Organic Geochemical Analysis of Oils and Condensates in the Northern North Sea

An inquiry in thermal maturation, organic facies, biodegradation, phase fractionation and migration

Tor Kristian Bogstrand

Master’s Thesis in Geosciences
Petroleum Geology and Petroleum Geophysics
30 Credits

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Trykk: Reprosentralen, Universitetet i Oslo
Abstract

Oils and condensates from 17 different northern North Sea wells have been studied and analyzed. The wells are geographically located in Quadrants 33, 34, 35, and 36, and span laterally across the north Viking Graben and Sogn Graben. The wells have been drilled on structural highs on the flanks of the graben structures, where oils and condensates have accumulated over time, generally due to secondary migration from the grabens in the area.

The geochemical analytical methods used in this thesis are GC-FID, GC-MS, and GC-MS/MS. The derived geochemical interpretation parameters provided information on thermal maturity, biodegradation, organic facies, migration paths, oil-oil and oil-source rock correlation, phase fractionation and age determination.

The samples display a distinct trend of increased thermal maturity for samples located proximal to the north Viking Graben. The three condensates from wells 34/10-23 (Va1), 34/11-1 (K1), and 34/11-2 S (N1), are interpreted to have been generated in the condensate/wet gas stage. The least mature samples appear to be located in the western part of the study area, but the maturity differences observed between the western flank (WF) samples and the eastern flank (EF) samples might be related to an increased amount of terrestrial input, which overestimates the maturity values.

A trend of increased terrestrial input in the eastern direction was observed during the organic facies analysis. WF samples display evidence of lower abundance of terrestrial input, with the exception of the Gullfaks Sør oils, which show significantly higher levels of terrestrial input. The vast majority of the samples have been correlated to mixed source input, which is defined as marine shales with minor terrestrial input. Most of the EF samples have been correlated to the Heather Fm., while the two WF oils (St1 and Sn1) have been correlated to the Draupne Fm. The Agat Fm. condensate (A1), from well 35/3-4, has been interpreted to be generated from a process known as phase fractionation. Fractionated condensates are linked to residual oils located at the original reservoir, or in a remigrated up-dip position. Thus, future oil discoveries in this general region are likely, and possible undiscovered oil accumulations in the Sogn Graben/Måløy Terrace area are tentatively proposed to exist. All samples have been interpreted to be sourced from Jurassic age source rocks based on the NDR parameters derived from the GC-MS/MS analysis.
Acknowledgements

First I would like to thank my supervisor, Professor Dag Arild Karlsen, who originally inspired me to choose organic geochemistry. My decision was based on my experience attending his Petroleum Systems course in the autumn semester 2015, where he quickly became my favorite professor. Thank you for enabling a great learning environment, and for being a kind and helpful supervisor throughout this entire process.

I would also like to acknowledge the petroleum geochemistry community at Blindern, who are a bunch of very friendly and welcoming people. Thank you Tesfamariam Berhane Abay, your help was indispensable. Kristian Backer-Owe, Zagros Matapour, and Benedikt Lerch, also deserve a special mention, as they all helped me at various stages during this thesis. Your guidance in the mechanics of lab work, and your response to my questions has been greatly appreciated.

I was also very lucky to be sharing the laboratory with last year’s MSc-thesis candidates Fredrik Wesenlund and Lars Jonas Jørgensen Narvhus at various times. Both of you were very generous in offering your advice, which has been very helpful.

Finally I would like to thank my family and friends. Your unconditional support has helped me greatly throughout the years, and made this degree possible.

Tor Kristian Bogstrand
Acronyms

BHT  Bottom hole temperature
CGC  Central Graben Condensates
CPI  Carbon Preference Index
DCM  Dichloromethane
DST  Drill stem test
EF   Eastern flank
FID  Flame ionization detection
Fm   Formation
GC   Gas chromatography
GOR  Gas to oil ratio
Gp   Group
HC   Hydrocarbon
i.d. Inner diameter
MA   Monoaromatic
MD   Measured depth
MDBT Methyl dibenzothiophene
MDR  Methyl dibenzothiophene ratio
MDT  Modular Dynamics Tester
MPI1 Methyl phenanthrene index
MPR  Methyl phenanthrene ratio
MS   Mass spectrometry
m/z  mass to ion charge number ratio
NCS  Norwegian continental shelf
NDR  Nordiacholestane ratio
NSO-1 Norwegian Standard Oil 1
OEP  Odd-to-even predominance
OM   Organic matter
Ph   Phytane
Pr   Pristane
ss   Sandstone
TA   Triaromatic
UCM  Unresolved complex mixture
WF   Western flank
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1 Introduction

1.1 Thesis outline

The thesis begins with the introduction to the study area, as well as a presentation of the main objectives of the thesis. Subsequently the regional geology is presented to provide the reader with an overview of the geological framework and tectonic evolution of the area. The third chapter provides a short overview of the sample set, as well as information regarding the wells where the samples were produced. Chapter 4 presents the analytical methods and lab procedures that produced the data set analyzed in this thesis. The next chapter describes the various interpretation parameters used to analyze the data set in a geological context. Subsequently the results are presented and discussed, before the summary and conclusions of the thesis are presented. The thesis ends with a short chapter about suggestions for future work in the study area.

1.2 The study area

This thesis analyzes samples retrieved from wells located in the northern North Sea. Since 1966, the exploration in the area has resulted in over 1700 exploration and appraisal wells drilled. This has led to close to 300 hydrocarbon discoveries, and the area has, and continues to be, a major hydrocarbon-producing region in the Norwegian petroleum exploration history. The study area is located directly west of Førde and Florø, and spans across four different Quadrants (Figure 1.1). The region has experienced several stages of tectonically very active periods. The tectonic evolution of the area, further explained in chapter 2, has created a complex and mature graben-topography.

1.3 Thesis objectives

The main objective of this thesis is to generate an extensive data set of different geochemical interpretation parameters in order to provide a comprehensive petroleum system analysis of the area. In particular this thesis will attempt to produce information regarding the following processes:
The development of aromaticity and paraffinicity as a result of geochemical alteration processes.

Thermal maturity

Organic facies

Oil-oil and oil-source rock correlation

The processes which generated the condensates

Age determination of the samples’ OM source

**Figure 1.1:** Structural map to provide overview of the study area (highlighted by blue borders). Note the two graben structures highlighted by the dark green color. Modified from (Folkestad et al., 2014).
2 Regional geology

2.1 Introduction

This chapter includes a summary of the tectonic evolution and stratigraphy of the study area. The chapter also presents a generalized overview of the northern North Sea petroleum systems, which includes the most important source rocks and reservoirs of the northern North Sea.

2.2 Tectonic evolution

The northern North Sea structural framework is a result of faults and shear zones formed by the Caledonian orogeny, and subsequent collapse of the orogenic belt in the Devonian period (Folkestad et al., 2014). The rift basin has also been affected by two major rifting stages, which occurred in the Permian to Early Triassic, and in the Late Mid-Jurassic to the Early Cretaceous period (Faleide et al., 2002). The subsidence history of the basin consists of short periods of active stretching, which is followed by a long period of passive subsidence caused by thermal contraction and relaxation of the heated lithosphere (Nøttvedt et al., 1995). The Permian to Early Triassic rifting stage resulted in large tilted fault blocks, which formed a north-south oriented basin in the Late Paleozoic. During the following subsidence created by the thermal relaxation of the crust, faulting occurred on the margins of the basin. This faulting of the margins was caused by lateral differences in sediment loading, thermal subsidence, compaction and flexure (Odinsen et al., 2000). The second major rifting stage began in the Late Bajocian – Early Bathonian, with the rotation of major fault blocks. Partial reactivation of master faults from the Triassic rifting stage attributed to the general structure of the basin, which includes segmentation and subsidence with opposing polarization in certain areas. The major graben features seen in the basin was created during the rifting climax in the Late Jurassic period. During this rifting climax, concentrated fault activity along the graben margins, created the mature graben topography seen today. This includes platforms, sub-platforms, marginal platform highs, and a graben with a complex centre of subsidence along the graben axis (Odinsen et al., 2000).
According to Bugge et al. (2001), the tectonic activity lasted longer in the northeastern part of the northern North Sea, and the area experienced less extensional and vertical tectonic activity throughout the Cretaceous period.

Figure 2.1 displays the general structural configuration seen in the northern part of the North Sea, including mature graben topography with platforms, sub-platforms and rotated fault blocks.

Figure 2.1: An overview of the structural elements present in the southern part of the study area. From Christiansson et al. (2000).
2.3 Stratigraphy

The oldest formations included in this report were deposited in the Triassic. Earlier deposits are not directly relevant to the present day petroleum systems of the northern North Sea, and are therefore not included. A general overview of the stratigraphic units of the northern North Sea can be seen in figure 2.2.

**Figure 2.2:** Stratigraphic overview of the North Sea. The Northern part is represented to the left in the figure. Green dots represent units known for oil production. Red dots represent units known for gas production. From Gautier (2005).
2.3.1 Triassic

Most of the Triassic period was dominated by continental deposition in a rapidly subsiding rift basin. The Hegre Group, which consists of the Teist, Lomvi and Lunde formations, are laterally extensive units present all over the northern part of the North Sea. The Hegre Group consists of intervals of interbedded sandstones, claystones and shales (Vollset and Doré, 1984).

2.3.2 Jurassic

During the Late Triassic to Early Jurassic period, i.e. during the Rhaetian to Sinemurian age, a 300-600 m thick sequence consisting of a silty/shaly unit, and the overlying Statfjord Formation, were deposited. This sequence is upwards coarsening. The lower part of the sequences consists of lacustrine, floodbasin, and brackish lagoonal deposits. Low-sinuosity braided rivers occur in the lower part of the Statfjord Formation, while shoreline processes influence the deposits towards the top of the Statfjord Formation. In general this depositional environment continued under the Toarcian age, with alternating sandy and shaly units. The Amundsen, Johansen and Burton formations are shale-dominated units, deposited during significant subsidence and eustatic sea-level rise. The sandstones in the Cook Formation extend far in to the basin, and represent a period with low rates of subsidence (Gabrielsen et al., 1990).

During the Toarcian and Bathonian age, the Drake Formation shales, and overlying sand rich Brent group were deposited. The sand rich units represent minimum subsidence deposits, while the Brent group also represents sediments from the basin margins. The maximum extent of sand occurred during the Bajocian time, where the sands reached the northern Tampen Spur area (Gabrielsen et al., 1990).

In the Late Jurassic there was an increase in fault activity, and the shaly Heather, and organic rich Draupne Formations, were deposited. During this time the sandy Krossfjord, Fensfjord and Sognefjord Formations were also deposited, but due to the high stand of the relative sea level, these sand units have limited geographical extent (Gabrielsen et al., 1990; Vollset and Doré, 1984).
2.3.3 Cretaceous

The Late Jurassic/Early Cretaceous period was a time of uplift and regression in the northwestern part of Europe. This created isolated sedimentary basins where deposition occurred in anaerobic environments. Amongst the formations deposited during this time, is the organic rich Draupne formation, a foremost source rock. This anaerobic environment came to an end during the Early Cretaceous. During the Valanginian to Barremian age, quiet conditions led to the deposition of the Åsgard and Mime Formations, which is part of the Cromer Knoll Group. The Åsgard Formation consists of calcereous claystones and marlstones, deposited in an open marine, low-energy shelf environment, with well-oxygenated bottom water conditions (Isaksen and Tonstad, 1989). According to Bugge et al. (2001), this period might have been less quiet than suggested by Isaksen and Tonstad (1989), but is represented by several tectonically induced gravity mass-flows, which deposited sand units. The Mime Formation consists of limestones and marlstones, and was deposited in a transgressional shallow marine environment. In the Mid-Late Aptian age a regression occurred, which led to erosion along the flanks of the basin and the deposition of the sandy Agat Formation. This regessional event was followed by a transgressional event of Albian age, where the sea flooded the structural highs. The Agat sandstones continued to be deposited along the structural flanks, and organic shales passed in to the calcereous Rødby Formation, which was also deposited during this time (Isaksen and Tonstad, 1989).

2.4 Petroleum geology

2.4.1 Source rocks

There are two main source rocks in the northern North Sea. The most prominent and important source rock is the oil-prone Draupne Formation, also known as Kimmeridge Clay. The other main source rock in the area is the gas-prone Heather Formation. There is also source rock potential in some coals, which are interbedded in the Ness Fm, known as the Brent coals (Lafargue and Behar, 1989; Goff, 1983).

Draupne Formation

The Draupne Formation/Kimmeridge Clay was deposited under anoxic conditions (Isaksen and Tonstad, 1989). This formation consists of type II kerogen, and is considered an excellent
oil generating source rock, which also generates gas at higher maturity levels. The Kimmeridge Clay has an average TOC of 2.7%, but the TOC content varies both laterally and vertically (Goff, 1983). The oils sourced from the Draupne Fm typically have Pr/Ph values between 1 and 1.5 (Gormly et al., 1994).

**Heather Formation**

The Heather Formation is considered an organically lean source rock, with only 1-2% TOC. The formation is, however, thick, around 1-2 km, and is capable of producing large amounts of dry gas (Goff, 1983). Oil/gas sourced from the Heather Fm. typically have Pr/Ph values between 2.15 and 4. Hydrocarbon samples with mixed signature have Pr/Ph values of 1.5 - 2.15 (Gormly et al., 1994).

**Brent Group**

The Brent Group coals are one of the most organic rich source rocks in the northern North Sea, and represent an excellent dry gas generating source rock. The delta plain facies of the Brent Groups contains 10 m thick layers of coal (Goff, 1983).

### 2.4.2 Reservoirs

This subchapter describes the Brent Groups reservoir qualities, as it is the most important reservoir rock in the region. Due to interesting findings surrounding the Agat condensate, the Agat Formation is also presented.

**Brent Group**

The Brent Group, consisting of the Broom, Rannoch, Etive, Ness and Tarbert formations are thick laterally extensive fluvial, deltaic and coastal deposits. At shallow depths the group has porosity values between 20 and 30 %. The Brent Group also shows high permeability values up to 500 mD in certain areas (Giles et al., 1992; Vollset and Doré, 1984).

**Agat Formation**

Isaksen and Tonstad (1989) argue that the Agat Formation was deposited as a submarine fan during a regression. Bugge et al. (2001), however, argue that the Agat sand formation is a
result of amalgamation of thin turbidite beds or sandy debris flows, which were deposited during a tectonically active period. Through examination of several wells in Quadrant 35, it appears to be no communication between the wells, and the sands have been interpreted to be isolated bodies.

2.4.3 Traps
Most of the traps in the northern North Sea are rotated fault blocks, where fine grain post rift sediments have been draped on top of the reservoirs and tilted fault blocks. In the specific case of the Brent group reservoirs, overlying Jurassic and Cretaceous shales seal vertically. The reservoirs are also sealed laterally by the juxtaposition of the shales and reservoir sandstones at fault contacts (Gautier, 2005).

2.4.4 Migration
Primary migration occurs when the hydrocarbons are expelled from the source rock. In the northern North Sea this occurs when enough petroleum has been formed, and is driven out of the source rock by a pressure driven flow through the pores of the source rock (Mackenzie et al., 1988).

Secondary migration refers to the migration from source rock to reservoir, and is a result of buoyant forces. Cornford (2009) established 5 modes of secondary migration that occurs in the North Sea, where migration into rotated fault blocks is the most common secondary migration mode in the northern North Sea.

Tertiary migration refers to remigration from reservoirs, and is related to the seals and traps, and their ability to retain the hydrocarbons within the reservoir. Most of the seals in the northern North Sea are mudstones. Mudstones are excellent seals for oil containing reservoirs, which is evident by the low levels of hydrocarbons in overlying sands, as well as absence of significant multipay reservoirs (Cornford, 2009).

2.5 Summary
The northern North Sea is a result of two major rifting events, which formed the mature graben topography. The area has produced several source rocks, but the Draupne
Formation/Kimmeridge Clay is the most important hydrocarbon source. The Brent Group is the most important reservoir sand, and consists of high porosity and high permeability sand at shallow depths. The Agat Formation sand units, however, appear to not be connected between wells. Most of the traps in the area are rotated fault blocks, which are vertically sealed by overlying mudstones, and laterally sealed by the juxtaposition of the sand and mudstones at fault contacts. Primary migration is a result of pressure driven flow through the pores of the source rock when hydrocarbon accumulations are at a sufficiently high enough level. Buoyant forces then force the hydrocarbons to migrate to the reservoirs, where the mudstone seals generally retain the hydrocarbons at the traps, and stop tertiary migration.
### 3 Sample set and well description

#### 3.1 Introduction

Chapter 3 presents the wells and sample set studied in this thesis. The chapter includes a brief visual description of the crude oils and condensates. The wells, from which the samples were produced, are also briefly discussed. A geographical overview of the hydrocarbon fields analyzed in this thesis is presented to enhance the readers understanding of the study area (Figure 3.2). All information in this chapter is gathered from the Norwegian Petroleum Directorate (NPD, 2017b).

#### 3.2 Description of sample set

The sample set includes a total of 17 samples (excluding NSO-1 reference sample), where 11 samples are crude oils and 6 samples are condensates. All of the samples originated in the northern North Sea and are located in Quadrants 33 to 36. The NSO-1, the Norwegian Geochemical Standard (North Sea Oil 1), originating in the Oseberg field further south, have been included in the sample set as a reference oil. The samples can be seen in figure 3.1, except the NSO-1 sample, which is stored in a non-transparent container.

##### 3.2.1 Crude oils

The crude oils display a dark brown/black color, and vary only slightly between the samples. The crude oils generally appear to have a higher viscosity than the condensates. The most viscous samples appear to be from the Gullfaks Sør field, from well 34/10-16 and 34/10-32R. Note the light coloration of Oil sample Sk1 from well 35/11-2 (Figure 3.1). The sample also displays low viscosity compared to the other oils.

##### 3.2.2 Condensates

The condensates display a generally lighter, more yellow color, and are less viscous than the oils. The most viscous condensate originated in the Valemon field (Well 34/10-23). Some color variations between the condensates are observable. The Vi2 (34/8-1) and K1 (34/11-1)
samples have a lighter color than the other condensates, which display a slightly more brown coloration (Figure 3.1).
Figure 3.1: Picture of the sample set analyzed in this thesis (Table 3.1). Note the light color of oil sample Sk1. The oils display a significantly darker color than the condensates.
Table 3.1: Overview of sample set and wells analyzed in this thesis. All information is gathered from NPD (n.d.). * m = meter, MD = Measured depth, Cond. = Condensate, DST = Drill Stem Test, MDT = Modular Dynamics Tester, ss = sandstone.

<table>
<thead>
<tr>
<th>Well</th>
<th>Sample</th>
<th>Test type</th>
<th>Test interval (m) (MD)</th>
<th>Phase</th>
<th>Unit</th>
<th>Field/Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>NSO-1</td>
<td>-</td>
<td>-</td>
<td>Oil</td>
<td>-</td>
<td>Oseberg field</td>
</tr>
<tr>
<td>33/9-14</td>
<td>St1</td>
<td>DST</td>
<td>2746.80 - 2759.80</td>
<td>Oil</td>
<td>Draupne Fm.</td>
<td>Statfjord N field</td>
</tr>
<tr>
<td>34/4-5</td>
<td>MH1</td>
<td>DST</td>
<td>3462.70 - 3480.70</td>
<td>Oil</td>
<td>Cook Fm.</td>
<td>Mort Horst (Location)</td>
</tr>
<tr>
<td>34/7-1</td>
<td>Sn1</td>
<td>DST</td>
<td>2574.00 - 2581.00</td>
<td>Oil</td>
<td>Unknown</td>
<td>Snorre field</td>
</tr>
<tr>
<td>34/8-1</td>
<td>Vi1</td>
<td>DST</td>
<td>2811.40 - 2814.40</td>
<td>Oil</td>
<td>Ness Fm.</td>
<td>Visund field</td>
</tr>
<tr>
<td>34/8-1</td>
<td>Vi2</td>
<td>DST</td>
<td>2726.80 - 2765.20</td>
<td>Cond.</td>
<td>Shetland Gp, Cromer Knoll Gp.</td>
<td>Visund field</td>
</tr>
<tr>
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<td>GS1</td>
<td>DST</td>
<td>3397.00 - 3407.00</td>
<td>Oil</td>
<td>Ness and Etive Fm.</td>
<td>Gullfaks Sør field</td>
</tr>
<tr>
<td>34/10-23</td>
<td>Val</td>
<td>DST</td>
<td>4085.00 - 4095.00</td>
<td>Cond.</td>
<td>Tarbert Fm.</td>
<td>Valenon field</td>
</tr>
<tr>
<td>34/10-32</td>
<td>GS2</td>
<td>DST</td>
<td>3368.00 - 3374.00</td>
<td>Oil</td>
<td>Nansen Fm.</td>
<td>Gullfaks Sør field</td>
</tr>
<tr>
<td>34/11-1</td>
<td>K1</td>
<td>DST</td>
<td>4114.00 - 4093.50</td>
<td>Cond.</td>
<td>Ness Fm.</td>
<td>Kvitebjorn field</td>
</tr>
<tr>
<td>34/11-2</td>
<td>N1</td>
<td>DST</td>
<td>4260.00 - 4185.00</td>
<td>Cond.</td>
<td>Ness, Etive, and Rannoch Fm.</td>
<td>Nokken Discovery</td>
</tr>
<tr>
<td>35/3-4</td>
<td>A1</td>
<td>DST</td>
<td>3445.00- 3471.00</td>
<td>Cond.</td>
<td>Agat Fm.</td>
<td>Agat field</td>
</tr>
<tr>
<td>35/9-1</td>
<td>G1</td>
<td>DST</td>
<td>2285.00 - 2291.80</td>
<td>Oil</td>
<td>Dunlin Gp.</td>
<td>Gjoa field</td>
</tr>
<tr>
<td>35/9-7</td>
<td>Sk1</td>
<td>MDT</td>
<td>2776.70</td>
<td>Oil</td>
<td>Intra Heather Fm. ss</td>
<td>Skarfjell field</td>
</tr>
<tr>
<td>35/11-2</td>
<td>Ve1</td>
<td>DST</td>
<td>3524.00 - 3542.00</td>
<td>Cond.</td>
<td>Oseberg Fm.</td>
<td>Vega field</td>
</tr>
<tr>
<td>35/11-15</td>
<td>F1</td>
<td>MDT</td>
<td>2941.00</td>
<td>Oil</td>
<td>Intra Heather Fm. ss</td>
<td>Fram H-Nord field</td>
</tr>
<tr>
<td>35/12-4</td>
<td>R1</td>
<td>DST</td>
<td>3127.00 - 3082.00</td>
<td>Oil</td>
<td>Ness Fm.</td>
<td>Ryggsteinen Ridge</td>
</tr>
<tr>
<td>36/7-1</td>
<td>G2</td>
<td>DST</td>
<td>2368.00 - 2363.00</td>
<td>Oil</td>
<td>Fensfjord Fm.</td>
<td>Gjoa field</td>
</tr>
</tbody>
</table>
3.3 Well description and sample retrieval

3.3.1 Well 33/9-14

Appraisal Well 33/9-14 was drilled on the Statfjord Nord field on Tampen Spur. Oil was discovered in the Draupne Formation at 2676 m. OWC (oil water contact) appears at 2747 m. Sample St1 was produced by Drill Stem Test (DST) Test 1 in the 2746.80 - 2759.80 m interval. DST reservoir temperature was 96 °C.

3.3.2 Well 34/4-5

Well 34/4-5 is a Wildcat well, and was drilled on the Mort Horst in the northeastern part of the block. The well spans geologic time range from perhaps as early as the Triassic to Pleistocene. Two DSTs have been carried out. The sample analyzed in this thesis came from test interval 3462.70 - 3480.70 m (MD) as part of the Cook Fm.
3.3.3 Well 34/7-1

Well 34/7-1 is a wildcat well, and was drilled on the E-structure in block 34/7. Three DSTs have been performed in the Oil bearing Triassic Lunde Fm. The sample analyzed in this thesis was produced from test interval 2574.00 - 2581.00 m (MD). During drilling bottom hole temperature (BHT) reached 96.1 ° C.

3.3.4 Well 34/8-1

Wildcat Well 34/8-1 was drilled on prospect “A”, the main prospect on the block. Main objective was to prove hydrocarbon accumulations in the Brent Gp. Two samples in this thesis were produced from this well. Sample Vi1 is an oil, and was acquired from DST test interval 2811.40 - 2814.40m (MD). Sample Vi1 is retained in the Ness Fm. Condensate sample Vi2 is produced from DST 3, in test interval 2726.80 - 2765.20 m (MD). The gas condensate is reserved in the Shetland Gp and Cromer Knoll Gp.

3.3.5 Well 34/10-16

Well 34/10-16 is an appraisal well, and was drilled on the Gullfaks Sør structure, approximately 8 km south of the Gullfaks field. The Brent Gp., which came in at 3171 m, contains both oil and gas. The oil sample GS1 analyzed in this thesis was produced from a DST, with test interval 3397.00 – 3407.00 m (MD). This depth corresponds to the Ness and Etive Fm.

3.3.6 Well 34/10-23

Well 34/10-23 is a wildcat well, and was drilled on the Gullfaks Gamma structure, south-south east of the Gullfaks Sør field. The sample analyzed in this thesis (Va1), was produced from a DST in the interval 4085.00 – 4095.00 m (MD). The condensate sample was reserved in the Tarbert Fm.
3.3.7 Well 34/10-32 R

Well 34/10-32 R is a re-entry well on the Gullfaks South structure. The oil sample analyzed in this thesis (GS2) was produced from a DST in the interval 3368.00 – 3374.00 m (MD). This depth interval corresponds to the Nansen Fm.

3.3.8 Well 34/11-1

Well 34/11-1 is a Wildcat well drilled on the Tjalve Terrace south-east of the Gullfaks field. The sample analyzed in this thesis, condensate K1, was produced from a DST in the interval 4114.00 - 4093.50 m (MD). This depth interval corresponds to the Ness Fm.

3.3.9 Well 34/11-2 S

Well 34/11-2 S is a Wildcat well drilled on the Tjalve Terrace east of the Gullfaks field. The sample analyzed in this thesis, condensate “N1”, was produced from a DST in the interval 4260.00 - 4185.00 m (MD). The condensate was reserved in the Ness Fm, Etive Fm, and Rannoch Fm.

3.3.10 Well 35/3-4

Well 35/3-4 is a Wildcat well drilled approximately 50 km east of Måløy, Norway. The sample analyzed in this thesis, condensate “A1”, was produced from a DST in the interval 3445.00- 3471.00 m (MD). This depth interval corresponds to the Agat Fm.

3.3.11 Well 35/9-1

Well 35/9-1 is a Wildcat well drilled approximately on the Måløy slope, north of the Horda platform. The well was drilled on an “A-structure”, which is an asymmetric horst, and is part of the Gjøa field. The sample analyzed in this thesis, the crude oil “G1”, was produced from a DST in the interval 2285.00 - 2291.80 m (MD). The oil sample was originally reserved in the Dunlin Gp.
3.3.12 Well 35/9-7

Well 35/9-1 is a Wildcat well drilled on the Skarfjell prospect on Ryggsteinen Ridge, south west of the Gjøa field. The sample analyzed in this thesis, the condensate “Sk1”, was produced from a Modular Dynamics Tester (MDT) at a depth of 2776.70 m (MD). The oil sample was originally reserved in the Intra Heather Fm. ss.

3.3.13 Well 35/11-2

Well 35/11-2 is a Wildcat well drilled on the boundary between the Horda Platform and the Viking Graben, north of the Troll field. The sample analyzed in this thesis, condensate “Ve1”, was produced from a DST in the interval of 3524.00 - 3542.00 m (MD). This depth interval corresponds to the Oseberg Fm.

3.3.14 Well 35/11-15 S

Well 35/11-15 S is a Wildcat well drilled on Fram/Astero area west of the Sognefjord. The sample analyzed in this thesis, the crude oil “F1”, was produced from a Modular Dynamics Tester (MDT) at a depth of 2941.00 m (MD). The oil was originally reserved in the Intra Heather Fm Ss.

3.3.15 Well 35/12-4 S

Well 35/12-4 S is a Wildcat well drilled on the Ryggsteinen Ridge/Uer Terrace. The sample analyzed in this thesis, crude oil “R1” was produced from a DST in the interval of 3127.00 - 3082.00 m (MD). This depth interval corresponds to the Ness Fm.

3.3.16 Well 36/7-1

Well 36/7-1 is a Wildcat well drilled on the Måløy Slope approximately 4 km south east of the Gjøa Discovery well 35/9-1. The sample analyzed in this thesis, crude oil “G2”, was produced from a DST in the interval of 2368.00 - 2363.00 m (MD). This depth interval corresponds to the Fensfjord Fm.
4 Analytical methods and laboratory procedures

4.1 Introduction

This chapter describes the lab procedures and analytical methods used to provide the molecular composition of the hydrocarbon samples. To determine the molecular composition, three methods are used:

1. Gas Chromatography- Flame Ionization Detection (GC-FID)
2. Gas Chromatography- Mass Spectrometry (GC-MS)
3. Gas Chromatography- Tandem Mass Spectrometry (GC-MS/MS)

The aforementioned methods allow for a qualitative analysis of the hydrocarbon samples to be completed by applying the interpretation parameters introduced in chapter 5. All lab procedures were completed in the Organic Geochemical Lab located in Geologibygningen, Blindern, University of Oslo.

4.2 GC-FID

Gas Chromatography – Flame Ionization Detection (GC-FID) is fast and comparatively inexpensive method to analyze hydrocarbon samples in order to show the main molecular groups that constitutes the petroleum sample. Typical compounds recorded are the isoprenoids pristane and phytane, and the overall n-alkane envelope. Often only the C10+ components are recorded, but in this thesis light HC parameters among the C6-7 HC species were recorded, which contains geochemical information about the main components, eg. n-alkanes, toluene, benzene, isoprenoids (Weiss et al., 2006).

The process begins with the injection of the analyte with a syringe through a septum into the GC-FIDs heated entry port, where the sample is vaporized. A carrier gas, in this analysis - N₂, transports the analyte. Inside the chromatographic column, a thin film layer acts as the stationary phase, which separates the analyte as it moves through the column. The analyte eventually flows through a Flame Ionization Detector (FID),
which records the response, and displays it on the computer as a chromatogram. In this study an open tabular column was used as the stationary phase. The film might, however, have been a little on the thin side for the light hydrocarbon analysis, and it might not have shielded the analyte against the silica surface of the column, which produced some peak-tailing in the chromatograms (Harris, 2010). A general overview of the process can be seen in Figure 4.1

Figure 4.1: Overview of GC-FID method. Figure from Pedersen (2002).

4.2.1 Technical information

All samples were analyzed on a Varian CP-3800 GAS CHROMATOGRAPH instrument equipped with an HP-ULTRA 1 column (50m×0.2mm i.d., film thickness 0.33 μm).

4.2.2 Light hydrocarbon GC-FID analysis – C7

Approximately 1 μL of pure crude oil or condensate sample was manually injected with a Hamilton 10-μL syringe. Because of the manual injection, human inconsistencies may arise, and the injected volume appears to vary to a degree throughout this analysis. The GC-FID column was first cleaned by a DCM injection
and quick run, before the samples were injected. All samples were analyzed with the following light hydrocarbon GC-FID program:

1. Initial temperature: 30 °C (Hold 4 min)
2. Temperature increased with 3 °C/min up to 90 °C.
3. Temperature increased with 20 °C/min up to 310 °C.
4. Entire program lasts 83 min

4.2.3 Medium range hydrocarbon GC-FID analysis

Two quick runs of DCM cleaned the column before the samples were injected. In this study the analyte was mixed with cyclohexane, and injected by an autosampler.

All sample runs were analyzed under the following settings:

1. Initial temperature: 80 °C (1 min hold)
2. Temperature increased with 4.5 °C/min up to 320 °C.
3. Temperature (320 °C) held for 25 min
4. Entire program lasts 80 min.

4.3 GC-MS and GC-MS/MS

The GC-MS and GC-MS/MS process works almost exactly the same as the GC-FID, except the method of detection is different. The carrier gas, in this case He, transports the analyte through the column, which separates the compounds within the analyte, which can be detected by a Mass Spectrometer (MS-Unit). The MS-unit is a sensitive detector capable of qualitative and quantitative information. The MS-unit ionizes the gaseous molecules, which are detected according to mass/charge (m/z) ratios. GC-MS/MS (SRM) only slightly deviates from regular GC-MS (SIM). Instead of monitoring selected ions, it monitors the transition from precursor ion (parent) to product ions, or daughter ions (Harris, 2010), and this helps in identifying small amount of compounds in a complex sample matrix. This is particularly useful for some age specific biomarkers. A general overview of the GC-MS process can be seen in figure 4.2.
4.3.1 Technical information

All samples were analysed on a Thermo Scientific TSQ 8000 Triple Quadropole MS instrument. The stationary column used was a Thermo TG-XLBMS (60 m × 0.25 mm i.d., film thickness 0.25 μm). The machine was cleaned with two quick runs of cyclohexane before the samples were run. All samples were injected by autosampler.


4.3.2 GC-MS analysis

Selected Ion Monitoring (SIM) mode, which monitors only selected m/z-ratios, was used in this thesis to study saturated and aromatic compounds. The mass/charge ratios monitored were 191, 217, 218, 231, 253, 178, 192, and 198.

All sample runs were analyzed under the following settings:

1. Initial temperature: 40 °C (Hold 1 min)
2. Temperature increased with 20 °C/min up to 180 °C.
3. Temperature increase of 1.7 °C/min up to 310 °C
4. Constant temperature of 310 °C for 40 minutes.
5. Cooling of column before next sample injection

4.3.3 GC-MS/MS analysis

Selected Reaction Monitoring (SRM) mode was used for the analysis of aliphatic compounds. In this thesis the reaction of m/z = 358 ➔ 217 was monitored to give information on the age biomarkers 24-nordiacholestanes and 27-nordiacholestanes. During GC-MS/MS analysis, argon was used as the collision gas.

All sample runs were analyzed under the following settings:

1. Initial temperature: 40 °C (hold 1 min)
2. Temperature increased with 20 °C/min up to 180 °C.
3. Temperature increase of 1.7 °C/min up to 310 °C
4. Constant temperature of 310 °C for 40 minutes.
5. Cooling of column before next sample injection

4.4 Sample preparation

All samples have been extracted from original containers (vial) sent from NPD, and injected into new vials, which acted as a working sample set during this thesis. This was done to avoid loss of light hydrocarbon compounds for future use.
4.4.1 GC-FID

This thesis used GC-FID analysis on two different occasions. One run was with intent to study the C7 compounds. The other GC-FID run – typically referred to as the C10+ run was completed with the intent to study the n-C17 to n-C34 compounds.

Light Hydrocarbon (C7 compounds)

During the light hydrocarbon analysis, approximately 1 μL of pure crude oil or condensate was manually injected into the GC-FID entry port, and the samples were not manipulated by preparation, excluding extraction from vials into GC-FID column.

Full range GC-FID

For the full range GC-FID analysis, approximately 1 pipette drop of pure crude oil or condensate was mixed with approximately 3 drops of cyclohexane in 4-mL vials. The vials were placed in the autosampler, which automatically injected 2 μL of each sample into the GC-FID column.

4.4.2 GC-MS and GC-MS/MS

For GC-MS and GC-MS/MS it is important to remove unwanted n-alkanes which are very abundant compared to biomarkers and often cause unwanted interference in the study of particular ions e.g. 191. This removal of n-alkanes was accomplished by a process achieved with molecular sieving. A spoon tip of “HiSiv 3000”, a framework MFI zeolite provided by Honeywell UOP, was inserted into a 15 mL vial. Approximately 2 drops of pure crude oil or condensate were mixed with 1 mL of cyclohexane used as solvent. Five pipette drops of this mixture were subsequently applied to the sieving powder in the 15 mL vial. The solution was then stirred together with the sieving powder, before being pumped with the pipette. This was done until the mixture was homogenized. The mixture was subsequently centrifuged at around 2000 rpm for 3 minutes. The process was repeated twice for each sample, before the analytes were transferred into 4 mL vials, which fit the autosampler. 2 μL analyte of each sample were injected during GC-MS and GC-MS/MS analysis.
5 Petroleum geochemical interpretation parameters

5.1 Introduction

Petroleum geochemical interpretation parameters refer to analytical interpretation parameters, which relate relative or absolute abundance of certain chemical compounds in the petroleum sample to one or more processes. These processes include e.g. migration and phase fractionation, thermal maturity and biodegradation. This chapter describes the various interpretation parameters used to analyze the petroleum samples, and introduces the theoretical background of these parameters.

5.2 Light hydrocarbon GC-FID analysis

In this thesis C7-compounds were analyzed during the light hydrocarbon GC-FID analysis. The compounds are listed in Table 5.1 and identified in figure 5.1.

Table 5.1: Overview of light hydrocarbon compounds analyzed in this thesis.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C7</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>MCYC6</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>Tol</td>
<td>Toluene</td>
</tr>
</tbody>
</table>
5.2.1 C7 compounds

The light hydrocarbon compounds studied have the same number of carbon atoms, but have a different chemical structure. The compound n-Heptane is a straight-chain alkane. Methylcyclohexane is a cyclohexane with a methyl-group, and is part of the saturated hydrocarbons. Toluene, also known as methylbenzene, is an aromatic compound. The chemical structures of the compounds are shown in figure 5.2 a, b, and c respectively (NCBI, 2017).

![Figure 5.1: Identified light hydrocarbon peaks on GC-FID chromatogram of reference sample NSO-1.](image)

![Figure 5.2: 2-D structures of C7-compounds (NCBI, 2017).](image)
5.2.2 Aromaticity and Paraffinicity

Aromaticity and paraffinicity are parameters introduced by Thompson (1987), and are defined as toluene/n-heptane ratio and n-heptane/methylcyclohexane ratio respectively. In this thesis, the parameters are used to infer the degree of evaporative fractionation, thermal maturity, biodegradation and water washing of the sample set. Evaporative fractionation leads to an increase in aromaticity, and a slight decrease in paraffinicity values. Thermal maturity will manifest itself in relation to an increase in paraffinicity and a slight increase in aromaticity, due to progressive thermal cracking. Biodegradation is related to a decrease in both parameters. Water washing will be associated with an increase in paraffinicity and a decrease in aromaticity. The decrease in aromaticity is due to stripping of low-molecular weight aromatic compounds (Canipa-Morales et al., 2003; Thompson, 1987; Thompson, 1983).

5.3 GC-FID

The following subchapter describes the analytical parameters used in GC-FID analysis, as well as an overview of the identified compounds (Table 5.2; Figure 5.2).

Table 5.2: Overview of compounds analyzed by GC-FID in this thesis.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pristane</td>
</tr>
<tr>
<td>Ph</td>
<td>Phytane</td>
</tr>
<tr>
<td>n-CX</td>
<td>n-alkane of carbon number “X”</td>
</tr>
</tbody>
</table>
Figure 5.3: Identified peaks on GC-FID chromatogram of reference sample NSO-1, which is an oil from the Oseberg Field.

5.3.1 Distribution of n-alkanes and presence of unresolved complex mixture (UCM)

The distribution and pattern of the n-alkanes seen on a GC-FID chromatogram can be used to gather information about maturity and organic facies of the samples. The peak heights generally decrease with an increase in carbon number, which leads to a concave curve on the chromatogram in the case of oils, which typically contain GC-FID resolvable n-alkanes out to C35. In case of condensates the peaks decrease more linearly and few alkanes are visible in GC-FID at higher carbon numbers than C25. A chromatogram with bimodal distribution has two maximum groups of n-alkanes, with a minimum between. Biodegradation can also be observed on the GC-FID chromatograms. This is evident when there is a relative rise in UCM compared to the n-alkanes, which show a relative decrease compared to isoprenoids and aromatic compounds. Heavily biodegraded samples show a great reduction in peak heights of n-alkanes typically around C10 for incipient biodegradation, or no peak to be detected of the important compounds pristane, phytane and n-alkanes (Sutton et al., 2005; Peters and Moldowan, 1993).
5.3.2 Carbon Preference Index (CPI) and Odd-Even Predominance (OEP)

The Carbon Preference Index, introduced by Bray and Evans (1961), takes the progressive evolution of the long-chained n-alkanes distribution to determine maturity and terrestrial input of OM. The CPI show certain molecular compounds displaying a specific carbon number configuration, where fatty acids displays a predominance for even numbers, and n-alkanes displays a predominance for odd numbers. Odd-carbon number predominance are either directly created from higher continental plants, or early diagenesis, where even numbered alcohols, acids and esters are transformed into odd carbon numbered n-alkanes. Sediments with both marine and terrestrial OM input, displays an odd over even predominance due to the terrestrial OM consisting of higher amounts n-alkanes than the marine OM (Tissot and Welte, 1984).

Carbonates show even number predominance. Shimoyama and Johns (1972) proposes that this is a result of the degradation of fatty acids, where calcium carbonate acts as a catalyst, and causes the loss of two carbon atoms by beta cleavage, leading to an even over odd carbon number predominance.

It is also proposed that the mineral montmorillonite acts as a catalyst for fatty acid degeneration, and causes the loss of one carbon-atom, leading to an odd over even predominance for siliciclastics

Even carbon number predominance for carbonates might also be caused by the lack of terrestrial OM input to a depositional environment which favors carbonate production (Powell and Mokirdy, 1973).

The CPI and OEP parameters are calculated from the equations (5.1 – 5.4) (Peters et al., 2007).

\[
\text{CPI} = \frac{1}{2} \left( \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}} \right)
\]  \hspace{1cm} (5.1)

\[
\text{CPI (1)} = 2 \left( \frac{C_{23}+C_{25}+C_{27}+C_{29}}{C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}} \right)
\]  \hspace{1cm} (5.2)
\[
OEP = \frac{C_{21}+6C_{23}+C_{25}}{4(C_{22}+C_{24})}
\]  \hspace{1cm} (5.3)

\[
OEP (1) = \frac{C_{25}+6C_{27}+C_{29}}{4(C_{26}+C_{28})}
\]  \hspace{1cm} (5.4)

### 5.3.3 Pristane/phytane ratio

Pristane (Pr) and phytane (Ph) are isoprenoid isoalkane compounds commonly derived from phytol, which is a side chain of chlorophyll. If phytol exists in an oxic environment it is oxidized to Pr, while an anoxic environment leads to phytol being reduced to Ph. This makes the Pr/Ph ratio an indicator of the redox potential of the depositional environment where the chlorophyll was deposited. Pr/Ph > 1 indicates a terrestrial depositional environment, while Pr/Ph < 1 indicates marine depositional environment (Peters et al., 2007). Pr/Ph = 1.3 – 1.7, indicates marine oil, Pr/Ph close to 2.5 indicates a marine environment with considerable terrestrial input, and Pr/Ph = 3 – 10 indicates coal/peat environment (Peters and Moldowan, 1993).

The Pr/Ph ratio can also be used as a maturity parameter, as the ratio will increase with maturity, due to the fact that phytane is a more unstable compound relative to pristane (Alexander et al., 1981).

There are however several limitations to the Pr/Ph ratio as a parameter. Peters and Moldowan (1993) argue that both Pr and Ph can have bacterial origin, which elevates the level of doubt regarding the determination of organic facies.

### 5.3.4 Pristane/n-C17 and Phytane/n-C18 ratios

Pr/n-C17 and Ph/n-C18 ratios are used to determine maturity, biodegradation and organic facies of hydrocarbons. The ratios are dependent on the input source of organic matter, and can be used in determining depositional environments (Alexander et al., 1981). The ratio is often used as a thermal maturity indicator, as the isoprenoids break down faster than n-alkanes, which implies that lower ratios indicate higher thermal maturity. It is vital that the parameter is used with care, given that both organic input and biodegradation affect the ratios (Peters and Moldowan, 1993).
5.3.5 Waxiness ratio

Higher molecular weight n-alkanes are represented more in terrestrial derived kerogen relative to marine kerogen (Tissot and Welte, 1984). Short-chained n-alkanes are shown to be of algal origin, thus a ratio between long-chained and short-chained n-alkanes can be used to indicate OM origin. The ratio is called waxiness, and is sensitive to thermal maturity and biodegradation, which should be considered when the parameter is used. The formula to calculate waxiness is shown in Eq. 5.5 (Justwan et al., 2005).

\[
\text{Waxiness} = \frac{n-C_{17}}{n-C_{17} + n-C_{27}}
\]  

(5.5)

5.4 GC-MS

GC-MS is used to identify ionized molecules with specific mass to charge (m/z) ratios. Specific organic compounds are identified as specific peaks on the chromatograms, and then quantified to determine the relative abundance of these different organic compounds. The NSO-1 chromatograms are used to display the identified and labeled chemical compounds. The m/z-ratios used during SIM mode to create GC-MS chromatograms are shown in Table 5.3.

Table 5.3: Overview of selected m/z-ratios and compounds used during GC-MS analysis

<table>
<thead>
<tr>
<th>m/z-ratio</th>
<th>Chemical compounds</th>
<th>Hydrocarbon fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>191</td>
<td>Terpanes</td>
<td></td>
</tr>
<tr>
<td>217</td>
<td>Steranes</td>
<td>Saturated hydrocarbons</td>
</tr>
<tr>
<td>218</td>
<td>Steranes</td>
<td></td>
</tr>
<tr>
<td>231</td>
<td>Triaromatic steroids</td>
<td></td>
</tr>
<tr>
<td>253</td>
<td>Monoaromatic steroids</td>
<td></td>
</tr>
<tr>
<td>178</td>
<td>Phenanthrene</td>
<td>Aromatic hydrocarbons</td>
</tr>
<tr>
<td>192</td>
<td>Methylphenanthrenes</td>
<td></td>
</tr>
<tr>
<td>198</td>
<td>Methyl dibenzothiophenes</td>
<td></td>
</tr>
</tbody>
</table>

5.4.1 Terpanes

Terpanes are part of the saturated hydrocarbon fraction, and are identified on m/z = 191. The terpanes are used for depositional environment indication and correlation (Peters et al., 2007a). The compounds analyzed in this study are shown in table 5.4 and figure 5.4.
5.4.2 Steranes

Steranes, which belong to the saturated hydrocarbon fraction, are identified on m/z = 217 and m/z = 218 chromatograms. The steranes are used to indicate maturity, organic facies and correlation. Steranes originates as products of sterols (Peters et al., 2007). The steranes analyzed in this study are shown in tables 5.5 and 5.6, and in figures 5.5 and 5.6.

Table 5.4: Overview of the terpane-compounds identified on m/z=191 chromatogram.

<table>
<thead>
<tr>
<th>Peak Label</th>
<th>Stereochemistry</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td></td>
<td>Tricyclic terpane</td>
</tr>
<tr>
<td>Q</td>
<td></td>
<td>Tricyclic terpane</td>
</tr>
<tr>
<td>R</td>
<td>(17R+17S)</td>
<td>Tricyclic terpane</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>Tetracyclic terpane</td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>Tricyclic terpane</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>Tricyclic terpane</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>18α (H)-trisnorneohopane</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>17α (H)-trisnorhopane</td>
</tr>
<tr>
<td>Z</td>
<td></td>
<td>17 α (H), 21β(H)-bisnorhopane</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>17α(H), 21β(H)-norhopane</td>
</tr>
<tr>
<td>29Ts</td>
<td></td>
<td>18α (H)-30-norneohopane</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>15α-methyl-17α (H)-27-diahopane</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>17β (H), 21α (H)-30-normorethane</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>17α (H), 21β (H)-hopane</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>17β (H), 21α (H)-moretane</td>
</tr>
<tr>
<td>G</td>
<td>22S</td>
<td>17α (H), 21β (H)-22-homohopane</td>
</tr>
<tr>
<td>H</td>
<td>22R</td>
<td>17α (H), 21β (H)-22-homohopane</td>
</tr>
</tbody>
</table>
Figure 5.4: NSO-1 chromatogram of m/z = 191 with identified peaks

Table 5.5: Overview of sterane-compounds identified on m/z = 217 GC-MS chromatogram.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Stereochemistry</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>20S</td>
<td>13β(H), 17α(H), 20(S)-cholestane (diasterane)</td>
</tr>
<tr>
<td>b</td>
<td>20R</td>
<td>13β(H), 17α(H), 20(R)-cholestane (diasterane)</td>
</tr>
<tr>
<td>q</td>
<td>20S</td>
<td>24-ethyl-5α(H), 14α(H), 17α(H), 20(S)-cholestane</td>
</tr>
<tr>
<td>r</td>
<td>20R</td>
<td>24-ethyl-5α(H), 14β(H), 17β(H), 20(R)-cholestane</td>
</tr>
<tr>
<td>s</td>
<td>20S</td>
<td>24-ethyl-5α(H), 14β(H), 17β(H), 20(S)-cholestane</td>
</tr>
<tr>
<td>t</td>
<td>20R</td>
<td>24-ethyl-5α(H), 14α(H), 17α(H), 20(R)-cholestane</td>
</tr>
</tbody>
</table>
Figure 5.5: NSO-1 chromatogram of m/z = 217 with identified peaks.

Table 5.6: Overview of regular sterane-compounds identified on m/z = 218 GC-MS chromatogram.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Stereochemistry</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>20S</td>
<td>C_{27} (5α(H), 14β(H), 17β(H), 20(S)-cholestanete)</td>
</tr>
<tr>
<td>o</td>
<td>20S</td>
<td>C_{28} (24-methyl-5α(H), 14β(H), 17β(H), 20(S)-cholestanete)</td>
</tr>
<tr>
<td>s</td>
<td>20S</td>
<td>C_{29} (24-ethyl-5α(H), 14β(H), 17β(H), 20(S)-cholestanete)</td>
</tr>
</tbody>
</table>
5.4.3 Triaromatic steroids

Triaromatic steroids are identified on chromatogram m/z = 231, and are part of the aromatic hydrocarbon fraction. Triaromatic steroids are used as maturity indicators, and are valid over a wide range of maturities (Figure 5.11). The triaromatic steroids analyzed in this thesis are shown in table 5.7 and figure 5.7 (Peters et al., 2007).

5.4.4 Monoaromatic steroids

Monoaromatic steroids are part of the aromatic hydrocarbon fraction, and can be identified on chromatogram m/z = 253. The monoaromatic steroids are used as maturity indicators in combination with triaromatic steroids (Peters et al., 2007). The monoaromatic compounds analyzed in this thesis are listed in table 5.8 and identified in figure 5.8.
Table 5.7: Overview of triaromatic steroids analyzed in this thesis. The compounds have been identified on GC-MS chromatogram m/z = 231.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>C_{20} triaromatic steroid (TA)</td>
</tr>
<tr>
<td>g1</td>
<td>C_{28} triaromatic steroid (TA)</td>
</tr>
</tbody>
</table>

Figure 5.7: NSO-1 GC/MS chromatogram of m/z = 231 with identified peaks.

Table 5.8: Monoaromatic steroid peak identified on GC-MS chromatogram m/z = 253.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>h1</td>
<td>C_{29} monoaromatic steroid (MA)</td>
</tr>
</tbody>
</table>
5.4.5 Phenantrene, methylphenantrenes and methyldibenzothiopenes

Phenantrene, methylphenantrenes, and methyldibenzothiopenes are aromatic hydrocarbons. They can be identified on chromatograms m/z = 178, 192 and 198 respectively. Chemical compounds identified on chromatograms m/z = 178, 192 and 198 have been listed in table 5.9. The identified phenantrene peak can be seen in figure 5.9. Methylphenantrenes and methyldibenzothiopenes are identified in figure 5.10.
Table 5.9: Overview of chemical compounds identified on GC-MS chromatograms m/z = 178, 192 and 198.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
<th>m/z-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Phenanthrene</td>
<td>178</td>
</tr>
<tr>
<td>3-MP</td>
<td>3-methylphenantrene</td>
<td>192</td>
</tr>
<tr>
<td>2-MP</td>
<td>2-methylphenantrene</td>
<td>192</td>
</tr>
<tr>
<td>9-MP</td>
<td>9-methylphenantrene</td>
<td>192</td>
</tr>
<tr>
<td>1-MP</td>
<td>1-methylphenantrene</td>
<td>192</td>
</tr>
<tr>
<td>4-MDBT</td>
<td>4-methyldibenzothiophene</td>
<td>198</td>
</tr>
<tr>
<td>(3+2) - MDBT</td>
<td>(3 and 2)-methyldibenzothiophene</td>
<td>198</td>
</tr>
<tr>
<td>1-MDBT</td>
<td>1-methyldibenzothiophene</td>
<td>198</td>
</tr>
</tbody>
</table>

Figure 5.9: Phenanthrene (P) identified on NSO-1 GC-MS chromatogram m/z = 178.
Figure 5.10: Identified methyldibenzothiophenes and methylphenantrenes peaks on GC-MS chromatograms m/z = 198 (Top) and 192 (lower).

5.4.6 Interpretation Parameters

This thesis uses a total of 27 GC-MS derived interpretation parameters (Table 5.10). This sub-chapter includes a short description of each parameter. Figure 5.11 displays valid maturity ranges for several of the parameters used in this thesis.
Table 5.10: GC-MS derived interpretation parameters used in this thesis.

<table>
<thead>
<tr>
<th>Number</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$T_s/(T_s + T_m)$ (Seifert and Moldowan, 1978)</td>
</tr>
<tr>
<td>2</td>
<td>Diahopane/(diahopane + normorethane) (Cornford et al., 1986)</td>
</tr>
<tr>
<td>3</td>
<td>$22S/(22S + 22R)$ of $C_{31} - 17\alpha$ (H), $21\beta$-hopanes (Mackenzie et al., 1980)</td>
</tr>
<tr>
<td>4</td>
<td>$C_{36}$-hopane/$C_{36}$-hopane + $C_{36}$-morethane (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>5</td>
<td>$C_{29}T_s/(C_{29}T_s + norhopane)$ (Moldowan et al., 1991)</td>
</tr>
<tr>
<td>6</td>
<td>Bisnorhopane/(bisnorhopane + norhopane) (Moldowan et al., 1984)</td>
</tr>
<tr>
<td>7</td>
<td>$C_{23}$-$C_{29}$ tricyclic terpanes/$C_{30}$ $\alpha\beta$-hopane (Mello et al., 1988)</td>
</tr>
<tr>
<td>8</td>
<td>$C_{24}$ tetracyclic terpane/$C_{30}$ $\alpha\beta$-hopane (Mello et al., 1988)</td>
</tr>
<tr>
<td>9</td>
<td>Hopane/sterane ratio (Mackenzie, 1984)</td>
</tr>
<tr>
<td>10</td>
<td>$\beta\beta/(\beta\beta + \alpha\alpha)$ of $C_{29}$ (20R + 20S) sterane isomers (Mackenzie et al., 1980)</td>
</tr>
<tr>
<td>11</td>
<td>$20S/(20S + 20R)$ of $C_{29}$ $5\alpha$ (H), $14\alpha$ (H), $17\alpha$ (H) steranes (Mackenzie et al., 1980)</td>
</tr>
<tr>
<td>12</td>
<td>Diasteranes/(diasteranes + steranes) (Seifert and Moldowan, 1978)</td>
</tr>
<tr>
<td>13</td>
<td>$% C_{27}$ of $C_{27} + C_{28} + C_{29}$ $\beta\beta$-cholestanes (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>14</td>
<td>$% C_{28}$ of $C_{27} + C_{28} + C_{29}$ $\beta\beta$-cholestanes (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>15</td>
<td>$% C_{29}$ of $C_{27} + C_{28} + C_{29}$ $\beta\beta$-cholestanes (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>16</td>
<td>$C_{20}$/(C20 + C28) triaromatic steroids (TA) (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>17</td>
<td>$C_{28}$ TA/(C28 TA + C29 MA) (Mackenzie et al., 1985)</td>
</tr>
<tr>
<td>18</td>
<td>Methylphenantrene ratio (MPR) (Radke et al., 1982b)</td>
</tr>
<tr>
<td>19</td>
<td>Methylphenantrene index 1 (MPI1) (Radke et al., 1982a)</td>
</tr>
<tr>
<td>20</td>
<td>Methylphenantrene distribution fraction 1 (MPDF1) (Kvalheim et al., 1987)</td>
</tr>
<tr>
<td>21</td>
<td>Methyl dibenzothiophene ratio (MDR) (Radke, 1988)</td>
</tr>
<tr>
<td>22</td>
<td>Calculated vitrinite reflection $R_m(1) = 1.1 * \log_{10} MPR + 0.95$ (Radke, 1988)</td>
</tr>
<tr>
<td>23</td>
<td>Calculated vitrinite reflection $% R_c = 0.6 * MPI1 + 0.4$ (Radke, 1988)</td>
</tr>
<tr>
<td>24</td>
<td>Calculated vitrinite reflection $% R_o = 2.242 * F_1 - 0.166$ (Kvalheim et al., 1987)</td>
</tr>
<tr>
<td>25</td>
<td>Calculated vitrinite reflection $R_m = 0.073 * MDR + 0.51$ (Radke, 1988)</td>
</tr>
<tr>
<td>26</td>
<td>$3$-methylphenanthrene/$4$-methyl dibenzothiophene (Hughes et al., 1995)</td>
</tr>
<tr>
<td>27</td>
<td>Methyl dibenzothiophenes/methylphenanthrenes (Radke et al., 2001)</td>
</tr>
</tbody>
</table>
Figure 5.11: Valid ranges for GC-MS biomarker interpretation parameters, which have been correlated with vitrinite reflection values and oil window stages. Note the non-linearity. From Peters et al. (2007).

**Parameter 1: Ts/(Ts+Tm)**

Parameter 1 is the ratio between C\textsubscript{27} 18α-trisnorhopane II (Ts) and C\textsubscript{27} 17α-trisnorhopane (Tm). An increase in this ratio is related to an increase in maturity, due to the fact that Tm is less stable than Ts (Peters et al., 2007). The ratio is however dependent on source input, and is also used to indicate the depositional environment of source rocks (Moldowan et al., 1986). The ratio is valid into the condensate/wet gas stage, which is useful in this thesis, as six of the samples are condensates (Figure 5.11).

**Parameter 2: Diahopane/(diahopane + normoretane)**

Parameter 2 is the ratio between C\textsubscript{30}-diahopane and C\textsubscript{29}-normoretane. The ratio increases with increasing maturity. This is the result of a relative decrease in C\textsubscript{29}-
normoretane abundance compared to the relative increase in C₃₀-diahopane. The ratio is affected by source input, and a high abundance of diahopane is related to oils with a significant terrestrial input (Peters et al., 2007).

**Parameter 3: 22S/(22S + 22R)**

Parameter 3 is the ratio between the 22S and 22R isomers of the C₃₁-17α (H), 21β(H)-hopanes. The 22S isomer is more unstable than the 22R isomer, and the ratio goes from 0 to ≈ 0.6 with increasing maturity. The ratio reaches equilibrium between 0.57 and 0.62 during thermal maturation, which has been found to correspond to ≈ 0.5 Rₒ. Thus the ratio is useful to analyze immature source rocks and early oil window samples, but not valid for samples of higher thermal maturity (Peters et al., 2007; Seifert and Moldowan, 1980).

**Parameter 4: C₃₀-hopane/(C₃₀-hopane + C₃₀-morethane)**

The C₃₀-hopane is more stable than the C₃₀-morethane, thus the ratio increases with increasing thermal maturity. It should be noted that the ratio is affected by source input (Peters et al., 2007; Rullkötter and Marzi, 1988).

**Parameter 5: C₂₉Ts/(C₂₉Ts + norhopane)**

C₂₉Ts is thermally more stable than norhopane, and the ratio will increase with increasing thermal maturity (Moldowan et al., 1991). The range the ratio is valid over is however unknown (Peters et al., 2007).

**Parameter 6: Bisnorhopane/(bisnorhopane + norhopane)**

High abundance of bisnorhopane indicates marine anoxic conditions, which makes this parameter a good facies indicator. The parameter is, however, affected by thermal maturation, which leads to a decrease in the ratio. This can be attributed to the bisnorhopane concentration being diluted by other terpanes during thermal maturation (Peters et al., 2007; Dahl, 2004).
**Parameter 7: $C_{23}$-C$_{29}$ tricyclic terpanes/C$_{30}$ αβ-hopane**

Parameter 7 is a good maturity indicator, due to the fact that the tricyclic terpanes are more thermally stable than the hopanes (Peters et al., 1990). There is a sudden drastic increase in the ratio for samples with vitrinite reflection values $> 0.75 \%R_0$, which makes the ratio valid for higher maturity values (van Graas, 1990). This parameter is of significant interest in this thesis, as it is affected by evaporative fractionation/phase fractionation (Karlsen et al., 1995).

**Parameter 8: $C_{24}$ tetracyclic terpane/C$_{30}$ αβ-hopane**

This ratio increases with maturity, due to the less thermal stable nature of C30- αβ-hopanes. However the ratio also increases with biodegradation, and should be used with care (Peters et al., 2007; Peters and Moldowan, 1993).

**Parameter 9: Hopane/sterane ratio**

Hopanes are mainly derived from bacteria, and steranes are mainly derived from algae and higher land plants, thus a high ratio indicates significant terrestrial input, and low ratios indicates planktonic input (Tissot and Welte, 1984). Lithology can also affect this ratio, where high ratio values are associated with carbonates, and low values are associated with shales (Peters et al., 2007).
Parameter 10: $\beta\beta/(\beta\beta + \alpha\alpha)$ of C$_{29}$ (20R + 20S) sterane isomers

Sterane isomerization at C14 and C17 increases the abundance of $\beta\beta$ relative to $\alpha\alpha$ with increasing thermal maturity. This implies an increase in the ratio corresponds to an increase in thermal maturity. The ratio has a range between 0 and $\approx 0.7$, and reaches equilibrium between 0.67 and 0.71. This range corresponds to $\approx 0.9 \% R_0$, which makes the ratio valid from immature source rock up to the late oil production stage (Figure 5.11). The ratio also appears to not be affected by source input, and is therefore a valuable control parameter (Peters and Moldowan, 1993; Seifert and Moldowan, 1986).

Parameter 11: $20S/(20S + 20R)$ of C$_{29}$ steranes

This ratio is a maturity parameter, which increases with maturity due to isomerization at C$_{20}$. The ratio increases from 0 to $\approx 0.5$, and reaches equilibrium between 0.52 – 0.55. The ratio is valid in the range between immature source rock and the peak oil production stage (Figure 5.11) (Peters et al., 2007).

Parameter 12: Diasteranes/(diasteranes + steranes)

The diasteranes to regular steranes ratio is used as a depositional environment indicator, where high ratio values are associated with clay-rich source rocks, and low ratios are associated with carbonates (Peters et al., 2007). The ratio is however affected by both thermal maturation, and biodegradation, where both processes increase the ratio (Peters and Moldowan, 1993).

Parameter 13, 14 and 15: Relative abundance (%) of C$_{27}$, C$_{28}$ and C$_{29}$ $\beta\beta$-steranes

The distribution between C$_{27}$, C$_{28}$ and C$_{29}$ $\beta\beta$-steranes, is used to correlate facies and depositional environment between the samples. The distribution is often plotted in a ternary diagram (Peters et al., 2007; Moldowan et al., 1985).

Parameter 16: C$_{20}$/(C$_{20} + C_{28}$) triaromatic steroids (TA)

Longer-chained (TA) steroids are less thermally stable than shorter-chain (TA) steroids, and cracking from longer-chain to shorter-chain compounds occurs as a result. Thus, an increase
in the ratio is related to increased thermal maturity (Mackenzie et al., 1985). The ratio is also sensitive to evaporative fractionation (Karlsen et al., 1995).

**Parameter 17: \( \frac{C_{28} TA}{C_{28} TA + C_{29} MA} \)**

The ratio between triaromatic steroids and monoaromatic steroids is another maturity parameter. During maturation monoaromatic steroids are rearranged into triaromatic steroids. Thus the ratio increases with maturity (Peters and Moldowan, 1993).

**Parameter 18: Methylphenantrene ratio (MPR)**

The MPR is a ratio between the 2-MP and 1-MP isomers. As the petroleum matures, a predominance of 2-MP develops, and the ratio increases (Radke et al., 1982b).

**Parameter 19: Methylphenantrene index 1 (MPI1)**

The MPI1 parameter is derived from the relation between phenantrene and four methylphenantrene isomers. The parameter have been correlated with vitrinite reflection data and provides a good maturity assessment (Radke et al., 1982a). The index does, however, have limitations, and the correlation with vitrinite reflection values is not linear (Figure 5.12). The MPI1 is also affected by source input, and does not provide quality maturity assessment of type II kerogen (Radke et al., 1986).
Parameter 20: Methylphenantrene distribution fraction 1 (MPDF₁)

MPDF₁ is relatively similar to MPI₁, however does not use phenantrene, but only methylphenantrenes (MPs) to indicate maturity. The fraction only increases with maturity, unlike the MPI₁ parameter (Kvalheim et al., 1987).

\[
MPDF₁ = \frac{3\text{MP} + 2\text{MP}}{3\text{MP} + 2\text{MP} + 9\text{MP} + 1\text{MP}}
\]  \hspace{1cm} (5.6)

Parameter 21: Methyldibenzothiophene ratio (MDR)

Radke et al. (1986) introduced another maturity parameter, which displays similarities to the MPR (Parameter 18). Above 0.8 %Rₘ, the concentration of 1-MDBT decreased with maturity. The parameter is also sensitive to source input, and displays different maturity trends for type II and type III kerogen during the early maturity stage. Thus the parameter can be used to indicate both facies and maturity (Radke et al., 1982a; Radke et al., 1986).

Parameter 22: Calculated vitrinite reflection Rₘ(1)
Calculated vitrinite reflection from MPR (Parameter 18) (Radke, 1988).

\[ R_m(1) = 1.1 \times \log_{10} MPR + 0.95 \]  \hspace{1cm} (5.7)

**Parameter 23: Calculated vitrinite reflection % \( R_c \)**

Calculated vitrinite reflection from MPI1 (Parameter 19) (Radke, 1988).

\[ R_c = 0.6 \times MPI1 + 0.4 \]  \hspace{1cm} (5.8)

**Parameter 24: Calculated vitrinite reflection % \( R_o \)**

Calculated vitrinite reflection from MPDF1 (Parameter 20) (Kvalheim et al., 1987).

\[ R_o = 2.242 \times MPDF1 - 0.166 \]  \hspace{1cm} (5.9)

**Parameter 25: Calculated vitrinite reflection \( R_m(2) \)**

Calculated vitrinite reflection from MDR (Parameter 21) (Radke, 1988).

\[ R_m(2) = 0.073 \times MDR + 0.51 \]  \hspace{1cm} (5.10)

**Parameter 26: 3-methylphenanthrene/4-methyldibenzothiophene**

This parameter was introduced by Hughes et al. (1995), and can be used to indicate facies. The parameter is commonly plotted vs. the Pr/Ph ratio.

**Parameter 27: Methyldibenzothiophenes/methylphenanthrenes**

This parameter is a ratio between methyldibenzothiophenes and methylphenanthrenes, and is used to determine facies. Like Parameter 26, the ratio is often plotted vs. the Pr/Ph ratio (Radke et al., 2001).
5.5 GC-MS/MS

In this thesis, the GC-MS/MS analysis is performed with the purpose of determining the age of the source rocks that produced the samples. The NSO-1 GC-MS/MS (SRM) 358 → 217 m/z parent-daughter chromatogram is used to show the identified and labeled chemical compounds (Figure 5.13). Table 5.11 provides an overview of the analyzed compounds used in this thesis. All information in this subchapter (5.5), have been gathered from Holba et al. (1998).

Table 5.11: Overview of C26 steranes identified on GC-MS/MS (SRM) 358 → 217 m/z chromatogram (Figure 5.13).

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24-nordiacholestane</td>
</tr>
<tr>
<td>2</td>
<td>24-nordiacholestane</td>
</tr>
<tr>
<td>3</td>
<td>27-nordiacholestane</td>
</tr>
<tr>
<td>4</td>
<td>27-nordiacholestane</td>
</tr>
</tbody>
</table>
Figure 5.13: Identified nordiacholestanes on GC-MS/MS (SRM) 358 → 217 m/z chromatogram of reference sample NSO-1.

5.5.1 Nordiacholestane ratio (NDR)

The nordiacholestane ratio (NDR) is calculated in order to provide information on the depositional age of the original source rock. The NDR is calculated as a ratio between 24-diacholestanes and 27-diacholestanes (Eq. 5.11). The 24-norcholestane compounds are believed to originate from diatoms. The diatoms were first observed in the fossil record in Jurassic rocks, but did not become abundant before the Cretaceous age. Thus a high ratio indicates Cretaceous age (Holba et al., 1998).

\[
\text{NDR} = \frac{[1+2]}{[1+2+3+4]} \quad (5.11)
\]
6 Results

6.1 Introduction

This chapter is an overview of the results gathered from the geochemical analysis performed, which is based on the theory presented in chapter 5. The results presented in this chapter include chromatograms and quantified parameter values for each sample. The first results presented are the chromatograms. Secondly the quantified data are presented in tables. Finally the quantified data are presented as box-whisker plots to provide an overview of the data set.

6.2 Chromatograms

6.2.1 GC-FID chromatograms

Figure 6.1: Chromatograms of sample NSO-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
Figure 6.2: Chromatograms of sample St1 from well 33/9-14. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.3: Chromatograms of sample MH1 from well 34/4-5. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.4: Chromatograms of sample Sn1 from well 34/7-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
Figure 6.5: Chromatograms of sample Vi1 from well 34/8-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.6: Chromatograms of sample Vi2 from well 34/8-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.7: Chromatograms of sample GS1 from well 34/10-16. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
Figure 6.8: Chromatograms of sample Va1 from well 34/10-23. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.9: Chromatograms of sample GS2 from well 34/10-32R. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.10: Chromatograms of sample K1 from well 34/11-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram
Figure 6.11: Chromatograms of sample N1 from well 34/11-2s. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.12: Chromatograms of sample A1 from well 35/3-4. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.13: Chromatograms of sample G1 from well 35/9-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
Figure 6.14: Chromatograms of sample Sk1 from well 35/9-7.  a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.15: Chromatograms of sample Ve1 from well 35/11-2.  a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.16: Chromatograms of sample F1 from well 35/11-15s.  a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
Figure 6.17: Chromatograms of sample R1 from well 35/12-4s. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.

Figure 6.18: Chromatograms of sample G2 from well 36/7-1. a) Light hydrocarbon range GC-FID chromatogram. b) Full range GC-FID chromatogram.
6.2.2 GC-MS and GC-MS/MS chromatograms

Figure 6.19: GC-MS Chromatograms of reference sample NSO-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.20: GC-MS Chromatograms of sample St1 from well 33/9-14. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.21: GC-MS Chromatograms of sample MH1 from well 34/4-5. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.22: GC-MS Chromatograms of sample Sn1 from well 34/7-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.23: GC-MS Chromatograms of sample Vi1 from well 34/8-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.24: GC-MS Chromatograms of sample Vi2 from well 34/8-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.25: GC-MS Chromatograms of sample GS1 from well 34/10-16. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.26: GC-MS Chromatograms of sample Va1 from well 34/10-23. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.27: GC-MS Chromatograms of sample GS2 from well 34/10-32 R. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.28: GC-MS Chromatograms of sample K1 from well 34/11-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.29: GC-MS Chromatograms of sample N1 from well 34/11-2 S. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.30: GC-MS Chromatograms of sample A1 from well 35/3-4. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.31: GC-MS Chromatograms of sample G1 from well 35/9-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.32: GC-MS Chromatograms of sample Sk1 from well 35/9-7. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.33: GC-MS Chromatograms of sample Ve1 from well 35/11-2. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.34: GC-MS Chromatograms of sample F1 from well 35/11-15 S. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 231, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.35: GC-MS Chromatograms of sample R1 from well 35/12-4 S. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z.
Figure 6.36: GC-MS Chromatograms of sample G2 from well 36/7-1. a) m/z = 191, b) m/z = 217, c) m/z = 218, d) m/z = 231, e) m/z = 253, f) m/z = 178, g) m/z = 198 and 192, h) GC-MS/MS (SRM) 358 – 217 m/z
6.2.3 Chromatogram observations

Light hydrocarbon GC-FID chromatogram observations

- Most of the crude oils appear to have a relative large methylcyclohexane peak compared to the condensates.
- Condensate samples K1 (Figure 6.10), N1 (Figure 6.11), and A1 (Figure 6.12) in particular, appear to contain more toluene than the other samples.

Full range GC-FID chromatogram observations

- Most of the condensates contain more of the light hydrocarbon compounds than the oils.
- From C15+, most of the samples display a progressive peak height decrease of n-alkanes with increasing carbon number. Most of the oils appear to have lower n-C5 – n-C13 peaks, which leads to a maximum peak around n-C15 for most of the samples.
- None of the samples appear to be significantly biodegraded - in the sense of significant removal of n-alkanes.

GC-MS and GC-MS/MS chromatogram observations

- All samples have identifiable and measurable peaks.
- Condensate samples Va1 (Figure 6.26), K1 (Figure 6.28), N1 (Figure 6.29) and A1 (Figure 6.30), all display a more significant UCM compared to the other samples.
- The condensates also display higher maturity due to the complete removal of triaromatic and monoaromatic compounds observed on m/z=231 and 253 GC-MS chromatograms (Ch. 6.2.2).
- All samples display the same signature on GC-MS/MS (SRM) chromatogram 358 → 217 m/z, with low 24-nordiacholestane peaks and high 27-nordiacholestane peaks.
6.3 Analytical assumptions, considerations and potential errors

There are several assumptions and considerations to recognize in this thesis. All of the parameter values have been calculated by manually measuring peaks with a ruler from a subjectively placed baseline. Chromatograms with a low signal-to-noise ratio make the baseline position ambiguous and uncertain.

It is assumed that the height of a peak is directly proportional to the abundance of the compound measured. This is, generally correct for peaks with approximately the same elution time. Some specific compounds can have the same retention time, which might lead to interference, but this problem is minimized due to measuring peak height rather than peak areas, and the peaks used are those with less interference.

Peaks might also experience “tailing” as a result of overloading the column. This is particularly a potential problem in the light hydrocarbon GC-FID analysis with manual injection of samples, but is not seen as problematic in the suite of petroleums analyzed.

Evaporative loss of compounds, due to sample storage, has not been accounted for in this thesis, and the geochemical composition of the samples might vary from the original hydrocarbon accumulation.
### 6.4 Quantified parameter values

#### 6.4.1 Quantified GC-FID parameter values

Table 6.1: Quantified parameter values from GC-FID analysis.

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<th>Sample</th>
<th>Well</th>
<th>Phase</th>
<th>n-C7/MCYC6</th>
<th>Tol/n-C7</th>
<th>Pr/Ph</th>
<th>Pr/n-C17</th>
<th>Ph/n-C18</th>
<th>CPI (I)</th>
<th>CPI</th>
<th>OEP (I)</th>
<th>OEP</th>
<th>Waxiness</th>
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<tbody>
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<td>Oil</td>
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<td>0.13</td>
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Table 6.1 Continuation

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### 6.4.2 Quantified GC-MS parameter values

Table 6.2: Quantified parameter values from GC-MS analysis (Parameters 1-15). * Cond. = Condensate.

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<td>0.61</td>
<td>38.8</td>
<td>29.1</td>
<td>32.1</td>
</tr>
<tr>
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<td>Cond.</td>
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<td>0.90</td>
<td>0.53</td>
<td>0.79</td>
<td>0.69</td>
<td>0.36</td>
<td>3.68</td>
<td>1.11</td>
<td>0.36</td>
<td>0.59</td>
<td>0.52</td>
<td>0.66</td>
<td>34.1</td>
<td>32.8</td>
<td>33.1</td>
</tr>
<tr>
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<td>0.75</td>
<td>0.61</td>
<td>0.91</td>
<td>0.41</td>
<td>0.16</td>
<td>0.72</td>
<td>0.22</td>
<td>1.84</td>
<td>0.62</td>
<td>0.46</td>
<td>0.56</td>
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<td>0.91</td>
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<td>2.40</td>
<td>0.63</td>
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</tr>
<tr>
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<td>0.72</td>
<td>0.58</td>
<td>0.88</td>
<td>0.41</td>
<td>0.20</td>
<td>0.26</td>
<td>0.07</td>
<td>2.14</td>
<td>0.59</td>
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<tr>
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<td>0.85</td>
<td>0.59</td>
<td>0.91</td>
<td>0.50</td>
<td>0.18</td>
<td>0.32</td>
<td>0.10</td>
<td>1.96</td>
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<td>29.2</td>
<td>38.7</td>
</tr>
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<td>R1</td>
<td>35/12-4 S</td>
<td>Oil</td>
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<td>0.74</td>
<td>0.58</td>
<td>0.87</td>
<td>0.39</td>
<td>0.15</td>
<td>0.24</td>
<td>0.07</td>
<td>2.24</td>
<td>0.58</td>
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<td>0.81</td>
<td>0.59</td>
<td>0.89</td>
<td>0.49</td>
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<td>0.48</td>
<td>30.6</td>
<td>29.5</td>
<td>39.9</td>
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</table>

| Average (Oil) | Oil | 0.66| 0.70| 0.59| 0.89| 0.39| 0.76| 0.30| 0.07| 1.81| 0.59| 0.43| 0.44| 32.39| 30.34| 37.27|
| Average (Cond.)| Cond. | 0.81| 0.84| 0.57| 0.84| 0.59| 0.70| 2.50| 0.75| 1.07| 0.62| 0.51| 0.59| 34.73| 29.32| 35.94|
Table 6.3: Quantified parameter values from GC-MS and GC-MS/MS analysis (Parameters 16-27 and NDR). * Cond. = Condensate.

<table>
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<tr>
<th>Sample</th>
<th>Well</th>
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<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
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</thead>
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<td>-</td>
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<td>0.86</td>
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<td>0.44</td>
<td>3.00</td>
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<td>0.66</td>
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<td>0.73</td>
<td>1.37</td>
<td>0.56</td>
<td>0.18</td>
</tr>
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<td>0.39</td>
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<td>0.65</td>
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<td>0.79</td>
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<td>0.19</td>
</tr>
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<td>0.76</td>
<td>0.79</td>
<td>0.43</td>
<td>0.42</td>
<td>3.82</td>
<td>0.84</td>
<td>0.66</td>
<td>0.78</td>
<td>0.79</td>
<td>1.26</td>
<td>0.53</td>
<td>0.21</td>
</tr>
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<td>0.78</td>
<td>0.76</td>
<td>0.41</td>
<td>0.41</td>
<td>3.65</td>
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<td>0.65</td>
<td>0.76</td>
<td>0.78</td>
<td>1.13</td>
<td>0.58</td>
<td>0.21</td>
</tr>
<tr>
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<td>34/8-1</td>
<td>Oil</td>
<td>0.65</td>
<td>0.69</td>
<td>0.82</td>
<td>0.42</td>
<td>0.43</td>
<td>4.91</td>
<td>0.86</td>
<td>0.65</td>
<td>0.80</td>
<td>0.87</td>
<td>1.65</td>
<td>0.40</td>
<td>0.20</td>
</tr>
<tr>
<td>Vi2</td>
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<td>Cond.</td>
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<td>0.66</td>
<td>0.89</td>
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<td>0.45</td>
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<td>0.83</td>
<td>0.84</td>
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<td>6.22</td>
<td>0.98</td>
<td>0.75</td>
<td>0.98</td>
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<td>0.28</td>
<td>0.21</td>
</tr>
<tr>
<td>Va1</td>
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<td>0.99</td>
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<td>0.59</td>
<td>0.55</td>
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<td>1.07</td>
<td>1.86</td>
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<td>0.21</td>
</tr>
<tr>
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<td>0.76</td>
<td>1.04</td>
<td>0.44</td>
<td>0.48</td>
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<td>0.66</td>
<td>0.91</td>
<td>0.92</td>
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<td>0.30</td>
<td>0.21</td>
</tr>
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<td>0.54</td>
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<td>1.10</td>
<td>0.77</td>
<td>1.06</td>
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<td>0.31</td>
<td>0.24</td>
</tr>
<tr>
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<td>Cond.</td>
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<td>0.54</td>
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<td>0.76</td>
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<td>1.45</td>
<td>3.35</td>
<td>0.23</td>
<td>0.22</td>
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<tr>
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<td>Cond.</td>
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<td>0.54</td>
<td>1.14</td>
<td>0.44</td>
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<td>4.77</td>
<td>0.92</td>
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<td>0.86</td>
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<td>0.31</td>
<td>0.21</td>
</tr>
<tr>
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<td>0.96</td>
<td>0.68</td>
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<td>3.79</td>
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</tr>
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<td>Oil</td>
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<td>0.97</td>
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<td>0.47</td>
<td>6.40</td>
<td>0.94</td>
<td>0.70</td>
<td>0.89</td>
<td>0.98</td>
<td>2.24</td>
<td>0.32</td>
<td>0.19</td>
</tr>
<tr>
<td>R1</td>
<td>35/12-4 S</td>
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<td>0.45</td>
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<td>0.93</td>
<td>0.45</td>
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<td>4.52</td>
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<td>0.22</td>
</tr>
<tr>
<td>G2</td>
<td>36/7-1</td>
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<td>0.64</td>
<td>1.04</td>
<td>0.49</td>
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<td>0.97</td>
<td>0.69</td>
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<td>0.45</td>
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<td>0.90</td>
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<td>0.85</td>
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<tr>
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<td>1.33</td>
<td>2.68</td>
<td>0.30</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>
6.5 Box-Whisker plots

This sub-chapter includes a total of three Box-Whisker plots, which are included to provide a better overview of the data set. The Box-Whisker plots are made with the quantified parameter values seen in Table 6.1, 6.2, and 6.3. All of the plots have been made with the Grapher 8 software. The plots include outliers, which have been excluded from the interquartile box and whisker calculations. The interquartile box represents the middle 50% of the data, while the whiskers represent the upper and lower 25% of the data. The line splitting the interquartile box in two pieces represents the median value.

6.5.1 Light hydrocarbon GC-FID Box-Whisker plot

![Box-Whisker plot of the light hydrocarbon parameter values (Table 6.1). Note sample A1, which is by far the biggest outlier in this plot. Also note that the three other outliers are condensates.](image)

**Figure 6.37:** Box-Whisker plot of the light hydrocarbon parameter values (Table 6.1). Note sample A1, which is by far the biggest outlier in this plot. Also note that the three other outliers are condensates.
Figure 6.37 displays the distribution of the parameter values from the light hydrocarbon GC-FID analysis. The n-heptane/methylcyclohexane (paraffinicity) parameter has in general a wider spread of values, however none of the samples appear as outliers, and the data set is rather continuous. The toluene/n-heptane (aromaticity) parameter has a very concentrated distribution of values, with the exception of the outliers. All of the outliers are condensates, however the A1 sample from well 35-3/4 is by far the biggest one. The condensates display higher values in paraffinicity and aromaticity on average (Table 6.1).

### 6.5.2 Full range GC-FID Box-Whisker plot

![Box-Whisker plot of the full range GC-FID parameter values.](image)

**Figure 6.38**: Box-Whisker plot of the full range GC-FID parameter values (Table 6.1). Note that samples A1 and St1 often appear on opposite sides of the spectrum as outliers. Also note that most of the parameters display a concentrated spread of values, except for the Pr/Ph ratio, which has larger range of values.
The A1 sample, from the Agat field, appears as an outlier for several parameters (Figure 6.38). The sample has the highest Pr/Ph ratio of the sample set, and by far the lowest Pr/n-C17 ratio. For several of the GC-FID parameters, the samples A1 and St1 appear as opposites, and for the CPI and OEP (1) parameters they are the only samples that differentiate themselves from the concentrated cluster (Table 6.1; Figure 6.38). The Pr/Ph ratio is the parameter that displays the widest range of values. The lowest values appear to belong to the samples with the lowest block numbers, which implies that there is a general trend of lower Pr/Ph values in the western part of the study area compared to the eastern part (Table 6.1).

There is a slight difference observed between average oil and average condensate values. The average condensate values indicate an increased terrestrial influence relative to the average oil values (Tissot and Welte, 1984).
6.5.3 GC-MS Box-Whisker plot

Figure 6.39: Box-Whisker plot of the GC-MS parameter values (Table 6.2 and 6.3). Note the repeated appearances as outliers by samples Va1, K1, and N1. Parameters 13, 14 and 15 have been multiplied by $10^{-2}$ to improve visibility. The outliers for P21 are not shown to increase visibility.

Figure 6.39 displays a Box-Whisker plot of the GC-MS parameter values from table 6.2 and 6.3. Condensate samples K1, N1 and Va1 stand out as outliers for several thermal maturity parameters that have a valid range into the condensate stage of petroleum production (Figure 5.11). The three condensates are also big outliers for P21, which is not shown in figure 6.39 to increase visibility. The condensate sample A1 from well 35/3-4 appear to have an increased value for thermal maturity parameters affected by evaporative fractionation, e.g. P7 and P16 (Table 6.2 and 6.3). Sample A1 does not exhibit the same behavior for thermal maturity parameters that
are unaffected by evaporative fractionation, eg. P2 and P5 (Table 6.2) (Karlsen et al., 1995).

Sample St1 stand out as an outlier for parameter 27, and is the only sample that indicates a carbonate source (Hughes et al., 1995).

The average condensates show higher maturity values compared to the crude oils (Table 6.2 and 6.3) (Peters et al., 2007).

All of the samples show similar NDR values (Table 6.3), where oils have an average NDR ratio of 0.21, and the condensates have an average value of 0.22.
7 Discussion

7.1 Introduction

This chapter contains an assessment of the results presented in chapter 6. The discussion involves thermal maturity, organic facies, biodegradation, water washing, and evaporative fractionation/phase fractionation of hydrocarbons. Chapter 7 includes several diagrams, which are included to increase the understanding and context of the results. The first results discussed are the light hydrocarbon GC-FID chromatograms and tables. Secondly GC-FID data on the C10+ fraction, and GC-MS biomarker data are used to discuss thermal maturity, organic facies, the continued evidence for evaporative fractionation, and review of previous migration studies in the area. The final results discussed are the GC-MS/MS age determination data.

7.2 Light hydrocarbon analysis

7.2.1 Introduction

Sub-chapter 7.2 includes the assessment and discussion of the light hydrocarbon GC-FID results. The focus of this analysis is a crossplot of paraffinicity vs. aromaticity (Figure 7.1) originally developed by Thompson (1987) and modified by (Canipa-Morales et al., 2003). The plot provides valuable insight into maturity, biodegradation, water washing and evaporative fractionation. It should be noted that the samples provided by NPD arrived with loosely sealed caps, and some samples showed visible leakage. It is possible that the geochemical composition might have been altered as a consequence, which could lead to misleading results, but this is not very likely. The cross plot displayed in figure 7.1, modified by Canipa-Morales et al. (2003), was originally based on a another sample set. The sample set consisted of oils from the Mexican Gulf, where the oils have been part of a petroleum system, which is much larger in geographical extent. The original composition of the sample set analyzed in this thesis, compared to the sample sets studied by Thompson (1987) and Canipa-Morales et al. (2003), might be very different, thus figure 7.1 might not accurately describe which process has altered the samples. One point worth
mentioning is that the Mexican Gulf petroleum systems seem much more influenced by phase fractionation than are the petroleum systems offshore Norway e.g. at Haltenbanken (cf. Karlsen and Skeie, 2006). The reason for the extraordinary degree of fractionation in the Gulf Cost systems has probably to do with very rapid and very deep burial.

Figure 7.1: Cross plot of paraffinicity (x-axis) and aromaticity (y-axis). Note sample A1, which displays an indication that evaporative fractionation has occurred. Also note the cluster forming close to origo, which indicates that biodegradation has occurred. Original diagram after Canipa-Morales et al. (2003). The term “D” which refers to original oils means unaltered oils. Water washing “C” is reflected in selective removal of the water-soluble compound toluene. Biodegradation is here reflecting removal of n-alkanes like n-heptane. The dataset of Dale (1997) comprising oils from Haltenbanken and would in this diagram plot inside the “D”-region, indicating tentatively that the present dataset is somewhat biodegraded, and some biodegradation in the Oseberg oil (NSO) is likely (Dahl and Speers, 1986).

7.2.2 Maturation of the light fraction – the C7 HCs

According to Thompson (1987), paraffinicity (n-heptane/methylcyclohexane) is a maturity parameter, where an increase in maturity is related to an increase in paraffinicity (Vector B, Figure 7.1). This has to do with the more stable carbon – carbon bonds in an n-alkane compared to the branched carbon-positions in methylcyclohexane. The samples analyzed in this study do not display any distinct indication of maturation related to thermal cracking, and an increase in light aromatic
compounds (Thompson, 1987). This suggest most likely that the sample set has a more modest maturity variation than the sample set of Thompson and Canipa-Morales. Thus, the diagram seems to suggest a modest maturity variation of the oil data set in this study. Still, one could consider that some of the n-alkanes were removed by biodegradation, as this would seemingly lower the maturity. However, n-alkanes are present in the C6-C7 range, and the biodegradation cannot have been a major factor. For biodegradation to occur, the petroleums would need to have accumulated in the reservoirs at depths less than approximately 2.2 km or equivalent to 70-80°C (Lerch et al., 2016b), and the petroleums in this thesis’ dataset are from reservoirs between 2.3 to 4.3 km. It is also noted that methylcyclohexane is in contrast usually dominating over n-C7 in Norwegian oils (Vobes, 1998; Dale, 1997), and this could point to a source specific element of simply that the oils on the NCS never gets to be super-mature condensates, a point brought out also by Karlsen et al. (1995).

7.2.3 Biodegradation of the light fraction – the C7 HCs

Biodegradation is a result of living organisms altering the composition of oils and condensates, destroying the lighter hydrocarbons, producing a denser composition of hydrocarbons (Head and Larter, 2003). Biodegradation is in particular related to removal of n-alkanes, hence the low n-heptane values (Thompson, 1983). Figure 7.1 show a cluster forming in the direction of origo, which indicates biodegradation has occurred. This is also supported by the fact that the Haltenbanken oil dataset of Dale, (1997) would plot inside the elongated circle “D” which includes “normal unaltered oils”. Still, the depths of the petroleums in this study are deeper than 2.2km, which reflect a burial depth temperature of approximately 70-80°C. With only sample G1 from a depth of about 2.3 km, biodegradation does not presently reflect the most likely alteration process to have significantly affected the sample set. It is clear that the chromatograms in general do not support extensive biodegradation. Most of the samples show limited signs of biodegradation, displaying low amounts of UCM, and low elevation of baseline. Still, it is possible that some of the petroleums from the more shallow traps were paleo-biodegraded, and a series of petroleums in this dataset originated from reservoirs at depth between 2.5-3.5 km. Extensive paleo-filling of traps was documented for the Ula field by Karlsen et al. (1993) and paleo-biodegradation was mentioned for e.g Norne and Draugen in Karlsen et al. (1993),
and in Karlsen and Skeie (2006). Matapour and Karlsen (2017) argue for palaeo-
biodegradation and a later recharge of fresh non-biodegraded oil into the trap when it
is deeper than the biodegradation seizure-sone, suggested for many oils in the Barents
Sea. It is proposed that something similar could have affected some of the petroleums
in this dataset. Still, one possible reason for the contradicting observations is that the
paraffinicity vs. aromaticity cross plot developed by Thompson (1987), was based on
a completely different sample set, but the dataset of Dale (1997) does not support this
entirely and it is concluded that the dataset in this study has to some extent
experienced paleo-biodegradation and a likely later recharge.

7.2.4 Water washing of the light fraction – the C7 HCs
Low amounts of toluene indicate that water washing and/or biodegradation has
occurred (Sarmah and Raju, 2016). All of the samples have low amounts of toluene
(compared to the “D” group), except sample A1 (Figure 7.1; Table 6.1). The sample
set also indicates that some level of biodegradation has occurred, and the depleted
toluene fraction is most likely a result of water washing and associated
biodegradation.

7.2.5 Evaporative fractionation of the light fraction – the C7
HCs
It was assumed for an extended period that condensates were exclusively of thermal
origin, generated by advanced cracking of oils. There are, however exceptions to this
process, where evaporative fractionation produce condensates with maturity values
within the oil window, typically between 0.5 – 1.2 % in vitrinite reflectance
(Thompson, 1987). In Figure 7.1, sample A1 is the only sample to indicate
evaporative fractionation. To further establish evaporative fractionation as the
generating mechanism to produce the A1 condensate, the sample should display oil
window maturity based on other parameters. Most of the maturity parameters valid
until the condensate stage indicate that the A1 condensate corresponds to oil window
maturity (see. Ch. 7.3). Thus it is implied that the A1 condensate is the only sample of
the sample set, which most likely is a result of phase fractionation.
7.3 Thermal maturity of the C10+ HC-fraction

This sub-chapter includes a thermal maturity discussion based on results from the GC-FID analysis of the C10+ fractions, as well as the GC-MS biomarker analysis. Some cross plots provide information about other alteration processes, which is mentioned briefly, however not discussed formally within this subchapter.

7.3.1 Pristane, phytane and n-alkanes

Pr/n-C17 and Ph/n-C18 ratios have average values of 0.67 and 0.39, and median values of 0.67 and 0.35 respectively (Table 6.1, Figure 7.2) Most of the samples have values close to the median and average values, however sample A1 appear as an outlier with Pr/n-c17 and Ph/n-c18 values of 0.37 and 0.13 respectively, which indicates that sample A1 is the most mature sample. It is clearly observed in figure 7.2 that the samples span some variation in either maturity and/or biodegradation. Average condensate values are 0.63 and 0.34 respectively, while the average oil values are 0.69 and 0.42 respectively, which indicates that the condensates are slightly more mature on average (Tissot and Welte, 1984). According to Peters et al. (2007), Pr/n-C17 and Ph/n-C18 ratios are more applicable for non-biodegraded oils. The ratios are sensitive to thermal maturation, OM-input and biodegradation. This could suggest that the low values observed for sample A1, is a result of other processes than thermal maturation.
Figure 7.2: Cross plot of Pr/n-C17 and Ph/n-C18. Note the distinct maturity trend where samples located in the eastern part of the study area seem to be the most mature. Also note the CGC samples, which display lower maturity values relative to EF samples. Most of the thermal maturity parameters analyzed in this thesis does not show the same trend, and this plot appears to be severely affected by source input. The plot displays a distinct trend of increased terrestrial input in the eastern part of the study area. This is the most likely cause of the EF samples relatively high maturity signature in this cross plot. Modified from (Shanmugam, 1985).

Figure 7.2 provides information about maturation, biodegradation, and organic facies. The maturity trends observed does not appear to be consistent with the overall maturity trend observed in chapter 6 and 7. A distinct pattern of increased terrestrial input in the eastern direction is observed (Figure 7.2). Most of the samples appear to originate from a mixed source transitional environment. The Gullfaks Sør field oils (GS1 and GS2) appear to be significantly influenced by terrestrial material, and plots in the peat-coal environment zone. Sample A1 appear to be much more mature than the other samples. The samples, which appear to contain more terrestrial material, also generally display higher thermal maturation values (Figure 7.2).
7.3.2 Terpanes and steranes

Figure 7.3 is a cross plot between $Ts/(Ts + Tm$, i.e. Parameter 1) and diasteranes/(diasteranes + steranes, i.e. Parameter 12), which is used to determine thermal maturity of hydrocarbon samples within the oil window range (Lerch et al., 2016a). The vast majority of the samples plot in the “Early Oil Zone”. Samples Va1 and N1, are the two most mature samples, both plotting in the “Peak Oil Zone”. The other condensates are plotted in the “Early Oil Zone”. The most mature oils appear to be G1 and G2, from the Gjøa field. Both samples are plotted close to the “Peak Oil Zone”. The rest of the oils plot in the “Early Oil Zone”, except GS1, which are the least mature sample. Most of the samples show predominance for the $Ts/(Ts + Tm)$ ratio, which indicates some source input influence (Peters et al., 2007).

Figure 7.4 is cross plot between $20S/(20S + 20R)$ ratio for $aaa-C_{29}$-steranes (parameter 11), and $\beta\beta/(aa + \beta\beta)$ ratio for $5\alpha-C_{29}$ steranes (parameter 10). Most of the oils and condensates display similar maturity. The majority of the samples are not yet fully isomerized, except four of the condensates, which have reached the isomerization equilibrium threshold. The least mature samples appear to be R1, Sk1, GS1 and NSO-1, but still plot relatively close to the other samples, which form a cluster close to the isomerization equilibrium threshold line (Figure 7.4).
Figure 7.3: Cross plot of $\frac{Ts}{(Ts+Tm)}$ (Seifert and Moldowan, 1978), and Diasteranes/(Diasteranes + Steranes) (Mackenzie et al., 1985). Borders separating oil zones have been adapted from (Lerch et al., 2016a). Note the general trend of condensates being more mature than oils. Also note that several condensates plot inside the “Early Oil Zone”. Gullfaks Sør oil samples are the least mature samples in the set. The arrow indicates a general maturity trend, and the moderate maturity of most of the samples seems striking in this diagram. Note that the Nøkken sample (N1 at 4.2km) and the almost equally deep Valemon (Va1 at 4.1km) plus the Kvitebjørn Field (K1 at 4.1km) are clearly the most mature and these are all condensates. The NSO marks an oil of about 0.7%Rc – a black oil from Oseberg, but with a complex filling history (Dahl and Speers, 1986).
Figure 7.4: Cross plot of 20S/(20S + 20R) ratio for C_{29}-steranes (parameter 11), and ββ/(αα + ββ) ratio for C_{29}-
eranes (parameter 10). The marked dashed lines displaying the isomerization equilibrium threshold interval
have been adapted from Lerch et al. (2016a). Note the four condensates that have reached the isomerization
equilibrium threshold. The NSO reference oil at approximately 0.7%Rc is again used a reference for maturity
indicating that most of the oils in the data set range between 0.7-0.8%Rc.

Figure 7.5 displays a trend, which is consistent with previously observed patterns. Both
parameters increase with maturity. The three condensates K1, N1, and Val (CGC), produced
from wells located in the central part of the graben, are the most mature samples observed and
are clearly past the main black-oil window. The samples produced from wells located on the
western flank (WF) of the Viking Graben, plot as the least mature samples. There is to some
extent here an interesting tentative regional trend: The oils located in the eastern part of the
study area (EF), from Quadrants 35 and 36, display an intermediate degree of maturation
relative to the two other sample clusters (Cornford et al., 1986; Moldowan et al., 1991). Also
note the relative low maturity of the A1 condensate (Figure 7.5).
Figure 7.5: Cross plot between diahopane/(diahopane + normoretan), (Cornford et al., 1986), and 29Ts/(29Ts + norhopane), (Moldowan et al., 1991). Note the development of three clusters, where the three central graben condensates are the most mature samples plotted. The least mature samples appear to be located in the western part of the study area. Also note that the condensate sample A1 appears as the least mature condensate, and plots close to several oils. Note that these parameters are, due to their similar boiling points, among the least affected by evaporative fractionation as discussed by Karlsen and Skeie (2006). A tentative maturity trend is indicated by the orange line. Three main maturity groups are suggested: The lower most at 0.7-0.8%Rc, the next at 0.9-1.1%Rc and the three condensates at 1.2 -1.4 or 1.5%Rc.
Figure 7.6 displays a cluster close to the y-axis. This is caused by the ratio equilibrium which occurs when the ratio ≈ 0.62. The parameter is unable to differentiate maturity past this point. All samples appear to be close to this equilibrium point. Four samples show a distinct difference to the other samples with the C_{24} tetracyclic terpane/C_{30} αβ-hopane (Parameter 8) ratio. An increase in this ratio occurs as the sample matures. The CGC samples are significantly more mature than the other samples, which Parameter 3 is unable to measure due to the ratio equilibrium being reached (Peters et al., 2007).

**Figure 7.6:** Cross plot between 22S/(22S+22R) of C_{31} 17a(H),21β(H)-hopanes (Parameter 3), (Mackenzie et al., 1980), and C_{24} tetracyclic terpane/C_{30} αβ-hopane (Parameter 8), (Mello et al., 1988). Both parameters increase as the thermal maturity increase. Note that most of the samples form a cluster close to the y-axis as all expelled oils are fully isomerized in the 22-hopane parameter. A1 differentiates itself slightly, with a higher parameter 8 value. Also note the 3 condensates with significantly higher Parameter 8 values, which could reflect either biodegradation or maturity, and given the depth of the traps, the latter is the most likely cause.
The vast majority of the samples has values between ≈ 0.8 and ≈ 0.95 in C30-hopane/morethane ratio, and displays a low range of values (Figure 7.7). Condensate sample K1 is the major outlier. The C30-hopane/morethane ratio (Parameter 4) is affected already at low temperatures. Isomerization of this ratio occurs at low temperatures due to the loss of C30-morethane, and it is proposed that the ratio is not reliable outside the “Early Oil Zone”, and the low value for sample K1 might be a result of high maturity, rather than immaturity (Rullkötter and Marzi, 1988) (Figure 7.7). The 29Ts/norhopane ratio (Parameter 5) increases with maturity, and with no or few source effects, and the parameter is also not influenced by phase fractionation as the numerator and denominator has very similar boiling points. This indicates that sample Va1 is the most thermally mature sample. The Gullfaks Sør field oils, GS1 and GS2, appear as the least mature in the sample set (Moldowan et al., 1991).
Figure 7.7: Maturity cross plot between the $29T_{s}/(29T_{s} + \text{norhopane})$, (Peters et al., 2007), and $C_{30}$-hopane/($C_{30}$-hopane + $C_{30}$morethane), (Mackenzie et al., 1985). Note the three condensates, which show a completely different behavior than the other samples. The condensates show high Parameter 5 values, but very varying Parameter 4 values.

7.3.3 Terpanes and aromatic steroids

Other processes, e.g. biodegradation and source input, often affect the maturation parameters used in this thesis. It is therefore important to minimize these effects by using several different parameters. Figure 7.7 displays a cross plot between diahopane/(diahopane + normorethane), i.e. Parameter 2 and $C_{20}/(C_{20}+C_{28})$ triaromatic steroids, i.e. Parameter 16. Parameter 2 is affected by source input (Peters and Moldowan, 1993). Parameter 16 is affected by evaporative fractionation in the sense that it displays an increased value for condensates relative to oils – and also shows systematically higher values for oils of
increasing GOR, and it is therefore providing insight into the origin of the condensates of this thesis (Karlsen et al., 1995).

The Gullfaks field oils (GS1) and (GS2), NSO-1 and WF-oils appear as less mature than the other samples. Condensate A1 has a diahopane/(diahopane + normoretane) ratio of 0.75, which corresponds to Early, Mid, and Late oil window (Karlsen et al., 1995). The A1 sample deviates from the general trend observed so far, and shows higher maturity levels if the parameters are affected by evaporative fractionation. This further indicates that evaporative fractionation is a possible process that formed the A1 condensate. If this is correct, then there could exist oil in the vicinity of the Agat discovery (Figure 7.8).
Figure 7.9: Cross plot between C28 TA/(C28 TA + C29 MA) i.e. Parameter 17 (Mackenzie et al., 1985), and bisnorhopane/(bisnorhopane + norhopane), i.e. Parameter 6 (Moldowan et al., 1984). Note the condensates plotted with significantly higher Parameter 17 values. The Parameter 17 values for the condensates have manually been set to 0.99. This is due to the complete removal of aromatic steroids observed in the GC-MS chromatograms for m/z = 231 and 253.

Parameter 6 is used to indicate organic facies, where low values indicate a marine oxic depositional environment. The ratio is however affected by thermal maturation, and should be used to compare samples of similar maturity. This sample set contains samples with varying degrees of maturity, and the parameter is therefore not necessarily reliable. With the previously mentioned variables in mind, the condensates show relatively high Parameter 17 values (Figure 7.9). This is the result of manually set Parameter 17 values, due to the lack of aromatic compounds present in the condensates. This is observed in the GC-MS chromatograms for m/z = 231 and 253 (Ch. 6.2.2). The three condensates have exhibited signs of high maturity previously in this chapter. The bisnorhopane/norhopane ratio decreases as the sample matures, which indicates that the CGC-condensates are likely sourced from a source rock with substantial marine input deposited under anoxic or suboxic conditions.
Figure 7.9 displays a trend where EF samples appear to have been sourced from source rocks deposited under more oxic conditions relative to the WF and CGC samples (Moldowan et al., 1984; Peters et al., 2007).

Figure 7.10: Cross plot between C23-C29 tricyclic terpanes/ C30 αβ-hopane, i.e. Parameter 7 (Mello et al., 1988), and C20/(C20 + C28) TA, i.e. Parameter 16 (Mackenzie et al., 1985). The parameters tend to show high scores for condensates and are generally correlating with GOR, despite having been constructed as maturity parameters. The CGCs attract attention with considerable high Parameter 7 values. Note sample A1, which appear more mature than previously observed.

Figure 7.10 displays the same patterns previously observed in the majority of cross plots presented in this chapter. The A1 condensate appears more mature in cross plots of parameters affected by evaporative fractionation. The CGC samples are the most mature samples of the sample set. The oils display varying degrees of thermal maturity, however samples GS1, NSO-1, St1 appear to be the least mature. As mentioned in chapter 5, according to van Graas (1990), Parameter 7 displays a sudden increase in the ratio value for samples...
with \( R_0 > 0.75 \% \). This indicates that the CGC samples have \( R_0 \) values > 0.75%, while the other samples have \( R_0 \) values < 0.75% (Figure 7.10).

### 7.3.4 Medium range aromatic parameters – C14-C15

Vitrinite reflectance (\( R_0 \)) values are used to indicate the thermal maturity of petroleum samples. Some of the medium range compound ratios among the phenantrenes and methylindbenzothiophenes can be converted to calculated vitrinite reflectivity values (\( R_c \)). This is of interest as these compounds are much more abundant in oils and condensates compared to phenathrenes, and they are, furthermore representing a lighter fraction compared to the generally C27-C35 range of the biomarkers. It is for this reason a comparison of the maturity sequence based on these parameters should be compared to that of the biomarkers when evaluating the potential that a given petroleum actually represents the blend between a black oil and a condensate in a trap. In this case the biomarker-maturity should be biased towards the black-oil, while the medium range parameters should be biased towards the condensate (Karlsen and Skeie, 2006). Figure 7.11 displays a thermal maturity pattern observed previously in this chapter, where the three CGC samples appear as the most mature samples of the sample set. The WF show indication of low maturity levels, except the Gullfaks Sør samples (GS1 and GS2), which appear more mature than what could be expected from previous plots.
Figure 7.11: Cross plot of calculated vitrinite reflection values $R_C$, i.e. Parameter 23 (Radke, 1988), and $R_0$, i.e. Parameter 24 (Kvalheim et al., 1987). Note that most of the samples cluster in the maximum oil generation area/peak oil zone. Also note the CGC samples appear as the most mature samples. One strange occurrence in this plot is the GS1 oil, which previously has indicated much lower maturity. It is possible that this oil is a blend between an early oil (lower biomarker maturity) and a more mature condensate.

Parameter 23 is derived from Parameter 19, which is affected by source input, and does not provide reliable thermal maturity information for samples derived from kerogen type II source rocks (Radke et al., 1986). Most of the oils in the area are supposedly sourced from kerogen type II source rocks, (Ch. 7.4). This implies that the parameter is not reliable in this thesis. This is also evident from figure 7.11, where Parameter 23 displays very little separation between samples that previously has indicated completely different maturity levels. Parameter 24 displays mostly the same patterns of thermal maturity as previously mentioned, with the exception of the Gullfaks Sor oils (GS1 and GS2), which appear much more mature than previous figures have indicated.
Figure 7.12: Cross plot of calculated vitrinite reflection values $R_m(1)$, i.e. Parameter 22 (Radke, 1988), and $R_m(2)$, i.e. Parameter 25 (Radke, 1988). Note the CGC samples with very high $R_m(2)$ values. Also note that the WF samples appear to be the least mature samples of the sample set.

The CGC samples are plotted as the most mature samples. Sample A1 also appear to be more mature than in figures 7.3, 7.4, and 7.5, but is still plotted within the oil window (Figure 7.12). There also appears to be a maturation trend, where the WF samples appear to be the least mature samples, with the exception of samples GS1 and GS2. The parameters are likely affected by source input, and the separation between WF and EF samples might be a consequence of varying degrees of terrestrial input (Radke et al., 1986).
7.4 Organic facies

This sub-chapter includes a discussion based on the calculated parameter values, which are influenced by organic facies. The subchapter begins with a discussion of n-alkanes and isoprenoids, before sterane distribution is discussed. The chapter continues with the presentation of aromatic compounds, and organic facies determination.

7.4.1 Isoprenoids and n-alkanes

Figure 7.13: Cross plot of Pr/n-C$_{17}$ and Ph/n-C$_{18}$. Note the trend of increased terrestrial input to the inferred source rock in the eastern direction of the study area, with the exception of the Gullfaks Sør samples (GS1 and GS2). The majority of the samples plot in a transitional environment with mixed organic sources. Also note sample A1, which appear as the most mature sample in this plot. The increased maturity values for EF samples appear to be related to the degree of terrestrial input to the source rocks. Modified from (Shanmugam, 1985).
In this thesis figure 7.13 is mainly used as an organic facies indicator. As mentioned in Ch. 7.3.1, a distinct trend of increased terrestrial input in the eastern direction is observed. The amount of terrestrial influence appears to affect the maturity estimates, and the EF samples maturity values are most likely overestimated. Figure 7.13 also displays an estimate of the redox-conditions. The values appear to be consistent with observations made in figure 7.9, where EF samples appear to be sourced from source rocks deposited in more oxidizing conditions relative to the WF samples.

### 7.4.2 Distribution of steranes

![Ternary plot of the relative distribution of C27, C28 and C29 ββ-steranes.](image)

**Figure 7.14**: Ternary plot of the relative distribution of C27, C28 and C29 ββ-steranes. Note that all samples form a cluster in the center of the diagram as typical for NCS samples, but there is a small possible trend along the C27-C29 axis, which reflects some variation in source rock kerogen composition. Still, as shown by Karlsen and Skeie (2006) are generally condensates enriched in C27 meaning that this effect must be compensated for. Adapted from (Shanmugam, 1985).
The relative distribution of C27, C28 and C29 ββ-steranes provides information about the depositional environment of the hydrocarbon source. It is assumed that the level of maturity does not significantly impact the distribution of the ββ-steranes (Peters et al., 2007). All of the samples plot as a concentrated cluster slightly closer to an estuarine environment than an open marine environment, which indicates some contribution of terrestrial material for most of the samples. One of the most important details to notice in this plot is the position of sample A1. The Agat condensate displays a significantly more marine signature in figure 7.14 compared to figure 7.13. A1 also has a Pr/Ph ratio = 3.3, which indicates a considerable terrestrial source (Table 6.1). The apparent different source input for isoprenoids/n-alkanes compared to the ββ-steranes biomarkers show mixing of different sources for the Agat condensate. Figure 7.14 also displays a familiar pattern of higher abundance of terrestrial input in the eastern part of the study area with the exception of the Gullfaks Sør field oils.

7.4.3 Aromatic hydrocarbons versus Pr/Ph

Figure 7.15 displays the methyldibenzothiophenes (MDBTs)/methylphenanthrenes (MPs) ratio plotted against the Pr/Ph ratio. The plot is used to determine lithological and organic facies differences between the samples. The vast majority of the sample set is plotted in zone 3, which indicates a marine shale environment. Samples A1 and Ve1 both plot in zone 4, which indicates that the samples are sourced from fluvio/deltaic environment, due to the increased Pr/Ph ratio values. In the context of this study, and the previously observed results, it is suggested that the A1 and Ve1 samples indicate a marine shale source with considerable terrestrial input (Figure 7.15). Oil sample St1, from the Statfjord field, displays a slightly different signature than the rest of the samples, and plots outside the marked zones. The relative high MDBTs/MPs ratio could indicate some carbonate influence (Hughes et al., 1995).
Figure 7.15: Cross plot between Pr/Ph ratio and methyl dibenzothiophenes/methylphenanthrenes (Parameter 27). Note that the majority of the samples plot inside zone 3. St1 is the only sample to plot outside the marked zones. Adapted from Hughes et al. (1995).

Albeit stable carbon isotopes was not part of this study, for time and cost reasons, it is worth noting that Chung et al. (1992) noted that the Agat petroleum is significantly more heavy than e.g. Gullfaks and Oseberg oils, with Snorre oils the isotopically lightest. The authors ascribed this trend as a pure Heather (heavy) to Draupne (light) signature (Figure 7.16).
Figure 7.16: Two illustrations from Chung et al. (1992) relating the significant regional isotope variation, and associated variation in the Pr/Ph values of oils and condensates (upper diagram) to the source rock signatures of the Heather versus the Draupne formations. Note the isotopically heavy Agat signature. This general regional trend in terrestrial- Heather signature, versus a distal-algal Draupne signatur is strongly supported by the parameters used in the current study.
7.5 Oil-oil and oil-source rock correlation

To correlate the samples in this study with known oil families and source rocks, geochemical data gathered by Gormly et al. (1994) is compared to the data acquired in this thesis (Table 7.1 and 7.2). There is a lack of comparable parameters from the study area, and the correlation is dependent on the Pr/Ph ratio. Ideally the correlation should be based on several different parameters calculated from different hydrocarbon fractions. This is evident from the large variations observed in previous figures.
Table 7.1: Pr/Ph ratio ranges gathered from Gormly et al. (1994).

<table>
<thead>
<tr>
<th>Oil family</th>
<th>Pr/Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draupne Fm. (Marine shale)</td>
<td>1.0 – 1.5</td>
</tr>
<tr>
<td>Mixed Source (Marine shale with minor terrestrial input)</td>
<td>1.5 – 2.15</td>
</tr>
<tr>
<td>Heather Fm. (Marine shale with strong terrestrial input)</td>
<td>2.15 – 4.0</td>
</tr>
</tbody>
</table>

Table 7.2: Oil-source rock correlation of thesis’ sample set and the information gathered from Gormly et al. (1994).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Well</th>
<th>Pr/Ph</th>
<th>Correlated oil family</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSO-1</td>
<td>-</td>
<td>1.75</td>
<td>Mixed source</td>
</tr>
<tr>
<td>St1</td>
<td>33/9-14</td>
<td>1.24</td>
<td>Draupne Fm.</td>
</tr>
<tr>
<td>MH1</td>
<td>34/4-5</td>
<td>1.60</td>
<td>Mixed Source/Draupne Fm.</td>
</tr>
<tr>
<td>Sn1</td>
<td>34/7-1</td>
<td>1.40</td>
<td>Draupne Fm.</td>
</tr>
<tr>
<td>Vi1</td>
<td>34/8-1</td>
<td>1.76</td>
<td>Mixed source</td>
</tr>
<tr>
<td>Vi2</td>
<td>34/8-1</td>
<td>1.65</td>
<td>Mixed source</td>
</tr>
<tr>
<td>GS1</td>
<td>34/10-16</td>
<td>2.18</td>
<td>Mixed source/Heather Fm.</td>
</tr>
<tr>
<td>Va1</td>
<td>34/10-23</td>
<td>2.05</td>
<td>Mixed source</td>
</tr>
<tr>
<td>GS2</td>
<td>34/10-32 R</td>
<td>2.46</td>
<td>Heather Fm.</td>
</tr>
<tr>
<td>K1</td>
<td>34/11-1</td>
<td>1.72</td>
<td>Mixed source</td>
</tr>
<tr>
<td>N1</td>
<td>34/11-2 S</td>
<td>1.96</td>
<td>Mixed source</td>
</tr>
<tr>
<td>A1</td>
<td>35/3-4</td>
<td>3.33</td>
<td>Heather Fm.</td>
</tr>
<tr>
<td>G1</td>
<td>35/9-1</td>
<td>2.43</td>
<td>Heather Fm.</td>
</tr>
<tr>
<td>Sk1</td>
<td>35/9-7</td>
<td>2.17</td>
<td>Mixed Source/Heather Fm.</td>
</tr>
<tr>
<td>Ve1</td>
<td>35/11-2 S</td>
<td>3.11</td>
<td>Heather Fm.</td>
</tr>
<tr>
<td>F1</td>
<td>35/11-15 S</td>
<td>2.00</td>
<td>Mixed source</td>
</tr>
<tr>
<td>R1</td>
<td>35/12-4 S</td>
<td>2.72</td>
<td>Heather Fm.</td>
</tr>
<tr>
<td>G2</td>
<td>36/7-1</td>
<td>2.45</td>
<td>Heather Fm.</td>
</tr>
</tbody>
</table>

Table 7.1 presents the oil family ranges proposed by Gormly et al. (1994). Table 7.2 shows terrestrial input is higher in the eastern part of the study area. The majority of the samples have been correlated as mixed source. It is important to note that the value ranges chosen by Gormly et al. (1994) are reasonable, but arbitrarily created. The Pr/Ph ratio is also affected by thermal maturation, and it is therefore quite possible that several of the samples displays overestimated levels of terrestrial input. This could be the case with the thermally mature CGC samples (K1, N1, and Va1), which have been correlated as mixed source, but could possibly be sourced from the Draupne Fm. According to Gormly et al. (1994), the oils located
in the western part of the study area, i.e. Visund, Snorre, Statfjord, are sourced from the Draupne Fm. The Gullfaks Sør field is the exception, and is sourced from both the Draupne Fm. and the Heather Fm. In the eastern part of the study area, the Agat Fm. is likely sourced from the Heather Fm., or the middle Jurassic coals. Most of the EF samples have been correlated to the Heather Formation.

7.6 Migration and phase fractionation

Former research in the area is reviewed and discussed in context of the new information attained in this thesis. Chapter 7 began with a notice on potential evidence for phase fractionation in figure 7.1. This subchapter tries to summarize and discuss the accumulated evidence for phase fractionation, and it’s potential implication on hydrocarbon migration in the study area.

The general migration patterns of the northern North Sea appear to be well known and documented. It generally involves a source rock, which have been exposed to higher temperatures in the center of the graben. The source rock expels the hydrocarbon, which laterally migrate through permeable beds and fault planes, into structural highs and traps located on the flanks of the graben (Cornford, 2009). The results and observations of this thesis appear to be in agreement with this general migration overview. There are, however, potential interesting consequences due to phase fractionation in the northern part of Quadrant 35.

7.6.1 Evidence for phase fractionation

A condensate is understood to arise generally via four different processes (Kingston, 1990).

1. Generation from type III kerogen source rocks throughout the oil window, i.e. a source rock control.
2. Generation from oil-prone or oil/gas-prone source rocks at late oil window levels, i.e. a maturity control.
3. Thermal cracking of oil in high-temperature reservoirs, i.e. an intrareservoir destruction process.
4. Evaporative fractionation/phase fractionation, i.e. a migration related process.
Condensates can be generated by phase fractionation when a charge of dry gas enters a trap already occupied by oil. The gas equilibrates with the light compounds of the oil, before the gas is vented from the reservoir migrating towards a shallower reservoir. At shallower depths the gas condensate out a liquid, which is referred to as a retrograde condensate. This process leads to two hydrocarbon accumulations. The high gravity retrograde condensate located at a shallower reservoir, and residual oil depleted in light paraffins located in the original reservoir (Thompson, 1988; Thompson, 1987).

Condensates generated by phase fractionation display certain defining characteristics. The samples should be depleted in light aromatic compounds relative to light saturated compounds. The samples should not indicate high maturity. Phase fractionation should also lead to a low abundance of biomarkers derived from higher plants relative to other biomarkers of similar molecular weight (Thompson, 1987; Thompson, 1988; Kingston, 1990).

Sample A1 from Agat displays several of these characteristics. The sample has a mixed source signature with a high Pr/Ph value and no significant signs of terrestrial influence from biomarker parameters. A1 also show signs of varying degrees of maturity, however, the parameters that indicate high maturity, appear to be affected by other processes (Ch. 7.4). It is therefore suggested that the maturity levels of sample A1 is consistent with evaporative fractionation. High levels of aromaticity (Ch. 7.2) also indicate evaporative fractionation.

There is also evidence that suggests that sample A1 could have been generated from a type III kerogen source rock. A condensate generated from type III kerogen source rocks has a very high Pr/Ph-ratio, and high abundance of light aromatic compounds (Snowdon and Powell, 1982). Sample A1 does indeed have a high Pr/Ph value, and relative high abundance of toluene. However, the mixed source signature tips the scale in favor of evaporative fractionation as the most likely process to generate the A1 condensate. A significant fractionation of Heidrun oils resulting in very high Pr/Ph values for a gas condensate above the main Jurassic structure was described in Karlsen et al. (1995). In that study the Pr/Ph value in the Jurassic traps was mostly around 1.3 to 1.4, with up to 4.2 in the condensate. In addition to the evidence presented in this thesis, Ohm et al. (2006) has found evidence of evaporative fractionation occurring at Marflo Ridge in block 35/1, located west of the Sogn Graben.
7.6.2 Reservoir infill and potential oil accumulations

Figure 7.17 displays a tentative reservoir sketch of the evaporative condensate accumulation in the Agat Fm., and a potential residual oil accumulation in the down-dip direction. Ohm et al. (2006) proposed a lateral migration pathway from a locally sourced atypical Jurassic source rock located in the Sogn Graben. The same is assumed to be true in this thesis, and according Thomas et al. (1985), the Agat kitchen is likely located in the central part of the Sogn Graben, where the Humber Group source rocks are assumed to be gas mature. It is proposed that a source rock, with significant terrestrial input (Heather Fm. or Brent Gp. Coals), generated dry gas, which migrated into a trap already occupied by oil (Figure 7.17, stage a). The gas subsequently equilibrates with the accumulated oil (Figure 7.17, stage b). Thompson (1988) describes the process of phase fractionation in detail. The essential element needed is a structural element, i.e. fault, which creates a zone of reduced pressure. If the reduced pressure zone is below the bubble point of the oil, exsolution of gas occurs immediately, and the gas migrates as vapor trough the fault plane (Figure 7.17, stage c). It is proposed that only saturated vapor migrates, which implies that the residual oil is depleted in light ends, due to fractionation. The vapor migrates through permeable beds and faults planes (Figure 7.17, stage d), and is condensed out from the vapor into the trap (Figure 7.17, stage e).
Figure 7.17: Tentative simplified migration model for the evaporative condensate accumulation in the Agat Fm.

Figure 7.17 is not intended to accurately describe the details of the Agat Fm. reservoir, but gives a broad and general overview of the process, which might have produced the Agat condensate. If this process has occurred, there is a potential for future oil discovery in the area. The potential residual oil accumulation is tentatively proposed to be in the down dip direction relative to the Agat condensate discovery.

Another possible migration scenario in the northern part of Block 35 is based on the theory of differential entrapment of hydrocarbons and migration of reservoir fluids presented by Gussow (1968) and Gussow (1954). The theory predicts oil accumulations in the up-dip direction of gas filled reservoirs. This is due to differential entrapment, where gas displaces oil, and the oil remigrates in the up-dip direction. In this model all cap rocks are treated as “perfect”. Variable cap rock properties can ensure that also gas traps leak and have room for an oil-leg, as often observed in traps on the NCS (Sales, 1997). The Gussow principle suggests that gas/condensate accumulations exist close to the graben, and oil accumulations in the up dip direction. This seem to fit with the general picture in this region for e.g. Stafjord, Oseberg and Gullfaks, which all leak gas (Sales, 1997). This is also interpreted to be the case
for the CGC samples, which are located in the traps closest to the graben, while oil have accumulated in traps further up-dip on structural highs (Matapour and Karlsen, 2017).

Figure 7.18: Simplified fill-spill migration system based on theory by Gussow (1968). Green indicates gas. Red indicates oil. Arrows describe the migration path of oil, which is either displaced by gas, or bypass the trap entirely. Oil migrates in a proximal direction, as suggested for e.g. Johan Sverdrup (Wesenlund, 2016).

The differential entrapment and fill-spill theory suggests potential oil discoveries in the up-dip proximal direction relative to the Agat Formation. If this is correct, appreciable amounts of oil from the Sogn Graben could exist in proximal basin directions (Figure 7.18).
7.7 Age determination

The 24-nordiacholestane/27-nordiacholestane (NDR) ratio is a parameter, which indicates the age of the deposited OM source. The 24-cholestane compounds are believed to be related to diatoms, which increased rapidly in abundance during the Cretaceous. The range of NDR values vary between 0.18 and 0.24 (Table 6.1). All of the samples appear to be sourced from Jurassic age source rocks (Holba et al., 1998), and no support is seen to suggest that e.g. the Agat sample, which occurs in a Cretaceous trap, could indeed be Cretaceous. Thus, compared to the Cretaceous oils off Mid-Norway described by Matapour and Karlsen (2017), nothing similar is observed for Agat.

7.8 Discussion summary

This subchapter includes a short summary of the most important findings, as well as tentative rankings of samples with regards to thermal maturity and organic facies. The subchapter begins with the light hydrocarbon analysis summary. Subsequently thermal maturity and organic facies are summarized. After the organic facies summary, the migration and evaporative fractionation summary finishes the chapter.

7.8.1 Light hydrocarbons

The Light HCs analysis provided the initial evidence for evaporative fractionation/phase fractionation. Sample A1 separated from the other samples with relatively high aromaticity values (Figure 7.1). Most of the samples from traps of shallow to intermediate depth, appeared to be significantly biodegraded in figure 7.1, however, the chromatograms does not appear to show significant biodegradation, and it is suggested that the biodegradation of the light HC fraction is a paleo-biodegradation event. As traps presently at approximately 4km and deeper do not contain these features, one could suggest that the inferred biodegradation event occurred when the traps were about 1.5km more shallow than today and it should be possible to estimate tentatively the time for this using a burial history from the region.

7.8.2 Thermal maturity

A distinct trend of higher maturity for samples located closer to the central part of the northern Viking Graben is observed. The EF samples might exhibit a slightly higher maturity
trend than the WF samples, but this has been interpreted to be a result of terrestrial input. Figure 7.19 displays a tentative subjective maturity ranking based on observations made. The CGC-samples are most likely generated in the late oil zone – condensate stage, and are the most mature samples. All the other samples are likely generated in the oil window. The most western samples appear to be the least mature and hence reflecting a more shallow source rock. This pattern could help in delineating migration patterns in the region.
### Figure 7.19: Tentative subjective thermal maturity rankings based on accumulated data in Ch. 7.3. Note that the least mature samples appear to be located in the western part of the study area. The most mature samples are CGC samples, which are located closest to the graben center.

<table>
<thead>
<tr>
<th>West / East</th>
<th>Stl</th>
<th>GS1</th>
<th>GS2</th>
<th>Sn1</th>
<th>MH1</th>
<th>Val</th>
<th>N1</th>
<th>Vi1</th>
<th>Vi2</th>
<th>K1</th>
<th>Ve1</th>
<th>F1</th>
<th>Sk1</th>
<th>R1</th>
<th>A1</th>
<th>G1</th>
<th>G2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower maturity / Higher maturity</td>
<td>GS1</td>
<td>Stl</td>
<td>Sn1</td>
<td>R1</td>
<td>MH1</td>
<td>GS2</td>
<td>Sk1</td>
<td>F1</td>
<td>Vi1</td>
<td>G2</td>
<td>G1</td>
<td>A1</td>
<td>Ve1</td>
<td>Vi2</td>
<td>N1</td>
<td>K1</td>
<td>Va1</td>
</tr>
<tr>
<td>Early oil zone – Peak oil zone</td>
<td>Early oil zone – Late oil zone</td>
<td>Late oil zone – Cond.</td>
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</table>

### Figure 7.20: Tentative terrestrial input rankings based on the correlation analysis completed in Ch. 7.5. The amount of terrestrial input might be overestimated for condensates. This is due to the extensive thermal maturation process some of the condensate samples have experienced, which affects the Pr/Ph ratio. Note the general trend of increased terrestrial input in the eastern direction. Also note the Gullfaks Sør oils (GS1 and GS2), which indicate higher amounts of terrestrial source rock input.

<table>
<thead>
<tr>
<th>West / East</th>
<th>Stl</th>
<th>Sn1</th>
<th>MH1</th>
<th>Vi2</th>
<th>K1</th>
<th>Vi1</th>
<th>N1</th>
<th>F1</th>
<th>Val</th>
<th>Sk1</th>
<th>GS1</th>
<th>G1</th>
<th>G2</th>
<th>GS2</th>
<th>R1</th>
<th>Ve1</th>
<th>A1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less terrestrial input / More terrestrial input</td>
<td>Draupne Fm.</td>
<td>Mixed source</td>
<td>Mixed/Heather Fm.</td>
<td>Heather Fm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
7.8.3 Organic facies and oil-source rock correlation

The organic facies analysis revealed a distinct trend of increased terrestrial input in the eastern direction (Figure 7.20). The vast majority of samples appear to be sourced from marine shales with varying degrees of terrestrial input. Samples St1 and Sn1 was correlated with the Draupne Fm. source rock, however most of the samples displayed a mixed source signature, which is defined by Gormly et al. (1994) as marine shale with minor terrestrial input. Six samples, mostly located in the eastern part of the study area, were correlated to the Heather Formation. The exceptions to this are the Gullfaks Sør oils, which display signs of even higher amounts of terrestrial input.

7.8.4 Evaporative fractionation and migration

This thesis argues that the A1 condensate from Agat was generated by evaporative fractionation. Low maturity, mixed source signature, low abundance of biomarkers derived from higher plants relative to other biomarkers of similar molecular weight, and high aromaticity values are indicative of evaporative fractionation. The evaporative fractionation process indicates a residual oil accumulation in the down dip direction relative to the Agat condensate discovery (Thompson, 1988). Still, the theory presented by Gussow (1968) tentatively suggest that there are potential oil accumulations in the up-dip proximal direction. What is common to both models is that the Agat condensate was co-genetic with oil, which should exist in the region.

The general migration patterns of the northern North Sea involve lateral migration to structural highs and traps located on flanks of the graben (Cornford, 2009).

7.8.5 Biodegradation

The light hydrocarbon analysis suggested that biodegradation had altered most of the petroleums in this study, however, the chromatograms suggest that only incipient amounts of biodegradation has occurred implying, the depths at which the reservoirs are situated are deemed too deep for biodegradation to occur today or recently. The thesis tentatively suggests that some form of palaeo-biodegradations has occurred (Matapour and Karlsen, 2017).
8 Summary and conclusions

A total of 18 samples, twelve oils and six condensates (including reference sample NSO-1), produced from 17 different wells located in the northern North Sea, were analyzed in this thesis. The study area spans four different quadrants in the northern part of the North Sea, from Quadrant 33 in the west to Quadrant 36 in the east. The area is structurally defined by a major orogenic collapse in the Devonian period. The orogenic collapse, in addition to two major rifting stages, which occurred in the Permian to Early Triassic, and in the late-Mid Jurassic to Early Cretaceous period, has created the mature graben topography of present day northern North Sea. The wells are drilled on structural highs on the flanks of the Viking Graben and Sogn Graben. As the source rock matures with depth in the graben during burial, it expels petroleum, which migrates laterally into rotated fault blocks located on the flanks.

The analytical methods used in this thesis are GC-FID, GC-MS and GC-MS/MS, which provided valuable information on the following subjects through interpretation parameters:

- The light hydrocarbon composition
- Thermal maturity
- Organic facies
- Oil-oil and oil-source rock correlation
- Evaporative/phase fractionation and migration
- Age determination of hydrocarbon sources

The light hydrocarbon analysis (Ch. 7.2) indicated that condensate sample A1 was generated by a process known as evaporative fractionation/phase fractionation.

The thermal maturity analysis that followed indicated oil window maturity for sample A1, which further supports phase fractionation as the generation process. The thermal maturity analysis also highlighted maturity differences based on longitude, where condensate samples located closest to the graben, also appeared as the most thermally mature. Samples located in
the western part of the study area indicated the lowest maturity levels, however, the maturity differences between the EF samples and the WF samples, might also be related to terrestrial input differences, as several facies parameters like the Pr/Ph ratio and also the ratio of C29 to C27 steranes are influenced by phase fractionation and maturity.

The terrestrial input increased in the eastern direction of the study area, and this is interpreted to be the cause of the increased maturity values for EF samples when parameters are significantly affected by source input. The Gullfaks Sør oils also appear to be affected by this effect, which overestimate the maturity on certain parameters affected by OM input. The Agat condensate (A1) displayed a mixed geochemical signature, with indications of moderate terrestrial input based on the ββ-sterane distribution, and very high Pr/Ph ratio value. The mixed signature further indicated evaporative fractionation as the most likely generation process for sample A1. The oil-oil and oil-source rock correlation was based on the Pr/Ph ratio. Samples St1 and Sn1 are the only samples that were correlated to the Draupne oil family and Draupne Fm. source rock. Most of the samples are correlated to a mixed source input, which is defined as a marine shale with minor terrestrial input. EF samples are generally correlated to the Heather oil family and Heather Fm. source rock, which is defined as a marine shale with major terrestrial input.

Based on accumulated information, the A1 sample is proposed as a phase fractionated condensate. This process suggests a residual oil might be located in the down dip direction of the Agat Fm. reservoir, or in an up-dip direction following the Gussow model.

GC-MS/MS analysis was performed to determine the age of the samples source rocks. The NDR ratio parameter indicates that all samples are sourced from Jurassic aged source rocks, with no evidence for Cretaceous sourced petroleum.
9 Future work

This thesis is based on the results calculated by a wide range of parameters derived from three analytical methods, e.g. GC-FID, GC-MS and GC-MS/MS. There are however several other methods and analytical parameters, which could improve the accumulated data set by further inquiry.

- A larger database of geochemical data from the study area would increase the understanding and confidence in the trends observed.

- Stable carbon isotopes is seen as the single most important parameter still left to investigate as it tends to carry a very conservative source rock information, not easily altered by migration, slight phase fractionation nor slight biodegradation. This could not be done in this study for time and cost reasons. One would expect Heather derived oils and condensates to be isotopically heavier than the Draupne derived petroleums.

- Thus, a wider range of comparable parameters with former studies in the area would also improve the confidence in the gathered results. In this particular study, the oil-oil and oil-source rock correlation were based on the samples Pr/Ph ratios. Ideally several parameters should be used, as it is evident several parameters are needed to isolate variables that influence the results. Former studies in the northern North Sea often incorporate carbon isotope data, API Gravity data and sulfur content. If these parameters were included in this study, correlation of several parameters with Schou et al. (1985), Gormly et al. (1994), and Keym et al. (2006), would greatly improve the confidence in the results obtained.

- TLC-FID Iatroscan analysis would reveal the gross composition of the petroleum samples. This would add information on thermal maturity, biodegradation, migration and compositional variations between the samples. It is also often improving the identification of phase fractionated samples (Karlsen et al., 1995).

- The northern North Sea is a severely faulted area with a complex tectonic history. Processes like burial history, petroleum generation, migration, and reservoir infill, are all notably affected by the complex variables related to the tectonic and depositional history of the area. The addition of seismic data, well log data, and structural mapping
of the area, would provide valuable information, which would aid the understanding of the processes involved in the outlined “Petroleum systems”.
Bibliography


Appendix A  GC-FID chromatograms
Sample: NSO-1
Sample: St1 (Well 33/9-14)
Sample: MH1 (Well 34/4-5)
Sample: Sn1 (Well 34/7-1)
Sample: Vi1 (Well 34/8-1)
Sample: Vi2 (Well 34/8-1)
Sample: GS1 (Well 34/10-16)
Sample: Va1 (Well 34/10-23)
Sample: GS2 (Well 34/10-32 R)
Sample: K1 (Well 34/11-1)
Sample: N1 (Well 34/11-2 S)
Sample: A1 (Well 35/3-4)
Sample: G1 (Well 35/9-1)
Sample: Sk1 (Well 35/9-7)
Sample: Ve1 (Well 35/11-2)
Sample: F1 (Well 35/11-15 S)
Sample: R1 (Well 35/12-4 S)
Sample: G2 (Well 36/7-1)
Appendix B  GC-MS chromatograms
Sample: NSO-1
Sample: St1 (Well 33/9-14)
Sample: MH1 (Well 34/4-5)
Sample: Sn1 (Well 34/7-1)
Sample: Vi1 (Well 34/8-1)
Sample: Vi2 (Well 34/8-1)
Sample: Va1 (Well 34/10-23)
Sample: GS2 (Well 34/10-32 R)
Sample: K1 (Well 34/11-1)
Sample: N1 (Well 34/11-2 S)
Sample: A1 (Well 35/3-4)
Sample: G1 (Well 35/9-1)
Sample: Sk1 (Well 35/9-7)
Sample: Ve1 (Well 35/11-2)
Sample: F1 (Well 35/11-15 S)
Sample: R1 (Well 35/12-4 S)
Sample: G2 (Well 36/7-1)
Appendix C  GC-MS/MS chromatograms
Sample: St1 (Well 33/9-14)
Sample: MH1 (Well 34/4-5)
Sample: Sn1 (Well 34/7-1)
Sample: Vi1 (Well 34/8-1)
Sample: Vi2 (Well 34/8-1)
Sample: GS1 (Well 34/10-16)
Sample: Va1 (Well 34/10-23)
Sample: GS2 (Well 34/10-32 R)
Sample: K1 (Well 34/11-1)
Sample: N1 (Well 34/11-2 S)
Sample: A1 (Well 35/3-4)
Sample: G1 (Well 35/9-1)
Sample: Sk1 (Well 35/9-7)
Sample: Ve1 (Well 35/11-2)
Sample: F1 (Well 35/11-15 S)
Sample: R1 (Well 35/12-4 S)
Sample: G2 (Well 36/7-1)