.08
34/10-35	0.28	0.41	0.23	0.19	0.14	0.05	0.17	0.43	0.29	1.32	0.40	2.38	0.32	0.04	0.05	0.13	0.10	0.00	0.38	0.18
6406/11-IS	2.38	1.40	0.73	0.71	0.78	0.27	0.38	0.31	0.56	0.55	0.22	1.02	0.60	0.23	0.28	0.62	0.16	1.08	1.09	0.40
6406/3-2	3.13	2.58	1.47	1.54	1.76	0.39	0.58	0.63	0.70	0.90	0.35	2.06	1.22	0.35	0.53	1.36	0.39	2.15	1.93	0.60
6407/7-4	1.43	2.10	0.99	1.14	0.91	0.42	0.91	0.80	1.16	1.10	0.40	2.30	1.52	0.40	0.51	1.09	0.27	0.68	0.70	0.24
6407/9-1	1.24	1.25	0.96	1.19	1.04	0.18	0.62	0.56	0.75	0.73	0.45	1.88	1.13	0.39	0.51	1.20	0.27	1.05	0.91	0.41
6506/11-2	0.87	0.72	0.52	0.65	0.49	0.12	0.36	0.29	0.43	0.35	0.23	0.84	1.43	0.18	0.23	0.44	0.14	0.41	0.74	0.17
6506/12-3	0.39	0.37	0.31	0.31	0.24	0.05	0.39	0.24	0.23	0.48	0.11	0.71	0.66	0.09	0.14	0.25	0.10	0.52	0.50	0.15
6507/3-1	2.31	2.34	1.21	1.29	1.02	0.28	1.02	0.88	1.17	1.28	0.52	2.02	1.05	0.38	0.43	0.86	0.23	0.62	0.37	0.14
6507/7-2 DST.2	4.42	1.38	1.16	1.54	1.08	0.44	0.87	0.49	0.59	0.66	0.73	2.03	0.87	0.39	0.45	1.06	0.72	1.24	0.65	0.31
6507/7-2 DST.3	8.10	3.84	3.01	5.13	3.24	0.44	3.41	1.65	1.49	5.64	2.47	8.36	3.63	0.97	0.74	3.37	1.82	-	-	-
6507/7-2 DST.4R	7.68	2.47	1.91	2.23	1.45	0.54	3.10	1.48	1.34	4.75	1.35	6.58	2.85	0.29	0.40	1.44	1.58	-	-	-
6507/7-3	0.50	0.49	0.36	0.30	0.25	0.07	0.42	0.20	0.22	0.46	0.13	0.61	0.30	0.10	0.07	0.24	0.13	0.57	0.33	0.23
6507/7-5 DST.1	24.97	13.75	9.65	12.22	9.69	1.46	5.99	4.46	4.89	9.55	2.97	15.64	5.66	2.97	3.89	9.82	2.87	-	-	-
6507/7-5 DST.2	20.63	11.11	7.71	9.78	7.92	1.61	7.84	4.73	5.04	10.48	4.33	14.80	5.99	2.57	3.96	8.22	2.36	-	-	-
6507/7-6 DST.1	46.69	26.45	23.95	29.93	26.06	4.30	22.76	12.97	15.58	27.02	10.94	39.36	18.34	7.32	10.50	27.43	6.11	-	-	-

Appendix 5a: Concentration of fluorenones and benzofluorenones

	F	1MF	2MF	3MF	4MF	1EtF	1,8DMF	C ₂ F1	C ₂ F2	C ₂ F3	C ₂ F4	C ₂ F5	C ₂ F6	C ₂ F7	C ₂ F8	C ₂ F9	C ₂ F10	BF[a]	BF[b]	BF[c]
6507/7-6 DST.2	36.70	20.42	17.74	21.79	19.17	3.16	11.09	7.45	9.06	10.19	6.80	26.33	9.25	6.33	7.58	20.72	4.41	-	-	-
6507/7-8 DST.1	44.02	11.89	9.44	10.87	8.84	3.17	15.17	7.81	6.41	20.17	5.60	26.87	9.47	3.28	3.66	10.05	5.03	-	-	-
6507/7-8 DST.2	14.51	5.52	4.05	5.05	4.15	3.22	9.78	4.19	3.18	10.71	3.47	11.99	6.65	1.52	1.77	4.68	3.87	-	-	-
6507/8-4 DST2	0.26	0.28	0.27	0.25	0.23	0.20	0.67	0.28	0.18	0.90	0.29	0.29	0.37	0.06	0.10	0.26	0.01	0.53	0.31	0.18
6507/8-4 DST.3	12.11	3.56	4.05	4.43	4.57	1.53	3.47	1.39	1.87	2.92	1.04	5.01	1.72	1.24	1.88	5.06	1.15	5.56	4.95	1.40
6507/8-4 DST.4	3.96	2.48	1.48	1.68	1.14	0.59	1.27	0.76	0.99	0.99	0.56	3.79	1.56	0.39	0.64	0.94	0.28	0.77	0.21	0.06
6507/11-3 DST.1	58.25	53.85	40.37	48.84	28.45	10.24	25.38	23.43	34.20	26.42	9.32	52.38	25.52	15.88	12.42	34.61	7.58	-	-	-
6507/11-3 DST.2	65.07	36.86	31.54	32.59	17.68	5.14	16.15	10.90	14.10	15.88	6.45	23.42	14.82	7.77	6.79	14.51	3.74	-	-	-
6507/11-3 DST.3	4.91	2.79	2.37	2.60	1.36	0.40	0.59	0.73	1.03	0.87	0.39	1.43	1.27	0.66	0.53	1.18	0.36	0.38	0.19	0.06
7120/1-2	0.19	2.43	0.15	0.17	0.18	0.26	1.37	0.73	1.13	1.14	0.10	2.78	0.72	0.08	0.13	0.22	0.06	0.54	0.18	0.11
7121/5-1	1.57	2.20	1.12	1.15	1.04	0.42	0.89	0.92	1.03	0.97	0.58	2.62	0.96	0.45	0.60	1.16	0.49	1.52	0.94	0.38
7124/3-1	6.73	8.34	4.59	5.26	4.99	2.20	3.89	3.00	3.18	4.83	1.88	7.71	3.24	1.69	2.10	5.33	1.02	4.10	3.57	1.41
Are 5647.15	68.81	42.38	22.67	23.73	7.49	1.64	7.59	5.61	9.78	10.26	0.88	6.61	3.93	4.01	1.81	3.67	0.87	134.96	42.35	12.26
Are 5647.60	358.40	134.86	79.13	105.84	20.33	1.38	18.36	14.20	26.79	26.92	2.10	11.61	8.62	11.69	3.62	14.05	2.97	365.75	143.61	40.15
Spekk 3744	391.46	297.43	127.44	127.66	102.57	49.57	36.67	39.94	42.38	57.01	24.14	101.29	41.78	21.07	17.76	50.74	16.25	77.58	24.66	24.36
Spekk 3744	232.24	186.65	92.51	90.97	68.04	33.94	24.22	30.97	34.79	46.75	21.34	86.10	33.32	17.72	15.42	41.69	13.71	68.45	21.37	23.87
Are 1406.40	1.83	1.76	0.67	0.64	0.67	0.22	0.30	0.16	0.19	0.22	0.16	0.46	0.40	0.10	0.08	0.11	0.08	0.37	0.39	0.53
Are 1406.50	1.15	0.42	0.29	0.26	0.31	0.12	0.16	0.09	0.09	0.16	0.09	0.33	0.60	0.06	0.09	0.15	0.07	0.65	1.16	0.65
Spekk 1623.30	57.30	80.05	27.79	31.03	20.62	13.00	11.99	13.85	16.41	17.81	5.66	25.22	12.45	6.12	3.88	11.28	3.29	4.54	1.97	2.38
Spekk 1627.50	9.96	7.92	2.72	3.21	2.06	1.04	1.40	1.42	1.79	1.99	0.53	2.68	1.14	0.63	0.42	1.16	0.34	0.63	0.25	0.28
Spekk 1675	33.74	52.02	19.49	21.49	14.95	8.42	9.73	11.03	13.02	14.03	4.06	20.27	10.66	4.50	3.31	8.50	2.34	3.13	1.53	2.87
Chareb oil 310°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb oil 330°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb oil 345°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb oil 355°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb oil 360°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb oil 365°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chareb bit. 310°C	4.20	1.61	2.46	3.13	6.38	0.28	0.05	0.53	0.84	2.68	0.68	4.07	4.41	1.73	1.77	8.96	1.01	0.48	0.77	0.73
Chareb bit. 330°C	1.32	0.47	0.89	1.15	2.47	0.17	0.03	0.25	0.37	0.90	0.35	1.80	1.73	0.87	0.93	3.84	0.51	0.23	0.31	0.31
Chareb bit. 345°C	2.30	0.75	1.59	1.72	3.34	0.20	0.04	0.35	0.41	1.25	0.29	2.13	2.77	0.88	1.27	4.70	0.62	0.08	0.45	0.43
Chareb bit. 355°C	45.01	16.73	25.72	33.96	48.22	0.86	0.78	5.50	11.51	28.56	7.39	44.50	31.11	15.38	14.18	78.11	11.07	5.53	5.29	7.59
Chareb bit. 360°C	24.52	25.01	11.93	15.85	29.01	5.78	9.74	6.57	5.06	13.68	3.07	25.52	12.05	6.28	5.92	29.52	3.72	5.32	2.95	4.07
Chareb bit. 365°C	11.47	10.20	4.69	5.42	12.15	2.39	4.34	2.81	1.74	5.20	0.94	11.63	12.95	4.15	2.87	9.40	2.29	1.48	0.60	1.01

Appendix 5b: Fluorenone and benzofluorenone ratios

	sumMF	sum C ₂ F	sum BF	BFa/ sumBF	BFb/ sumBF	BFc/ sumBF	BFa(a+c)	BFa(a+b)	BFb(b+c)	F/sumMF	F/sumC ₂ F	F/sumBF	sumMF/ sumC ₂ F	sumMF/ sumBF	sumC ₂ F/ sumBF	1EtF/(1EtF +1,8DNF)	1MF/ (1MF+F)
2/2-5	0.32	0.85	0.49	0.60	0.19	0.21	0.74	0.76	0.48	0.77	0.30	0.50	0.38	0.65	1.71	0.18	0.26
2/4-14	124.10	230.75	8.88	0.48	0.34	0.18	0.73	0.58	0.66	0.19	0.10	2.62	0.54	13.98	25.98	0.10	0.73
6/3-1	1.10	3.01	0.60	0.59	0.25	0.16	0.79	0.71	0.61	0.26	0.09	0.47	0.37	1.83	4.99	0.30	0.66
7/7-2	5.33	7.55	2.51	0.49	0.27	0.24	0.68	0.64	0.54	0.38	0.27	0.80	0.71	2.12	3.00	0.56	0.49
9/2-1	1.33	2.47	1.20	0.61	0.26	0.13	0.83	0.70	0.68	0.40	0.21	0.44	0.54	1.10	2.05	0.17	0.44
15/12-5	0.73	2.67	0.65	0.58	0.19	0.22	0.73	0.75	0.47	0.32	0.09	0.36	0.27	1.12	4.09	0.25	0.60
15/12-6	0.70	2.83	0.60	0.60	0.25	0.15	0.81	0.70	0.64	0.27	0.07	0.32	0.25	1.17	4.75	0.24	0.63
25/5-1	0.85	1.64	1.68	0.63	0.26	0.11	0.85	0.71	0.70	0.49	0.25	0.25	0.52	0.51	0.98	0.24	0.37
25/11-T-21A	0.17	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.21	-	0.56	-	-	0.24	0.59
NSO-1	13.33	34.19	16.10	0.65	0.20	0.14	0.82	0.76	0.58	0.26	0.10	0.22	0.39	0.83	2.12	0.43	0.57
30/9-10	17.37	30.36	7.10	0.50	0.35	0.15	0.76	0.59	0.70	0.27	0.15	0.65	0.57	2.45	4.27	0.42	0.58
30/9-1[OL]	186.70	246.38	27.45	0.69	0.17	0.14	0.83	0.80	0.55	0.24	0.18	1.65	0.76	6.80	8.98	0.39	0.69
30/9-1[TM]	225.48	324.74	34.17	0.69	0.17	0.15	0.83	0.81	0.53	0.24	0.17	1.58	0.69	6.60	9.50	0.38	0.69
31/2-G-3H	0.06	0.29	-	-	-	-	-	-	-	0.36	0.08	-	0.21	-	-	0.24	0.54
35/3-4	36.76	39.75	3.05	0.62	0.26	0.12	0.84	0.70	0.69	0.40	0.37	4.79	0.92	12.03	13.01	0.31	0.52
35/11-4	10.85	16.53	4.01	0.59	0.30	0.11	0.85	0.66	0.74	0.36	0.24	0.98	0.66	2.70	4.12	0.29	0.52
6201/11-1	1.56	4.56	0.35	0.74	0.18	0.08	0.90	0.81	0.68	0.07	0.02	0.31	0.34	4.43	12.96	0.13	0.92
33/9-12	0.91	2.28	0.25	0.53	0.23	0.24	0.69	0.70	0.49	0.27	0.11	1.00	0.40	3.70	9.27	0.25	0.52
33/9-14	10.51	15.05	6.76	0.42	0.39	0.19	0.69	0.52	0.67	0.33	0.23	0.52	0.70	1.55	2.23	0.43	0.47
34/4-6	0.97	3.48	0.61	0.56	0.26	0.18	0.76	0.68	0.60	0.27	0.07	0.43	0.28	1.58	5.70	0.11	0.60
34/7-4	2.09	4.64	1.05	0.81	0.08	0.11	0.88	0.91	0.42	0.27	0.12	0.54	0.45	2.00	4.44	0.29	0.61
34/7-6	1.07	2.57	0.73	0.75	0.21	0.04	0.95	0.78	0.84	0.23	0.10	0.34	0.42	1.46	3.51	0.29	0.66
34/7-8	1.02	2.23	0.49	0.47	0.25	0.28	0.63	0.65	0.48	0.32	0.15	0.67	0.45	2.08	4.57	0.39	0.54
34/7-10	11.18	23.67	3.57	0.71	0.15	0.14	0.83	0.83	0.50	0.12	0.06	0.39	0.47	3.13	6.62	0.42	0.84
34/7-13 DST.1.1	2.60	4.81	2.24	0.56	0.27	0.17	0.77	0.68	0.62	0.36	0.19	0.41	0.54	1.16	2.15	0.29	0.46
34/7-13 DST.1	3.71	7.31	-	-	-	-	-	-	-	0.48	0.24	-	0.51	-	-	0.34	0.32
34/7-14	0.94	2.36	0.72	0.53	0.20	0.27	0.66	0.73	0.42	0.30	0.12	0.40	0.40	1.32	3.30	0.10	0.54
34/7-16 DST.3	0.33	1.49	0.45	0.74	0.15	0.12	0.86	0.83	0.56	0.36	0.08	0.26	0.22	0.74	3.29	0.19	0.48
34/7-16 DST.2	0.25	0.64	-	-	-	-	-	-	-	0.32	0.13	-	0.39	-	-	0.21	0.46
34/7-18	0.32	0.70	-	-	-	-	-	-	-	0.34	0.16	-	0.46	-	-	0.28	0.46
34/7-21	1.75	4.19	0.89	0.51	0.27	0.22	0.70	0.66	0.55	0.26	0.11	0.52	0.42	1.97	4.70	0.16	0.59

Appendix 5b: Fluorenone and benzofluorenone ratios

	sumMF	sum C ₃ F	sum BF	BFa/ sumBF	BFb/ sumBF	BFc/ sumBF	BFa(a+c)	BFa(a+b)	BFb(b+c)	F/sumMF	F/sumC ₃ F	F/sumBF	sumMF/ sumC ₃ F	sumMF/ sumBF	sumC ₃ F/ sumBF	1EtF/(1EtF +1,8DNF)	1MF/ (1MF+F)
34/7-22	0.45	1.03	-	-	-	-	-	-	-	0.28	0.12	-	0.44	-	-	0.35	0.54
34/7-23A	0.42	1.00	-	-	-	-	-	-	-	0.29	0.12	-	0.42	-	-	0.48	0.49
34/7-26A	0.20	0.56	-	-	-	-	-	-	-	0.29	0.10	-	0.35	-	-	0.26	0.49
34/8-8R	4.52	8.92	3.12	0.52	0.36	0.12	0.82	0.59	0.76	0.32	0.16	0.47	0.51	1.45	2.86	0.23	0.55
34/10-1	1.81	3.61	1.31	0.47	0.36	0.17	0.73	0.56	0.68	0.26	0.13	0.36	0.50	1.39	2.76	0.24	0.59
34/10-3 DST2	9.03	13.94	4.12	0.46	0.37	0.16	0.74	0.55	0.70	0.25	0.16	0.55	0.65	2.19	3.38	0.49	0.59
34/10-3 DST3	2.21	3.69	1.22	0.49	0.34	0.17	0.74	0.59	0.67	0.32	0.19	0.57	0.60	1.81	3.02	0.41	0.49
34/10-7	1.23	2.33	0.63	0.58	0.27	0.15	0.80	0.68	0.64	0.27	0.14	0.52	0.53	1.95	3.68	0.45	0.60
34/10-8	2.28	3.49	1.11	0.47	0.34	0.19	0.72	0.58	0.65	0.35	0.23	0.73	0.65	2.06	3.14	0.46	0.49
34/10-9	2.99	5.11	1.52	0.51	0.31	0.17	0.75	0.62	0.64	0.25	0.15	0.49	0.58	1.97	3.37	0.52	0.58
34/10-14	1.27	2.76	0.82	0.64	0.20	0.15	0.81	0.76	0.57	0.27	0.13	0.42	0.46	1.55	3.36	0.43	0.56
34/10-A-1H	0.53	1.20	0.11	0.70	0.05	0.25	0.74	0.93	0.16	0.28	0.12	1.38	0.44	4.97	11.19	0.38	0.51
34/10-17	10.35	18.27	3.72	0.45	0.39	0.16	0.74	0.53	0.71	0.27	0.16	0.76	0.57	2.78	4.91	0.29	0.57
34/10-30	19.44	37.85	3.59	0.58	0.25	0.16	0.78	0.70	0.61	0.14	0.07	0.74	0.51	5.42	10.55	0.23	0.81
34/10-32R	0.58	2.13	0.85	0.63	0.22	0.15	0.80	0.74	0.59	0.24	0.07	0.17	0.27	0.69	2.50	0.25	0.68
34/10-34	1.15	1.77	0.42	0.56	0.25	0.19	0.75	0.69	0.57	0.64	0.42	1.75	0.65	2.72	4.19	0.45	0.35
34/10-35	0.97	5.68	0.56	0.00	0.68	0.32	0.00	0.00	0.68	0.29	0.05	0.50	0.17	1.74	10.19	0.24	0.60
6406/11-1S	3.62	5.17	2.57	0.42	0.42	0.16	0.73	0.50	0.73	0.66	0.46	0.93	0.70	1.41	2.02	0.42	0.37
6406/3-2	7.35	9.48	4.67	0.46	0.41	0.13	0.78	0.53	0.76	0.43	0.33	0.67	0.78	1.57	2.03	0.40	0.45
6407/7-4	5.15	10.89	1.62	0.42	0.43	0.15	0.74	0.49	0.74	0.28	0.13	0.88	0.47	3.18	6.74	0.32	0.60
6407/9-1	4.44	8.66	2.38	0.44	0.38	0.17	0.72	0.54	0.69	0.28	0.14	0.52	0.51	1.87	3.64	0.23	0.50
6506/11-2	2.38	5.04	1.31	0.31	0.56	0.13	0.71	0.36	0.82	0.36	0.17	0.66	0.47	1.82	3.85	0.25	0.45
6506/12-3	1.22	3.45	1.16	0.44	0.43	0.13	0.78	0.51	0.77	0.32	0.11	0.34	0.35	1.05	2.96	0.11	0.48
6507/3-1	5.85	10.11	1.13	0.55	0.33	0.12	0.82	0.62	0.73	0.40	0.23	2.04	0.58	5.17	8.93	0.22	0.50
6507/7-2 DST.2	5.17	9.31	2.21	0.56	0.29	0.14	0.80	0.66	0.67	0.86	0.48	2.00	0.55	2.34	4.22	0.33	0.24
6507/7-2 DST.3	15.22	33.98	-	-	-	-	-	-	-	0.53	0.24	-	0.45	-	-	0.11	0.32
6507/7-2 DST.4R	8.06	25.70	-	-	-	-	-	-	-	0.95	0.30	-	0.31	-	-	0.15	0.24
6507/7-3	1.41	2.95	1.13	0.51	0.29	0.20	0.72	0.63	0.59	0.36	0.17	0.45	0.48	1.25	2.61	0.15	0.49
6507/7-5 DST.1	45.31	70.18	-	-	-	-	-	-	-	0.55	0.36	-	0.65	-	-	0.20	0.36
6507/7-5 DST.2	36.52	71.93	-	-	-	-	-	-	-	0.56	0.29	-	0.51	-	-	0.17	0.35
6507/7-6 DST.1	106.40	202.63	-	-	-	-	-	-	-	0.44	0.23	-	0.53	-	-	0.16	0.36

Appendix 5b: Fluorenone and benzofluorenone ratios

	sumMF	sum C ₂ F	sum BF	BFa/ sumBF	BFb/ sumBF	BFc/ sumBF	BFa(a+c)	BFa(a+b)	BFb(b+c)	F/sumMF	F/sumC ₂ F	F/sumBF	sumMF/ sumC ₂ F	sumMF/ sumBF	sumC ₂ F/ sumBF	1EtF/(1EtF +1,8DNF)	1MF/ (1MF+F)
6507/7-6 DST.2	79.12	122.36	-	-	-	-	-	-	-	0.46	0.30	-	0.65	-	-	0.22	0.36
6507/7-8 DST.1	41.03	116.69	-	-	-	-	-	-	-	1.07	0.38	-	0.35	-	-	0.17	0.21
6507/7-8 DST.2	18.77	65.03	-	-	-	-	-	-	-	0.77	0.22	-	0.29	-	-	0.25	0.28
6507/8-4 DST.2	1.03	3.61	1.02	0.52	0.31	0.17	0.75	0.63	0.64	0.25	0.07	0.26	0.29	1.01	3.52	0.23	0.52
6507/8-4 DST.3	16.61	28.29	11.92	0.47	0.42	0.12	0.80	0.53	0.78	0.73	0.43	1.02	0.59	1.39	2.37	0.31	0.23
6507/8-4 DST.4	6.78	12.76	1.05	0.74	0.20	0.06	0.92	0.79	0.76	0.58	0.31	3.79	0.53	6.49	12.20	0.32	0.39
6507/11-3 DST.1	171.51	277.37	-	-	-	-	-	-	-	0.34	0.21	-	0.62	-	-	0.29	0.48
6507/11-3 DST.2	118.67	139.65	-	-	-	-	-	-	-	0.55	0.47	-	0.85	-	-	0.24	0.36
6507/11-3 DST.3	9.13	9.42	0.64	0.60	0.30	0.10	0.86	0.66	0.76	0.54	0.52	7.69	0.97	14.31	14.76	0.40	0.36
7120/1-2	2.92	8.74	0.82	0.65	0.21	0.13	0.83	0.75	0.62	0.06	0.02	0.23	0.33	3.57	10.67	0.16	0.93
7121/5-1	5.51	11.08	2.85	0.53	0.33	0.13	0.80	0.62	0.71	0.29	0.14	0.55	0.50	1.93	3.89	0.32	0.58
7124/3-1	23.18	40.06	9.07	0.45	0.39	0.16	0.74	0.53	0.72	0.29	0.17	0.74	0.58	2.55	4.41	0.36	0.55
Åre 5647.15	96.27	56.65	189.58	0.71	0.22	0.06	0.92	0.76	0.78	0.71	1.21	0.36	1.70	0.51	0.30	0.18	0.38
Åre 5647.60	340.16	142.29	549.51	0.67	0.26	0.07	0.90	0.72	0.78	1.05	2.52	0.65	2.39	0.62	0.26	0.07	0.27
Spekk 3744	655.11	498.60	126.61	0.61	0.19	0.19	0.76	0.76	0.50	0.60	0.79	3.09	1.31	5.17	3.94	0.57	0.43
Spekk 3744	438.17	399.97	113.69	0.60	0.19	0.21	0.74	0.76	0.47	0.53	0.58	2.04	1.10	3.85	3.52	0.58	0.45
Åre 1406.40	3.73	2.48	1.29	0.28	0.30	0.41	0.41	0.49	0.42	0.49	0.74	1.42	1.51	2.90	1.93	0.42	0.49
Åre 1406.50	1.28	2.01	2.46	0.27	0.47	0.26	0.50	0.36	0.64	0.89	0.57	0.46	0.64	0.52	0.82	0.43	0.27
Spekk 1623.30	159.49	140.96	8.90	0.51	0.22	0.27	0.66	0.70	0.45	0.36	0.41	6.44	1.13	17.93	15.85	0.52	0.58
Spekk 1627.50	15.92	14.55	1.16	0.54	0.22	0.24	0.69	0.71	0.47	0.63	0.68	8.56	1.09	13.69	12.51	0.43	0.44
Spekk 1675	107.96	109.87	7.53	0.42	0.20	0.38	0.52	0.67	0.35	0.31	0.31	4.48	0.98	14.34	14.60	0.46	0.61
Ghareb oil 310°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb oil 330°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb oil 345°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb oil 355°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb oil 360°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb oil 365°C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ghareb bit. 310°C	13.58	26.99	1.98	0.24	0.39	0.37	0.40	0.38	0.52	0.31	0.16	2.12	0.50	6.87	13.65	0.84	0.28
Ghareb bit. 330°C	4.98	11.76	0.86	0.27	0.36	0.37	0.43	0.43	0.50	0.26	0.11	1.53	0.42	5.81	13.71	0.84	0.26
Ghareb bit. 345°C	7.41	14.90	0.96	0.09	0.47	0.45	0.16	0.15	0.51	0.30	0.15	2.34	0.50	7.70	15.50	0.85	0.25
Ghareb bit. 355°C	124.63	248.96	18.41	0.30	0.29	0.41	0.42	0.51	0.41	0.36	0.18	2.44	0.50	6.77	13.52	0.52	0.27
Ghareb bit. 360°C	81.80	126.91	12.34	0.43	0.24	0.33	0.57	0.64	0.42	0.30	0.19	1.99	0.64	6.63	10.29	0.37	0.50
Ghareb bit. 365°C	32.47	60.71	3.10	0.48	0.19	0.33	0.59	0.71	0.37	0.34	0.18	3.57	0.53	10.49	19.61	0.36	0.47

Appendix 5c: Fluorenone and benzofluorenone ratios

	1/(1+4) MF	1/ sumMF	1/(1+2) MF	1/(1+3) MF	2/(2+3) MF	2/(2+4) MF	3/(3+4) MF	1,8/ (1,8+4)	1EtF/ (1EtF+ 1MF)	1EtF/ (1EtF+ 4MF)
2/2-5	0.55	0.27	0.52	0.51	0.49	0.53	0.54	0.58	0.20	0.23
2/4-14	0.84	0.51	0.73	0.71	0.47	0.66	0.68	0.77	0.06	0.26
6/3-1	0.74	0.50	0.75	0.76	0.51	0.48	0.47	0.59	0.18	0.38
7/7-2	0.55	0.36	0.69	0.65	0.45	0.35	0.40	0.16	0.17	0.20
9/2-1	0.56	0.32	0.59	0.60	0.51	0.46	0.46	0.51	0.14	0.17
15/12-5	0.69	0.47	0.76	0.73	0.46	0.41	0.45	0.69	0.25	0.42
15/12-6	0.70	0.45	0.72	0.72	0.50	0.47	0.47	0.69	0.24	0.42
25/5-1	0.55	0.29	0.56	0.55	0.49	0.49	0.50	0.38	0.14	0.16
25/11-T-21A	0.83	0.55	0.70	0.83	0.68	0.68	0.50	0.68	0.12	0.40
NSO-1	0.63	0.34	0.61	0.59	0.48	0.53	0.55	0.45	0.26	0.38
30/9-10	0.63	0.37	0.66	0.61	0.45	0.47	0.52	0.30	0.15	0.24
30/9-[OL]	0.83	0.54	0.75	0.76	0.51	0.62	0.61	0.57	0.14	0.45
30/9-[TM]	0.82	0.53	0.75	0.74	0.48	0.60	0.62	0.59	0.16	0.47
31/2-G-3H	0.78	0.44	0.66	0.66	0.50	0.64	0.64	0.85	0.34	0.64
35/3-4	0.73	0.43	0.68	0.66	0.48	0.56	0.58	0.38	0.09	0.22
35/11-4	0.68	0.39	0.65	0.64	0.49	0.54	0.55	0.39	0.11	0.21
6201/11-1	0.94	0.83	0.94	0.93	0.44	0.48	0.53	0.88	0.07	0.53
33/9-12	0.60	0.30	0.49	0.59	0.60	0.61	0.51	0.59	0.24	0.33
33/9-14	0.54	0.30	0.60	0.55	0.46	0.44	0.48	0.23	0.16	0.18
34/4-6	0.68	0.41	0.67	0.67	0.50	0.51	0.51	0.68	0.11	0.21
34/7-4	0.68	0.42	0.69	0.67	0.48	0.49	0.51	0.47	0.15	0.27
34/7-6	0.71	0.45	0.72	0.70	0.47	0.48	0.51	0.48	0.14	0.28
34/7-8	0.66	0.39	0.64	0.66	0.51	0.52	0.51	0.32	0.14	0.24
34/7-10	0.83	0.64	0.87	0.84	0.44	0.42	0.49	0.57	0.17	0.49
34/7-13 DST.1.1	0.55	0.31	0.59	0.57	0.47	0.46	0.49	0.36	0.15	0.18
34/7-13 DST.1	0.45	0.22	0.47	0.47	0.50	0.48	0.48	0.35	0.25	0.22
34/7-14	0.61	0.35	0.62	0.62	0.49	0.49	0.50	0.55	0.08	0.12
34/7-16 DST.3	0.61	0.33	0.60	0.58	0.48	0.51	0.53	0.77	0.33	0.43
34/7-16 DST.2	0.55	0.28	0.56	0.50	0.44	0.49	0.55	0.52	0.19	0.22
34/7-18	0.57	0.29	0.52	0.57	0.55	0.55	0.50	0.55	0.26	0.32
34/7-21	0.63	0.37	0.67	0.63	0.45	0.46	0.51	0.57	0.13	0.20

	1/(1+4) MF	1/ sumMF	1/(1+2) MF	1/(1+3) MF	2/(2+3) MF	2/(2+4) MF	3/(3+4) MF	1,8/ (1,8+4)	1EtF/ (1EtF+ 1MF)	1EtF/ (1EtF+ 4MF)
34/7-22	0.61	0.33	0.60	0.58	0.48	0.51	0.53	0.55	0.30	0.40
34/7-23A	0.56	0.28	0.56	0.51	0.45	0.51	0.55	0.49	0.41	0.47
34/7-26A	0.59	0.28	0.50	0.55	0.55	0.60	0.55	0.69	0.34	0.43
34/8-8R	0.68	0.40	0.66	0.65	0.48	0.52	0.54	0.50	0.13	0.23
34/10-1	0.63	0.38	0.67	0.64	0.46	0.45	0.49	0.46	0.14	0.21
34/10-3 DST.2	0.62	0.37	0.67	0.63	0.46	0.45	0.49	0.24	0.16	0.24
34/10-3 DST.3	0.55	0.30	0.60	0.55	0.45	0.45	0.50	0.32	0.21	0.24
34/10-7	0.67	0.40	0.69	0.65	0.45	0.47	0.52	0.36	0.19	0.32
34/10-8	0.58	0.34	0.66	0.59	0.43	0.42	0.49	0.22	0.15	0.19
34/10-9	0.59	0.35	0.65	0.60	0.45	0.44	0.49	0.23	0.18	0.24
34/10-14	0.57	0.34	0.68	0.59	0.40	0.38	0.48	0.35	0.23	0.29
34/10-A-1H	0.57	0.29	0.60	0.48	0.39	0.48	0.59	0.50	0.31	0.38
34/10-17	0.68	0.37	0.62	0.60	0.47	0.56	0.59	0.47	0.14	0.26
34/10-30	0.84	0.59	0.80	0.79	0.48	0.57	0.58	0.64	0.09	0.35
34/10-32R	0.80	0.51	0.75	0.73	0.48	0.57	0.59	0.78	0.24	0.55
34/10-34	0.64	0.34	0.61	0.59	0.48	0.53	0.55	0.30	0.17	0.26
34/10-35	0.75	0.43	0.65	0.68	0.54	0.62	0.59	0.55	0.11	0.28
6406/11-1S	0.64	0.39	0.66	0.66	0.50	0.48	0.48	0.33	0.16	0.26
6406/3-2	0.59	0.35	0.64	0.63	0.49	0.46	0.47	0.25	0.13	0.18
6407/7-4	0.70	0.41	0.68	0.65	0.47	0.52	0.55	0.50	0.17	0.31
6407/9-1	0.54	0.28	0.56	0.51	0.45	0.48	0.53	0.37	0.13	0.15
6506/11-2	0.60	0.30	0.58	0.53	0.45	0.52	0.57	0.42	0.15	0.20
6506/12-3	0.61	0.30	0.54	0.54	0.50	0.57	0.57	0.62	0.12	0.17
6507/3-1	0.70	0.40	0.66	0.64	0.48	0.54	0.56	0.50	0.11	0.22
6507/7-2 DST.2	0.56	0.27	0.54	0.47	0.43	0.52	0.59	0.45	0.24	0.29
6507/7-2 DST.3	0.54	0.25	0.56	0.43	0.37	0.48	0.61	0.51	0.10	0.12
6507/7-2 DST.4R	0.63	0.31	0.56	0.53	0.46	0.57	0.60	0.68	0.18	0.27
6507/7-3	0.66	0.35	0.57	0.62	0.55	0.59	0.55	0.63	0.13	0.23
6507/7-5 DST.1	0.59	0.30	0.59	0.53	0.44	0.50	0.56	0.38	0.10	0.13
6507/7-5 DST.2	0.58	0.30	0.59	0.53	0.44	0.49	0.55	0.50	0.13	0.17
6507/7-6 DST.1	0.50	0.25	0.52	0.47	0.44	0.48	0.53	0.47	0.14	0.14

Appendix 5c: Fluorenone and benzofluorenone ratios

	1/(1+4) MF	1/ sumMF	1/(1+2) MF	1/(1+3) MF	2/(2+3) MF	2/(2+4) MF	3/(3+4) MF	1,8/ (1,8+4)	1EtF/(1EtF+1MF)	1EtF/(1EtF+4MF)
6507/7-6 DST.2	0.52	0.26	0.54	0.48	0.45	0.48	0.53	0.37	0.13	0.14
6507/7-8 DST.1	0.57	0.29	0.56	0.52	0.46	0.52	0.55	0.63	0.21	0.26
6507/7-8 DST.2	0.57	0.29	0.58	0.52	0.44	0.49	0.55	0.70	0.37	0.44
6507/8-4 DST.2	0.55	0.27	0.52	0.53	0.51	0.53	0.52	0.74	0.41	0.46
6507/8-4 DST.3	0.44	0.21	0.47	0.45	0.48	0.47	0.49	0.43	0.30	0.25
6507/8-4 DST.4	0.68	0.37	0.63	0.60	0.47	0.56	0.59	0.53	0.19	0.34
6507/11-3 DST.1	0.65	0.31	0.57	0.52	0.45	0.59	0.63	0.47	0.16	0.26
6507/11-3 DST.2	0.68	0.31	0.54	0.53	0.49	0.64	0.65	0.48	0.12	0.23
6507/11-3 DST.3	0.67	0.31	0.54	0.52	0.48	0.64	0.66	0.30	0.12	0.23
7120/1-2	0.93	0.83	0.94	0.93	0.47	0.46	0.49	0.89	0.10	0.59
7121/5-1	0.68	0.40	0.66	0.66	0.49	0.52	0.53	0.46	0.16	0.29
7124/3-1	0.63	0.36	0.65	0.61	0.47	0.48	0.51	0.44	0.21	0.31
Are 5647.15	0.85	0.44	0.65	0.64	0.49	0.75	0.76	0.50	0.04	0.18
Are 5647.60	0.87	0.40	0.63	0.56	0.43	0.80	0.84	0.47	0.01	0.06
Spekk 3744	0.74	0.45	0.70	0.70	0.50	0.55	0.55	0.26	0.14	0.33
Spekk 3744	0.73	0.43	0.67	0.67	0.50	0.58	0.57	0.26	0.15	0.33
Are 1406.40	0.73	0.47	0.72	0.73	0.51	0.50	0.49	0.31	0.11	0.25
Are 1406.50	0.57	0.33	0.59	0.61	0.52	0.48	0.46	0.34	0.22	0.28
Spekk 1623.30	0.80	0.50	0.74	0.72	0.47	0.57	0.60	0.37	0.14	0.39
Spekk 1627.50	0.79	0.50	0.74	0.71	0.46	0.57	0.61	0.40	0.12	0.34
Spekk 1675	0.78	0.48	0.73	0.71	0.48	0.57	0.59	0.39	0.14	0.36
Chareb oil 310°C	-	-	-	-	-	-	-	-	-	-
Chareb oil 330°C	-	-	-	-	-	-	-	-	-	-
Chareb oil 345°C	-	-	-	-	-	-	-	-	-	-
Chareb oil 355°C	-	-	-	-	-	-	-	-	-	-
Chareb oil 360°C	-	-	-	-	-	-	-	-	-	-
Chareb oil 365°C	-	-	-	-	-	-	-	-	-	-
Chareb bit. 310°C	0.20	0.12	0.40	0.34	0.44	0.28	0.33	0.01	0.15	0.04
Chareb bit. 330°C	0.16	0.09	0.35	0.29	0.43	0.26	0.32	0.01	0.26	0.06
Chareb bit. 345°C	0.18	0.10	0.32	0.30	0.48	0.32	0.34	0.01	0.21	0.06
Chareb bit. 355°C	0.26	0.13	0.39	0.33	0.43	0.35	0.41	0.02	0.05	0.02
Chareb bit. 360°C	0.46	0.31	0.68	0.61	0.43	0.29	0.35	0.25	0.19	0.17
Chareb bit. 365°C	0.46	0.31	0.68	0.65	0.46	0.28	0.31	0.26	0.19	0.16

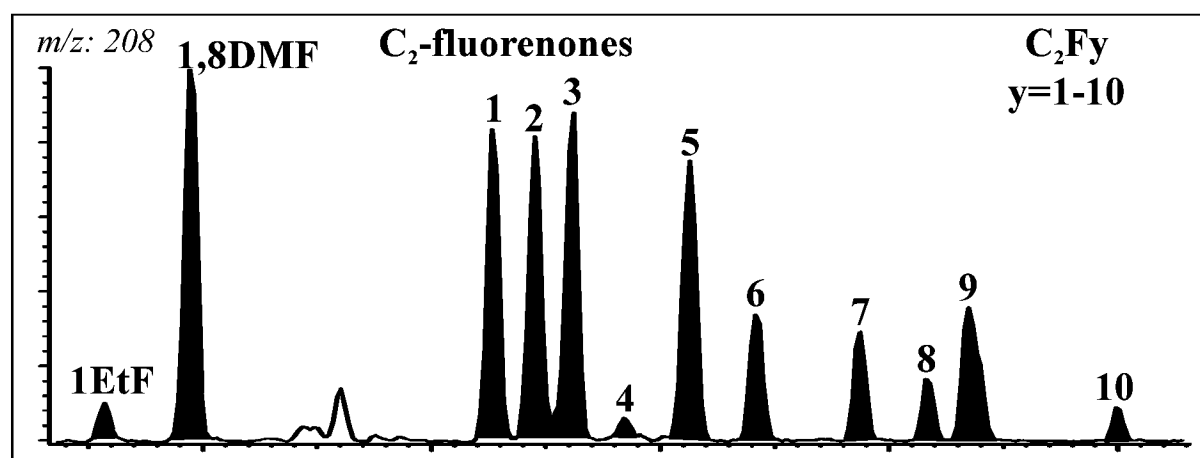
F : fluorenone

MF : methylfluorenone

DMF : dimethylfluorenone

EtF : ethylfluorenone

BF : benzofluorenone

C₂F : C₂-fluorenones

Appendix 6a: Concentration of xanthenes

[µg/g oil]	X	1-MX	4-MX	2-MX	3-MX	C _{2a} -X	C _{2b} -X	C _{2c} -X	C _{2d} -X	C _{2e} -X	C _{2f} -X	C _{2g} -X	C _{2h} -X	C _{2j} -X	C _{2k} -X	C _{2l} -X	C _{2m} -X
2/2-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2/4-14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6/3-1	1.14	0.27	0.33	0.43	0.23	0.03	0.04	0.10	0.01	0.09	0.22	0.20	0.14	0.09	0.06	0.01	0.11
7/7-2	0.97	0.05	0.23	0.21	0.12	0.02	0.01	0.05	0.09	0.02	0.01	0.04	0.19	0.16	0.11	0.02	0.05
9/2-1	0.93	0.14	0.85	0.98	0.54	0.03	0.03	0.16	0.13	0.05	0.19	0.31	0.70	0.59	0.33	0.05	0.16
15/12-5	2.75	0.08	0.99	1.14	0.73	0.06	0.07	0.12	0.08	0.05	0.07	0.11	0.57	0.57	0.32	0.07	0.10
15/12-6	3.42	0.19	1.21	1.55	1.06	0.06	0.03	0.12	0.14	0.09	0.15	0.16	0.82	0.84	0.37	0.14	0.26
25/5-1	0.92	0.11	0.99	0.97	0.45	0.05	0.07	0.13	0.14	0.05	0.08	0.14	0.81	0.68	0.31	0.03	0.25
25/11-T-21A	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NSO-1	56.39	1.20	24.93	21.59	17.09	1.01	0.31	1.31	2.65	1.05	2.16	2.05	15.97	16.16	6.76	2.03	3.12
30/9-10	6.74	0.51	3.34	2.98	1.98	0.01	0.03	0.07	0.03	0.04	0.01	0.12	2.36	2.15	0.46	0.26	0.30
30/9-1[OL]	2.92	1.41	2.58	2.91	2.70	0.77	1.23	0.23	1.25	1.19	0.74	1.63	0.73	2.62	1.64	1.39	1.27
30/9-1[TM]	2.18	0.37	2.70	2.17	1.52	0.21	1.25	0.73	1.49	1.46	0.62	1.35	0.38	2.90	1.13	0.98	1.60
31/2-G-3H	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
35/3-4	1.50	0.24	0.97	0.90	0.51	0.04	0.07	0.06	0.14	0.08	0.07	0.15	0.45	0.28	0.10	0.02	0.06
35/11-4	1.03	0.36	0.49	0.90	0.31	0.03	0.02	0.15	0.09	0.14	0.18	0.15	0.73	0.18	0.13	0.00	0.03
6201/11-1	1.82	0.25	0.91	0.60	0.87	0.03	0.10	0.07	0.02	0.05	0.15	0.12	0.21	0.26	0.16	0.09	0.16
33/9-12	0.77	0.07	0.59	0.52	0.33	0.07	0.07	0.09	0.07	0.06	0.04	0.06	0.51	0.44	0.27	0.01	0.09
33/9-14	1.07	0.20	0.33	0.61	0.13	-	-	-	-	-	-	-	-	-	-	-	-
34/4-6	3.36	0.16	1.83	1.21	1.58	0.05	0.13	0.05	0.10	0.04	0.08	0.12	0.49	0.72	0.42	0.16	0.47
34/7-4	2.64	0.13	1.32	0.93	0.81	0.06	0.07	0.07	0.08	0.05	0.08	0.17	0.45	0.54	0.25	0.04	0.24
34/7-6	1.96	0.08	1.06	0.79	0.64	0.01	0.04	0.04	0.06	0.05	0.04	0.05	0.35	0.44	0.27	0.02	0.21
34/7-8	7.97	0.73	2.06	2.60	0.49	0.13	0.24	0.35	0.07	0.18	0.27	0.31	0.69	0.69	0.28	0.06	0.15
34/7-10	5.14	0.42	0.64	0.71	0.18	-	-	-	-	-	-	-	-	-	-	-	-
34/7-13 DST.1.1	2.26	0.15	1.47	1.21	0.89	0.03	0.03	0.07	0.22	0.04	0.07	0.08	1.01	0.96	0.38	0.09	0.19
34/7-13 DST.1	5.39	0.30	4.52	3.69	3.19	0.59	0.22	0.42	0.60	0.20	0.50	0.08	3.43	4.10	2.46	0.22	1.36
34/7-14	1.26	0.17	0.96	0.97	0.55	0.03	0.03	0.09	0.11	0.07	0.09	0.11	0.98	0.95	0.37	0.09	0.14
34/7-16 DST.3	0.41	0.03	0.34	0.29	0.19	0.07	0.09	0.06	0.03	0.03	0.01	0.06	0.27	0.24	0.22	0.03	0.11
34/7-16 DST.2	0.45	0.03	0.39	0.34	0.25	0.07	0.06	0.03	0.06	0.02	0.02	0.08	0.29	0.31	0.12	0.04	0.14
34/7-18	0.54	0.05	0.58	0.45	0.35	0.10	0.09	0.04	0.08	0.05	0.04	0.15	0.55	0.58	0.38	0.07	0.16
34/7-21	1.72	0.25	1.23	1.13	0.66	0.07	0.09	0.27	0.17	0.14	0.15	0.21	0.97	0.90	0.39	0.07	0.15

Appendix 6a: Concentration of xanthenes

[µg/g oil]	X	1-MX	4-MX	2-MX	3-MX	C _{2a} -X	C _{2b} -X	C _{2c} -X	C _{2d} -X	C _{2e} -X	C _{2f} -X	C _{2g} -X	C _{2h} -X	C _{2j} -X	C _{2k} -X	C _{2l} -X	C _{2m} -X	C _{2n} -X
34/7-22	0.81	0.06	0.72	0.62	0.43	0.12	0.11	0.06	0.10	0.07	0.10	0.13	0.64	0.69	0.55	0.40	0.12	0.16
34/7-23A	0.78	0.06	0.71	0.63	0.45	0.12	0.07	0.05	0.09	0.06	0.05	0.08	0.55	0.66	0.52	0.32	0.07	0.19
34/7-26A	0.12	0.03	0.16	0.09	0.07	0.11	0.09	0.02	0.03	0.02	0.02	0.02	0.14	0.13	0.12	0.16	0.01	0.04
34/8-8R	5.43	0.17	2.03	1.65	1.50	0.07	0.07	0.12	0.12	0.07	0.12	0.12	0.63	0.52	0.62	0.34	0.07	0.23
34/10-1	2.29	0.28	1.92	1.66	1.05	0.06	0.06	0.15	0.25	0.14	0.18	0.18	1.80	1.62	1.13	0.62	0.15	0.20
34/10-3 DST2	4.06	0.47	3.55	2.73	2.00	0.10	0.07	0.22	0.62	0.26	0.34	0.26	3.48	2.74	2.22	0.99	0.35	0.27
34/10-3 DST3	2.75	0.46	2.41	1.99	1.50	0.14	0.10	0.37	0.39	0.25	0.30	0.25	2.31	2.08	1.58	0.79	0.25	0.23
34/10-7	5.15	0.16	2.82	2.06	2.45	0.06	0.06	0.11	0.16	0.06	0.14	0.11	1.06	1.21	1.26	0.62	0.29	0.41
34/10-8	1.64	0.16	1.38	1.03	0.75	0.05	0.03	0.10	0.18	0.06	0.09	0.07	1.17	1.02	0.74	0.37	0.12	0.13
34/10-9	4.32	0.30	3.15	2.40	2.06	0.11	0.07	0.19	0.38	0.13	0.21	0.18	2.40	2.22	1.74	0.86	0.30	0.30
34/10-14	2.94	0.33	2.62	2.01	1.58	0.19	0.15	0.25	0.30	0.16	0.32	0.21	2.33	2.14	1.41	0.68	0.19	0.16
34/10-A-1H	0.93	0.10	0.91	0.73	0.56	0.16	0.15	0.09	0.11	0.08	0.14	0.15	0.86	0.97	0.64	0.43	0.06	0.15
34/10-17	2.16	0.59	1.92	2.28	1.36	0.06	0.10	0.18	0.22	0.20	0.37	0.22	1.82	1.11	1.32	0.72	0.16	0.27
34/10-30	38.71	0.43	5.77	3.55	2.87	0.02	0.09	0.13	0.23	0.19	0.31	0.25	1.01	1.04	0.96	0.28	0.02	0.20
34/10-32R	2.52	0.13	1.34	1.14	0.72	0.07	0.11	0.17	0.11	0.08	0.15	0.19	0.74	0.73	0.71	0.34	0.05	0.31
34/10-34	0.13	0.09	0.12	0.20	0.04	0.06	0.01	0.07	0.03	0.06	0.02	0.05	0.31	0.13	0.11	0.07	0.01	0.03
34/10-35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6406/11-1S	0.21	0.11	0.35	0.30	0.16	0.02	0.04	0.06	0.09	0.05	0.04	0.09	0.34	0.23	0.23	0.00	0.02	0.01
6406/3-2	0.40	0.06	0.72	0.29	0.13	0.05	0.05	0.10	0.17	0.02	0.02	0.17	0.40	0.62	0.14	0.10	0.01	0.10
6407/7-4	4.78	0.74	2.76	3.09	1.79	0.07	0.15	0.50	0.30	0.28	0.48	0.34	2.18	1.38	1.66	0.67	0.17	0.30
6407/9-1	1.61	0.30	1.39	1.14	0.84	0.01	0.04	0.20	0.17	0.12	0.14	0.21	1.29	0.85	0.71	0.41	0.05	0.20
6506/11-2	2.02	0.50	1.27	1.81	1.07	0.03	0.08	0.15	0.17	0.06	0.13	0.19	1.20	0.38	0.61	0.29	0.03	0.15
6506/12-3	1.17	0.27	0.90	1.12	0.74	0.06	0.08	0.17	0.12	0.04	0.08	0.11	1.00	0.34	0.50	0.22	0.07	0.02
6507/3-1	0.15	0.04	0.31	0.20	0.13	0.02	0.06	0.09	0.06	0.02	0.02	0.13	0.20	0.28	0.10	0.06	0.01	0.04
6507/7-2 DST.2	0.29	0.07	0.24	0.21	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-
6507/7-2 DST.3	0.61	0.06	0.54	0.47	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-
6507/7-2 DST.4R	0.42	0.04	0.42	0.33	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-
6507/7-3	0.92	0.06	0.52	0.51	0.32	0.07	0.02	0.08	0.06	0.05	0.03	0.10	0.39	0.36	0.28	0.01	0.04	0.15
6507/7-5 DST.1	3.45	1.10	2.66	2.34	1.45	0.10	0.14	0.25	0.30	0.33	0.32	0.43	1.61	1.07	1.00	0.39	0.08	0.17
6507/7-5 DST.2	3.10	0.64	2.52	1.92	1.24	0.13	0.08	0.28	0.31	0.22	0.17	0.29	1.54	1.15	0.91	0.49	0.07	0.13
6507/7-6 DST.1	7.85	1.02	6.09	4.43	2.87	0.22	0.18	0.33	0.71	0.29	0.34	0.43	3.03	2.34	1.78	0.99	0.24	0.25

Appendix 6a: Concentration of xanthenes

[µg/g oil]	X	1-MX	4-MX	2-MX	3-MX	C _{2a} -X	C _{2b} -X	C _{2c} -X	C _{2d} -X	C _{2e} -X	C _{2f} -X	C _{2g} -X	C _{2h} -X	C _{2i} -X	C _{2j} -X	C _{2k} -X	C _{2l} -X	C _{2m} -X	C _{2n} -X
6507/7-6 DST.2	5.82	1.22	4.33	3.28	2.13	0.11	0.12	0.65	0.60	0.36	0.34	0.46	2.29	1.55	1.26	0.65	0.18	0.17	0.15
6507/7-8 DST.1	3.20	0.59	2.51	2.14	1.31	0.36	0.40	0.49	0.27	0.21	0.26	0.54	1.62	1.44	0.97	0.72	0.05	0.27	0.32
6507/7-8 DST.2	1.67	0.17	1.49	1.15	0.72	0.43	0.44	0.18	0.20	0.08	0.07	0.49	0.97	0.86	0.60	0.39	0.05	0.02	0.27
6507/8-4 DST.2	0.07	0.12	0.37	0.09	0.21	0.15	0.15	0.13	0.13	0.08	0.03	0.08	0.83	0.43	0.41	0.23	0.05	0.11	0.06
6507/8-4 DST.3	0.11	0.18	1.05	0.31	0.71	0.10	0.06	0.09	0.30	0.10	0.15	0.14	1.61	1.18	1.07	0.45	0.23	0.21	0.16
6507/8-4 DST.4	0.06	0.15	0.31	0.09	0.17	0.03	0.05	0.07	0.07	0.03	0.05	0.08	0.29	0.17	0.17	0.02	0.01	0.03	0.03
6507/11-3 DST.1	4.17	0.76	5.31	4.67	2.68	0.46	0.40	0.93	0.80	0.32	0.55	0.68	4.48	4.17	3.56	1.37	0.41	0.42	0.32
6507/11-3 DST.2	1.79	0.41	1.68	1.57	0.97	0.17	0.13	0.28	0.26	0.17	0.22	0.29	1.24	1.05	0.89	0.30	0.12	0.11	0.13
6507/11-3 DST.3	0.16	0.03	0.18	0.17	0.10	0.03	0.02	0.02	0.03	0.03	0.04	0.05	0.17	0.17	0.09	0.06	0.02	0.03	0.03
7120/1-2	1.64	0.21	0.90	0.56	0.89	0.04	0.11	0.07	0.04	0.05	0.12	0.08	0.25	0.25	0.31	0.17	0.10	0.21	0.15
7121/5-1	1.67	0.42	3.84	2.00	0.86	0.09	0.07	0.76	0.64	0.23	0.39	0.39	2.81	5.42	1.92	0.80	0.16	0.38	0.39
7124/3-1	8.85	1.32	13.51	7.84	3.36	0.20	0.17	1.70	2.51	0.71	0.84	0.65	9.13	14.85	5.46	1.69	0.40	1.06	0.64

Appendix 6b: Xanthone ratios

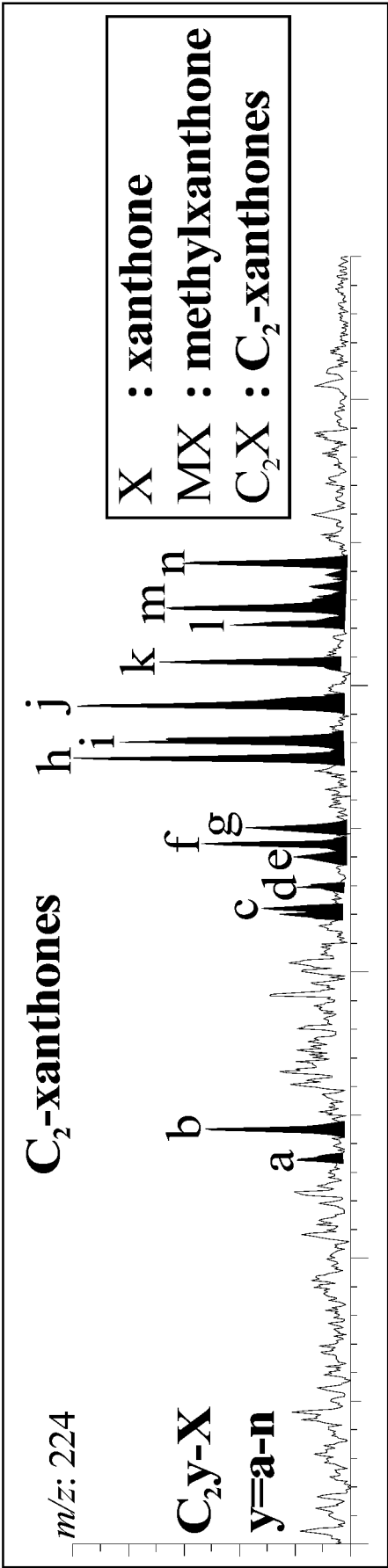
	sumC ₂ -X	sumMX	(1+4)/(2+3)MX	sumMX/ sumC ₂ X	X/(sumC ₂ X)	X/(sumMX)	1/(1+4)MX	1/(1+2)MX	X/(X+4MX)	4/(4+3)MX	4/(4+2)MX	1/(1+3)MX
2/2-5	-	-	-	-	-	-	-	-	-	-	-	-
2/4-14	-	-	-	-	-	-	-	-	-	-	-	-
6/3-1	1.45	1.26	0.92	0.87	0.79	0.90	0.45	0.39	0.77	0.59	0.44	0.54
7/7-2	0.87	0.61	0.85	0.70	1.12	1.59	0.17	0.18	0.81	0.66	0.53	0.28
9/2-1	3.60	2.51	0.65	0.70	0.26	0.37	0.14	0.12	0.52	0.61	0.46	0.21
15/12-5	3.06	2.93	0.57	0.96	0.90	0.94	0.08	0.07	0.74	0.58	0.46	0.10
15/12-6	4.32	4.00	0.54	0.93	0.79	0.86	0.13	0.11	0.74	0.54	0.44	0.15
25/5-1	3.92	2.52	0.78	0.64	0.24	0.37	0.10	0.10	0.48	0.69	0.51	0.20
25/11-T-21A	-	-	-	-	-	-	-	-	-	-	-	-
NSO-1	72.88	64.81	0.68	0.89	0.77	0.87	0.05	0.05	0.69	0.59	0.54	0.07
30/9-10	7.02	8.82	0.78	1.26	0.96	0.76	0.13	0.15	0.67	0.63	0.53	0.21
30/9-1[OL]	16.72	9.60	0.71	0.57	0.17	0.30	0.35	0.33	0.53	0.49	0.47	0.34
30/9-1[TM]	16.86	6.77	0.83	0.40	0.13	0.32	0.12	0.15	0.45	0.64	0.55	0.20
31/2-G-3H	-	-	-	-	-	-	-	-	-	-	-	-
35/3-4	1.90	2.62	0.86	1.38	0.79	0.57	0.20	0.21	0.61	0.66	0.52	0.32
35/11-4	2.36	2.06	0.70	0.87	0.43	0.50	0.43	0.29	0.68	0.61	0.35	0.54
620/11-1	1.85	2.62	0.79	1.42	0.99	0.69	0.22	0.30	0.67	0.51	0.60	0.23
33/9-12	2.28	1.51	0.77	0.66	0.34	0.51	0.10	0.11	0.57	0.64	0.53	0.17
33/9-14	-	1.27	0.70	-	-	0.84	0.38	0.25	0.77	0.71	0.35	0.60
34/4-6	3.81	4.78	0.71	1.25	0.88	0.70	0.08	0.12	0.65	0.54	0.60	0.09
34/7-4	2.69	3.20	0.83	1.19	0.98	0.83	0.09	0.12	0.67	0.62	0.58	0.14
34/7-6	2.15	2.57	0.80	1.19	0.91	0.76	0.07	0.09	0.65	0.63	0.57	0.11
34/7-8	4.13	5.89	0.90	1.43	1.93	1.35	0.26	0.22	0.79	0.81	0.44	0.60
34/7-10	-	1.95	1.19	-	-	2.63	0.40	0.37	0.89	0.78	0.47	0.70
34/7-13 DST.1.1	4.11	3.72	0.77	0.91	0.55	0.61	0.09	0.11	0.61	0.62	0.55	0.14
34/7-13 DST.1	18.72	11.69	0.70	0.62	0.29	0.46	0.06	0.07	0.54	0.59	0.55	0.09
34/7-14	3.94	2.66	0.74	0.67	0.32	0.47	0.15	0.15	0.57	0.64	0.50	0.24
34/7-16 DST.3	1.52	0.85	0.77	0.56	0.27	0.49	0.09	0.10	0.55	0.64	0.54	0.14
34/7-16 DST.2	1.64	1.01	0.71	0.61	0.28	0.45	0.07	0.08	0.54	0.61	0.53	0.11
34/7-18	2.88	1.43	0.79	0.50	0.19	0.38	0.08	0.10	0.48	0.63	0.56	0.13
34/7-21	4.39	3.26	0.82	0.74	0.39	0.53	0.17	0.18	0.58	0.65	0.52	0.27

Appendix 6b: Xanthone ratios

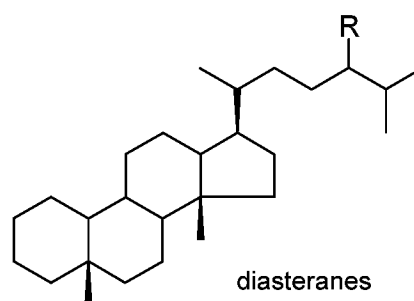
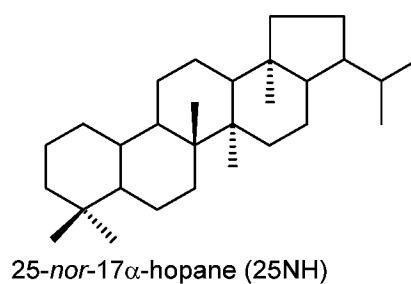
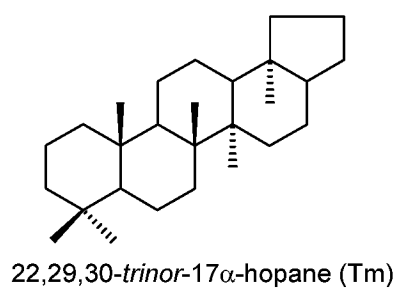
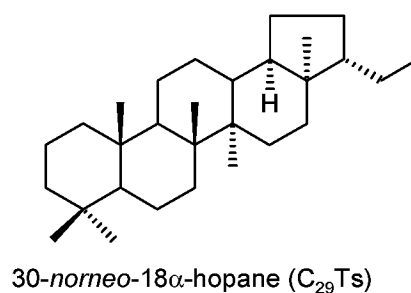
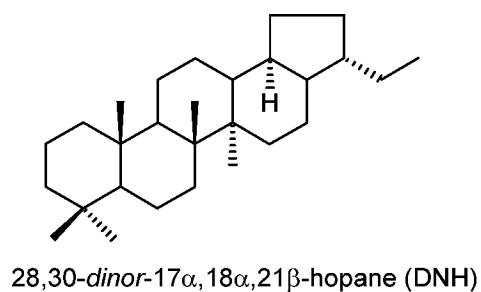
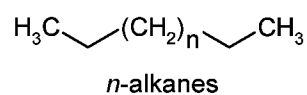
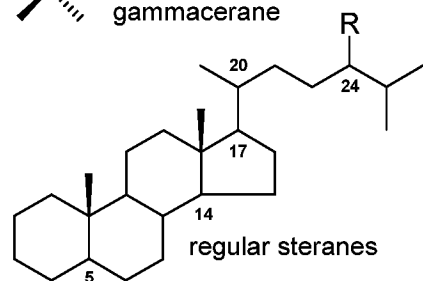
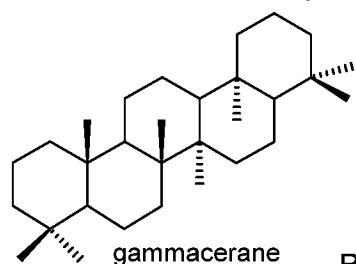
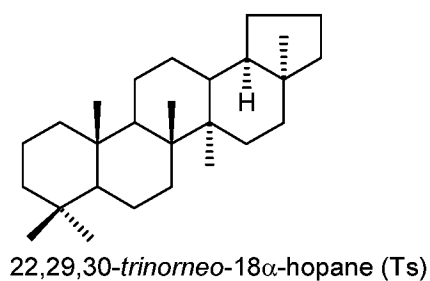
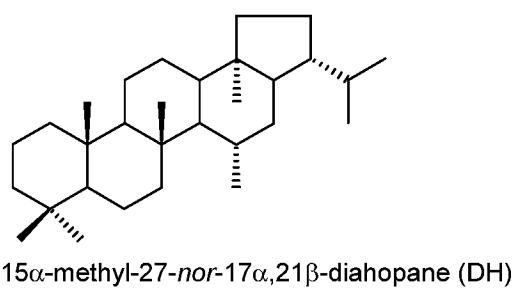
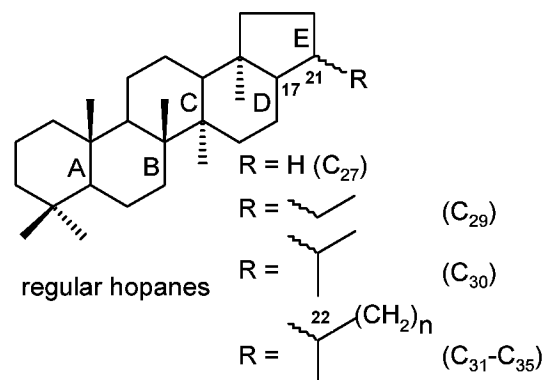
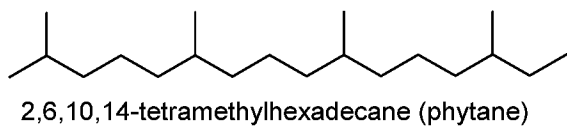
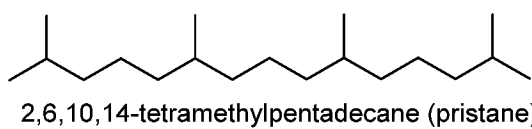
	sumC ₂ -X	sumMX	(1+4)/(2+3)MX	sumMX/ sumC ₂ X	X/(sumC ₂ X)	X/(sumMX)	1/(1+4)MX	1/(1+2)MX	X/(X+4MX)	4/(4+3)MX	4/(4+2)MX	1/(1+3)MX
34/7-22	3.42	1.83	0.74	0.53	0.24	0.44	0.07	0.08	0.53	0.63	0.54	0.12
34/7-23A	3.00	1.86	0.72	0.62	0.26	0.42	0.08	0.09	0.52	0.61	0.53	0.12
34/7-26A	0.94	0.36	1.14	0.38	0.13	0.33	0.16	0.24	0.43	0.69	0.63	0.30
34/8-8R	3.30	5.34	0.69	1.62	1.64	1.02	0.08	0.09	0.73	0.57	0.55	0.10
34/10-1	6.72	4.92	0.81	0.73	0.34	0.47	0.13	0.14	0.54	0.65	0.54	0.21
34/10-3 DST2	12.30	8.75	0.85	0.71	0.33	0.46	0.12	0.15	0.53	0.64	0.57	0.19
34/10-3 DST3	9.35	6.37	0.82	0.68	0.29	0.43	0.16	0.19	0.53	0.62	0.55	0.23
34/10-7	6.15	7.50	0.66	1.22	0.84	0.69	0.05	0.07	0.65	0.53	0.58	0.06
34/10-8	4.26	3.31	0.86	0.78	0.39	0.50	0.10	0.13	0.54	0.65	0.57	0.17
34/10-9	9.54	7.91	0.77	0.83	0.45	0.55	0.09	0.11	0.58	0.60	0.57	0.13
34/10-14	8.75	6.55	0.82	0.75	0.34	0.45	0.11	0.14	0.53	0.62	0.57	0.17
34/10-A-1H	4.07	2.30	0.78	0.57	0.23	0.40	0.10	0.13	0.51	0.62	0.55	0.16
34/10-17	6.99	6.15	0.69	0.88	0.31	0.35	0.24	0.21	0.53	0.58	0.46	0.30
34/10-30	4.90	12.61	0.97	2.57	7.90	3.07	0.07	0.11	0.87	0.67	0.62	0.13
34/10-32R	3.89	3.33	0.79	0.86	0.65	0.76	0.09	0.10	0.65	0.65	0.54	0.15
34/10-34	0.97	0.44	0.87	0.46	0.13	0.29	0.42	0.30	0.51	0.76	0.38	0.69
34/10-35	-	-	-	-	-	-	-	-	-	-	-	-
6406/11-IS	1.26	0.92	0.99	0.73	0.17	0.23	0.24	0.27	0.38	0.68	0.54	0.40
6406/3-2	2.09	1.20	1.88	-	-	0.33	0.07	0.16	0.36	0.85	0.71	0.31
6407/7-4	8.78	8.38	0.72	0.95	0.55	0.57	0.21	0.19	0.63	0.61	0.47	0.29
6407/9-1	4.60	3.67	0.85	0.80	0.35	0.44	0.18	0.21	0.54	0.62	0.55	0.26
6506/11-2	3.60	4.65	0.61	1.29	0.56	0.43	0.28	0.21	0.61	0.54	0.41	0.32
6506/12-3	2.91	3.02	0.63	1.04	0.40	0.39	0.23	0.19	0.57	0.55	0.44	0.26
6507/3-1	1.13	0.68	1.08	-	-	0.22	0.12	0.18	0.33	0.70	0.61	0.25
6507/7-2 DST.2	-	0.67	0.86	-	-	0.44	0.23	0.25	0.55	0.62	0.53	0.33
6507/7-2 DST.3	-	1.30	0.86	-	-	0.47	0.10	0.11	0.53	0.70	0.54	0.21
6507/7-2 DST.4R	-	0.98	0.91	-	-	0.43	0.09	0.11	0.50	0.70	0.56	0.18
6507/7-3	1.71	1.42	0.71	0.83	0.54	0.65	0.11	0.11	0.64	0.62	0.51	0.17
6507/7-5 DST.1	6.37	7.55	0.99	1.19	0.54	0.46	0.29	0.32	0.56	0.65	0.53	0.43
6507/7-5 DST.2	5.92	6.31	1.00	1.07	0.52	0.49	0.20	0.25	0.55	0.67	0.57	0.34
6507/7-6 DST.1	11.44	14.41	0.97	1.26	0.69	0.54	0.14	0.19	0.56	0.68	0.58	0.26

Appendix 6b: Xanthone ratios

	sumC ₂ -X	sumMX	(1+4)/(2+3)MX	sumMX/ sumC ₂ -X	X/(sumC ₂ X)	X/(sumMX)	1/(1+4)MX	1/(1+2)MX	X/(X+4MX)	4/(4+3)MX	4/(4+2)MX	1/(1+3)MX
6507/7-6 DST.2	8.88	10.96	1.03	1.23	0.66	0.53	0.22	0.27	0.57	0.67	0.57	0.36
6507/7-8 DST.1	7.90	6.56	0.90	0.83	0.41	0.49	0.19	0.22	0.56	0.66	0.54	0.31
6507/7-8 DST.2	5.03	3.53	0.89	0.70	0.33	0.47	0.10	0.13	0.53	0.67	0.57	0.19
6507/8-4 DST2	2.86	0.79	1.62	0.28	0.02	0.09	0.25	0.57	0.15	0.63	0.80	0.36
6507/8-4 DST.3	5.87	2.24	1.21	0.38	0.02	0.05	0.14	0.37	0.10	0.60	0.77	0.20
6507/8-4 DST.4	1.11	0.72	1.72	0.65	0.06	0.08	0.32	0.61	0.16	0.64	0.77	0.46
6507/11-3 DST.1	18.85	13.42	-	-	-	-	-	-	-	-	-	-
6507/11-3 DST.2	5.36	4.63	0.83	0.86	0.33	0.39	0.20	0.21	0.52	0.63	0.52	0.30
6507/11-3 DST.3	0.79	0.49	0.76	0.62	0.20	0.32	0.13	0.14	0.46	0.64	0.51	0.21
7120/1-2	1.95	2.57	0.76	1.32	0.85	0.64	0.19	0.27	0.65	0.50	0.62	0.19
7121/5-1	14.44	7.12	1.49	0.49	0.12	0.23	0.10	0.17	0.30	0.82	0.66	0.33
7124/3-1	40.00	26.03	1.33	0.65	0.22	0.34	0.09	0.14	0.40	0.80	0.63	0.28



Appendix 7: Structures of important compounds



Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft



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