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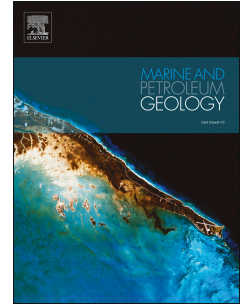
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Unravelling maturity- and migration-related carbazole and phenol distributions in Central Graben crude oils

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Abstract

In this contribution we present the results of an integrated investigation of selected nitrogen- and oxygen-bearing compounds in Norwegian Central Graben crude oils. We first provide an interpretation framework built on hydrocarbon biomarkers, and then use this framework to relate polar compound geochemistry to the influences of source facies (Farsund versus Mandal Formations), maturity, migration and reservoir lithology.

Oil maturity could be assessed using established changes in carbazole annelation (N_1 DBE 9 vs. 12 vs. 15 classes), as well as hydrocarbon biomarkers. $29Ts/(29Ts+NH)$ correlated best with the polar compound maturity data. Secondary migration fractionation appears nevertheless to have played a role, as seen by increased DBE 9 and 12 carbazole and benzocarbazole proportions and a loss of C_{2-3} DBE 12 homologues within carbonate reservoirs as compared to intraformational Upper Jurassic siliciclastic reservoirs. Thus migration distances, pathways and wettability of carrier systems ostensibly play a significant role in carbazole distributions of the Central Graben oils, manifesting itself as apparent maturity retardation. In an attempt to eliminate the migration component from maturity assessment, we here present a novel ternary diagram including dibenzocarbazoles (N_1 DBE 15) and phenolic species (O_1 DBE 4 and 5) based on a single measurement using the FT-ICR-MS. However, the integration of such results into 3D-modelling software must be conducted to clarify source kitchen, migration pathways and distances.

1. Introduction

Petroleum consists of an exceedingly complex mixture of hydrocarbons and non-hydrocarbons, extending from methane to macromolecular aggregates such as asphaltenes. The relative proportions of these components are quite variable and depend initially on the type of organic matter in the parent source rock, its level of maturity at the time of expulsion, and subsequently upon secondary effects including phase behaviour (Silverman, 1965; England et al., 1987; England and Mackenzie, 1989; Larter and Mills, 1991; di Primio and Skeie, 2004), fractionation during expulsion (Han et al., 2015; Ziegs et al., 2017), biodegradation and water washing (Connan, 1984; e.g. Ahsan et al., 1998) and in-reservoir maturation (Gabrielsen et al., 1985; Horsfield et al., 1992). The mixing of charges from co-sources (e.g. Ohm et al., 2012) and the acquisition of organics along migration routes (Curiale and Bromley, 1996) also occur. Deciphering these various influences remains a key challenge in petroleum geochemistry. Recognising and predicting the occurrence of migration fractionation is an important element in petroleum system assessment, because the processes, strongly influenced by water-oil and rock-oil interactions (Li et al., 1994; Larter et al., 1996; Mann et al., 1997), can alter the physicochemical properties of crude oils appreciably. Being of low polarity, hydrocarbon biomarkers reflect source and maturity and are not suitable for tracing fractionation (Peters et al., 2005). Polar compounds on the other hand lend themselves well to this application.

Early attempts to integrate the alkylcarbazoles and alkylphenols into petroleum geochemistry protocols were made by the Newcastle Research Group (Li et al., 1994; Stoddart et al., 1995; Larter et al., 1996; Li et al., 1997) using gas-chromatography mass-spectrometry (GC-MS) data. The main concept was that migration-related fractionation is controlled by the surface activity of polar compound isomers, as determined by the local chemical environment of the functional group or polar atom. Shielding effects of

fused/annelated rings or alkyl side chains and therefore, the molecular size and shape of individual molecules, influence polarity and thus have been proposed as maturity-independent measures of migration distance. They are affected by sorption onto clay minerals or into solid organic matter (Stoddart et al., 1995; e.g. Larter et al., 1996) or by oil-water-partitioning (van Duin and Larter, 2001). Li et al. (1994) and (1995) suggested that migration fractionation has a more remarkable impact on pyrrolic nitrogen abundances and distributions than source environments. Varying lithology and geometry along the migration pathway affect distributions (Li et al., 1998). Nevertheless, the preferential removal of the rod-shaped [a] isomer relative to the sub-spherical [c] configuration, originally considered to be migration-driven (Larter et al., 1996), can be influenced by **maturity** (Li et al., 1997; Clegg et al., 1998a; Clegg et al., 1998b; Horsfield et al., 1998), and **facies** (Bakr and Wilkes, 2002) in vertically drained petroleum systems. This is also the case for the predominant enrichment of alkylcarbazoles over alkylbenzocarbazoles and generally an enrichment of more methylated over less methylated homologues. Clegg et al. (1997) compared relative abundances of alkylated carbazoles in the carbonate-rich Keg River Formation and found that C₄₋₅ carbazoles prevailed in the lower transgressive facies but C₀₋₁ carbazoles dominate the upper regressive facies. Source and maturity variations can also have a strong impact on the hydrocarbon fraction, but not on the pyrrolic N fraction of crude oils in the Rainbow-Shekilie-Zama sub-basins, NW Alberta, Canada (Li et al., 1999). Due to short migration distances, strong correlations between oil maturity and carbazole distributions were shown for the marine carbonate Tithonian source rocks of the Sonda de Campeche (Clegg et al., 1998b; Horsfield et al., 1998).

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) has offered new insights into polar compound geochemistry (e.g. Hughey et al., 2002; Marshall and Rodgers, 2008). While it cannot identify stereochemical isomers, FT-ICR MS offers the big advantage of extending the molecular weight range up to 1000 Da. In

addition, it differentiates between the multitudes of N-, S- and O-compounds in complex mixtures according to aromaticity, annulation and aliphaticity. The ESI negative mode is able to ionize acidic ring structures with one or more nitrogen (N_1 to N_2), oxygen (O_1 to O_x) and sulphur atoms (S_1 to S_z) or combinations of all three (N_yO_x , N_yS_z or S_zO_x classes). Double Bond Equivalents define the structure of these compounds by the number of aromatic and saturated rings plus unsaturated carbon bonds incorporated into the core structure and attached side chains (Oldenburg et al., 2014; Poetz et al., 2014), thus defining their aromaticity (Hughey et al., 2002; Hughey et al., 2004). The relative abundance of carbazoles, benzo- and dibenzocarbazoles in a North Sea Viking Graben oil series, as determined using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, showed a strong dependence on maturity (FT-ICR-MS, Oldenburg et al., 2014). The term aliphaticity has been used to define the chain length distribution (short, intermediate, long) of the side chains attached to a given core structure (Mahlstedt et al., 2016), this being relatable to similar structural moieties in kerogens (cf. Muscio et al., 1991).

Here we present the results of an integrated investigation of selected polar compounds of Central Graben crude oils, utilising FT-ICR MS data. Importantly, we first provide an interpretational context for the petroleum system using hydrocarbon biomarkers, and then use this framework to relate polar compound geochemistry to the influences of source facies, maturity, migration fractionation and reservoir lithology. An assessment of expulsion efficiency and factors controlling adsorption has already been presented (Ziegs et al., 2017).

2. Geological setting & hydrocarbon habitat

The Central Graben is an intracratonic basin forming the southern branch of the North Sea triple rift complex (Fig. 1, inset) whose Norwegian part is bounded by the Mid-North Sea High to the southwest and the Coffee Soil Fault to the northeast (e.g. Gowers et al., 1993; Japsen et al., 2003; Møller and Rasmussen, 2003). The Mandal High in the southernmost part of the Norwegian sector split the main graben, having evolved as an extensional basin, from the adjacent Søgne Basin which developed as a half-graben (Rossland et al., 2013). Its present-day configuration results from failed rift development starting during Permian times and culminating during the Upper Jurassic (Ziegler, 1988; e.g. Glennie, 1990, 1990; Gowers et al., 1993), followed by a thermal sag phase from the Cretaceous up to the present day. The deposition of thick Zechstein salt successions during prolonged extension in Permian-Triassic times is followed by a Triassic sequence of continental red-bed mudstones, siltstones and minor sandstones. Lower Jurassic successions are largely missing due to pre-rift doming which represents the earliest stage of the main extensional phase (Ziegler, 1990; Underhill and Partington, 1993; Andsbjerg et al., 2001; Andsbjerg and Dybkjaer, 2003; Nielsen, 2003). Middle Jurassic shallow-marine shaly-coaly sandstones of the Lulu and Bryne Formations constitute the first horizons of the Jurassic extensional phase, followed by the deposition of thick, OM-rich, marine black shales in the Upper Jurassic/basal Cretaceous. The opening of the Atlantic Ocean during the Early Cretaceous completely changed the regional stress regime causing the cessation of rifting and flooding of the basin with fresh water, marking the initiation of the post-rift thermal subsidence. The sequential deposition of Lower Cretaceous organic-lean, marine shales, Upper Cretaceous chinks and limestones, and thick Cenozoic shales successions, resulted in the progressive burial and thermal maturation of Upper Jurassic source rocks in the Central Graben. Present-day burial depths along the graben axis are ~4700 m and up to 3300 m

along the flanks. Chalk sequences represent the major reservoir type in the Central Graben axis (Ziegler, 1990; Cornford, 1994), e.g. the Ekofisk, Eldfisk, and Valhall fields, which account for 72% of the Central Graben's initial petroleum in-place reserves (npd.no, Dec 2015). At marginal basin locations (light grey in Fig. 1), clean, shallow-marine sandstones of the Ula Formation were deposited during Middle and Upper Jurassic times constituting important reservoirs (dark grey in Fig. 1).

Upper Jurassic black shales are subdivided into the Haugesund, Farsund and Mandal Formations in the Norwegian part of the Central Graben. The Mandal Formation constitutes the principal source rock in the graben centre containing Type II algal marine OM. The Farsund Formation, a less prolific source rock which contains higher terrigenous input, has charged individual petroleum accumulations (e.g. 2/2-1, Gabrielsen et al., 1985), generally at marginal locations where the Mandal is thin or eroded. Although being a TOC-rich source rock, the Mandal Formation possesses a low efficiency in expelling its generated products which was attributed to enhanced generation of heavy, involatile and thus less movable petroleum fractions in which volatile products are partially retained (Ziegs et al., 2017). Different mechanisms for retention of oil and gas may as well affect the gas-oil-ratio of expelled products.

3. Samples & Methods

3.1. Sample set

Crude oils were selected based on publically available screening data in the online database of the Norwegian Petroleum Directorate (NPD), including fluid test type, reservoir depth and stratigraphy, API gravity and GOR. A screening database provided

by Aker BP ASA contained supplementary bulk compositional data. The oils obtained from drill stem tests (DST) were provided by the NPD.

Twenty-four DST oils from 20 well locations were selected as representing the API and likely maturity range typical for the Central Graben. Cornford (1998) identified the main mode of North Sea oils representing a full maturity spectrum at 38° API. The sample choice included oils potentially sourced from the Mandal Formation that is the principal source rock in the Mandal-Ekofisk petroleum system (Cornford, 1994). Three oils which have been generated by source rocks with different organic matter types were selected as a compositional comparison to intra-Mandal facies variations. The 2/2-5 oil was generated from a source rock formed under locally restricted, hypersaline and highly anoxic depositional environment (Pedersen et al., 2006). The Farsund Formation, a marine shale with a higher input of terrigenous organic matter, has charged the 2/2-1 discovery (Gabrielsen et al., 1985). The Trym condensate play (well 3/7-4) was sourced by the coaly Middle Jurassic Lulu Formation from the Danish part of the Søgne Basin and represents the only active petroleum system there (Petersen and Brekke, 2001). The sampled crude oils were collected from either Upper Cretaceous to Lower Palaeocene carbonate reservoirs or Devonian to Upper Jurassic (silici)clastic reservoirs.

Five petroleum provinces have been distinguished in the Norwegian Central Graben (NCG) based on literature (Cooper and Barnard, 1984; e.g. Gabrielsen et al., 1985; Hughes et al., 1985; Petersen and Brekke, 2001; Ohm et al., 2012): Chalk and limestone reservoir occur in (1) deep axial regions developed in the southwest of the NCG (Greater Ekofisk area) but as well (2) at the Steinbit Terrace. (3) Shallow-marine sandstone reservoirs are restricted to shallower, marginal areas in the north/northeast, called here the “Extended Ula Trend”, (4) In the Søgne Basin no active Upper Jurassic sourced petroleum system has been identified, despite sufficient source rock presence and maturity (Petersen et al., 2013; Ziegls et al., 2017). The Trym condensate (well 3/7-4),

on the other hand, is charged from the marine-influenced, coaly Lulu Formation. The 2/6-5 discovery is located within the structural borders of the Søgne Basin but oil-source correlation is to-date unclear. (5) Although structurally located in the basin axis, the 2/7 oils of the siliciclastic Embla field (SW region) are distinguishable due to a mixed origin with minor input of Palaeozoic oils that were biodegraded before receiving fresh, undegraded petroleum from the Upper Jurassic Farsund Formation (Ohm et al., 2012). Furthermore but not linked to a source kitchen, the Mjølner oil field close to the Danish border has been produced from shoreline sandstones of the Eldfisk Formation which was deposited synchronously to the Haugesund Formation (Söderström et al., 1991).

3.2. Analytical methods

Geochemical data of conventional geochemical analyses on crude oils are provided by the project partner Aker BP ASA and measured by APT Norway AS. FT-ICR-MS measurements are conducted at GFZ.

For GC-FID on whole oils, an Agilent 7890 A instrument is used. The column is a HP PONA, length 50 m, i.d. 0.2 mm, film thickness 0.5 μm . 2,2,4-tri-methyl-pentane is used as an internal standard. The Temperature programme is as follows: 30 °C (10 min. isothermal) - 2 °C/min. - 60 °C (10 min.) - 2 °C/min - 130 °C (0 min.)-4 °C/min. - 320 °C (25 min.). The oils were fractionated into aliphatic, aromatic and polar fractions using an automated medium pressure liquid chromatography (MPLC) procedure (Radke et al., 1980). Sample weights of the individual fractions were used for the chemical gross composition. GC-MS was conducted on the saturate and aromatic fraction, but only the former fraction was useful for interpretation. For GC-MS analysis of the saturate fraction, a Micromass ProSpec high resolution instrument is used. The instrument is tuned to a resolution of 3000 and data is acquired in Selected Ion Recording (SIR) mode.

The column used is a 60 m CP-Sil-5 CB-MS with an i.d. of 0.25 mm and a film thickness 0.25 μm . $\delta 4\text{-}27\alpha\text{dR}$ is used as internal standard for quantification. The temperature programme is the following: 50 $^{\circ}\text{C}$ (1 min.) - 20 $^{\circ}\text{C}/\text{min}$. - 120 $^{\circ}\text{C}$ - 2 $^{\circ}\text{C}/\text{min}$ - 320 $^{\circ}\text{C}$ (20 min.).

Mass analyses on the polar compounds were performed with a 12 T FT-ICR mass spectrometer in negative ion ESI mode equipped with an Apollo II ESI source both from Bruker Daltonik GmbH (Bremen, Germany). Details on the analytical procedure, mass calibration and subsequent data analysis were described in Mahlstedt et al. (2016). Consequently developing and adjusting the method to the needs of the samples, we have used stock solutions with a concentration of 1000 $\mu\text{g}/\text{ml}$ MeOH:Tol [1:1, v:v] + 10 μl aqueous NH_3 solution to facilitate deprotonation). The mass spectra, having been accumulated in a mass range from m/z 147 to 750 Da during 200 scans, were internally recalibrated using known homologous series of saturated fatty acids and carbazoles with one, two, and three additional fused aromatic rings. A quadratic calibration mode was chosen for all samples. Elemental formulas were assigned to the recalibrated m/z values with a maximal error of 0.5 ppm using S/N ratio of 12 and allowing 0- ∞ C, 0- ∞ H, 0-8 O, 0-2 N, 0-2 S, and 0-1 Na atoms as well as 0-2 ^{13}C isotopes. The number of assigned signals, mostly above 80% of all detected peaks, the mean molecular weight (normalized to # of signals, M_n , and molecular weight, M_w), and the relative monoisotopic ion abundances of major compound classes are listed in Table 2, whereby the subscripts denote the number of heteroatoms incorporated into individual chemical structures. Elemental classes, compound classes and individual compounds are given as Total Monoisotopic Ion Abundance (% TMIA) representing a relative abundance of individual compounds based on all detected compounds, excluding the ^{13}C species.

4. Results & Discussion

4.1. Oil and condensate properties using conventional parameters

4.1.1. Variations of API with depth

The sample set covers a wide range of API gravities from different regions of the Norwegian Central Graben encompassing 29° API black oils (Krabbe discovery, 7/8-3) to 55° API condensates of the Tommeliten Alpha field (1/9-1). Present-day bottom hole temperatures (BHT) of selected DSTs do not fall below 80 °C (Table 1), drastically reducing the likelihood of biodegradation as a compositional alteration factor.

Crude oils in sandstone reservoirs of the Ula, Bryne, Sandnes Formations or Rotliegend Group show API gravities that are increasing as a function of depth with a gradient of 2° API/100 m. These results are similar to those of Justwan et al. (2006) and Barnard and Bastow (1991) for the southern Viking Graben (N, GB) showing a gradient of 3° and 6° API/100 m, respectively. However, oil qualities in Upper Cretaceous to Lower Palaeocene chalk and limestone reservoirs (Ekofisk and Tor Formations) show a wide API gravity range independent of depth (Fig. 2) and reservoir temperature. Based on the general relationship between API gravity and maturity (e.g. Peters et al., 2005), and thus depth of generation and expulsion, crude oils in carbonate reservoirs must have experienced vertical and/or longer migration distances than those in clastic reservoirs which are, in most cases, in close juxtaposition to the source rocks.

The trends are likely related to facies and maturity of the source kitchens, though phase behaviour cannot be ruled out. Cretaceous and Tertiary horizons are lean in organic matter, and thus contamination during secondary migration (Curiale and Bromley, 1996) can be ruled out. Measured BHTs of sampled DSTs range between 80 and 165°C and thus only oils in wells 1/3-3 and 2/7-22 are near the temperature range

needed for in-reservoir thermal alteration (165-174°C; Horsfield et al., 1992; Pepper and Dodd, 1995; Isaksen, 2004). However, phase separation might be a factor influencing physical behaviour and chemical composition. In well 1/9-1, three DST oils from different carbonate reservoir intervals have been sampled with API densities (35 and 55° API) and GOR's increasing up-well. In between oil-filled intervals, dry horizons are present, thus intra-reservoir equilibration or evaporative fractionation can be ruled out, but lateral hydraulic connection could be possible.

4.1.2. Gross Chemical Composition

Fig. 3 shows that increasing API gravity is accompanied by an increase in the relative abundance of saturated hydrocarbons, describing a single trend for oils produced from both clastic and carbonate reservoirs.

Oils in clastic reservoirs generally follow a maturity trend becoming increasingly lighter and more enriched in saturate compounds as a function of maturity. On the other hand, oils from carbonate reservoirs are characterized by regional differences. While compositionally similar within the regional sub-sample sets, oils at the eastern margins contain less saturates than those from the western basin centre (green and blue circles, respectively).

Although describing a general maturity trend by decreasing density, secondary alteration processes can affect the composition. The increased NSO content of the lowermost reservoir interval in well 1/9-1 explains the reduced API gravity (see chapter 4.1.1) and can affect phase behaviour (Bailey et al., 1973; Bennett et al., 2007a). If these compartments are hydraulically connected, this feature could point to phase separation during secondary migration and charging of the reservoir horizons.

Other samples falling apart from the general trend are characterized by facies differences. While oils charged from more terrigenous-influenced source rocks (2/2-1, 3/7-4) contain higher aromatic proportions, the hypersaline 2/2-5 oil is richer in the NSO fraction.

4.1.3. Molecular geochemistry of hydrocarbons

The primary factors influencing crude oil compositions are the organofacies and maturity of the source rock. The secondary influence of biodegradation can be eliminated due to a lack of 25-NH and no alteration of *n*-alkanes. The principal source rock in the Norwegian Central Graben is the Upper Jurassic marine Hot Shale of the Mandal Formation containing 5 – 6% TOC and a generation potential of ~450 mg HC/g TOC in its immature to early mature sections (e.g. Cornford, 1994; Ziegs et al., 2017). Though having a high overall source potential containing Type II kerogen, the Mandal Formation consists of alternating sequences with high and low source potential due to fluctuations in redox conditions during deposition, while the quality of marine zoo- and phytoplanktonic input remained consistent (Herbin et al., 1993). Fig. 4a illustrates this biological uniformity, while Fig. 4b shows the fluctuations in chemical conditions of the source intervals having principally charged oil accumulations. Oils along the northern margins of the Central Graben and the 2/2-5 discovery have been charged by highly anoxic to mixed anoxic/dysoxic source intervals with anoxia increasing further northwards. Petroleum accumulations in the SW basin centre and margins were charged from compositionally variable Type II facies. Interestingly, the eastern carbonate-reservoired oils (2/5-7, 2/5-11 and 2/6-5) show identical properties of marine anoxic facies (Fig. 4b, green circle), this being a hint that the northern Søgne Basin well 2/6-5 has been sourced from the Central Graben or an equivalent facies. The 2/2-1 discovery charged by the Farsund Formation shows higher terrigenous organic matter

input in a more dysoxic marine environment. The Trym condensate (3/7-4) is indicated to be charged from a source rock with increased marine organic matter input in a more oxic marine environment. The T-seams of the coaly Lulu Formation in the Danish part of the Søgne Basin were accumulated during a high-standing water table resulting in stronger marine influence to the peat mires (Petersen and Brekke, 2001).

When assessing both depositional environment and maturity, it has to be kept in mind that all crude oils just represent cumulative mixtures of generated petroleum portions having been expelled from a potentially inhomogeneous source rock at different maturity levels (Wilhelms and Larter, 2004).

A cross plot of the %20S and % $\beta\beta$ sterane maturity biomarker (Fig. 5a) shows that most of the Central Graben crude oils have reached the stage where chemical equilibrium of the α sterane isomerization (%20S > 0.55) has taken place, but % $\beta\beta$ which is more effective at slightly higher maturities (Peters et al., 2005) ranges between 0.57 and 0.65 indicating the beginning of peak oil generation, according to correlations in Waples and Machihara (1990). The samples plot in a very confined area and do not show any specific trend related to spatial or stratigraphic occurrence. The oil from well 2/2-5 is the only oil falling away from the general trend showing values of 0.52 (%20S) and 0.47 (% $\beta\beta$) indicating expulsion at an early maturity level.

According to a cross-plot of $T_s/(T_s+T_m)$ and $29T_s/(29T_s+NH)$ (Fig. 5b) the oils can be separated into peak- to late oil window maturity, high mature and supermature ranges. Crude oils in siliciclastic Jurassic reservoirs show a very broad maturity range whereas Cretaceous carbonate reservoir oils lie in a confined, high maturity range between 0.40 and 0.51 in their $29T_s/(29T_s+NH)$ ratio. While the 1/9-1 oils (Tommeliten Alpha field) are principally of the same maturity, the Tommeliten Gamma crudes are very different. 1/9-4 DST 4 (50.5° API) is indicated as lower mature than the deeper DST 1 (46° API) and 1/9-6 S (30° API), a side track of the 1/9-4 well, which are both similar to

the Albuskjellet condensate, the highest mature crude in the Greater Ekofisk area trend (Hughes et al., 1985). The eastern carbonate reservoirs 2/6-5 and 2/5-7 contain oils of the similarly high maturity, while the 2/5-11 oil is of intermediate maturity within the carbonate-reservoired oils.

Crude oils from the Steinbit Terrace, north of the Mandal High, block 2/2, are least mature, according to sterane epi-and isomerization indicators (Fig. 5a). Still, the maturity of the 2/2-5 oil might be overestimated using C₂₉ steranes and Ts/(Ts+Tm) (Fig. 5b) due to its hypersaline source environment (Peters et al., 2005; Pedersen et al., 2006). Oils from the Jæren High (wells 7/7-2 and 7/8-3) were expelled at a late maturity stage (Fig. 5b). Also, the Trym condensate, sourced by the coaly Jurassic Lulu Formation from the south, seems to be charged from source intervals with intermediate maturity of the hopanes (Fig. 5b). Oils in siliciclastic reservoirs from the basin-marginal Ula Trend, comprising wells 7/12-6, 1/3-3 and 2/1-9, and the Mjølner field seem to be charged from a highly mature source rock. Here, well 1/3-3 crude oil is at the supermature stage similar to the Middle Jurassic and Rotliegend reservoirs in block 2/7, wells -20, -21 S and -27 S, at the western margin of the Central Graben.

Oil-water interactions typically accompany biodegradation of petroleum and results in the selective loss of light hydrocarbons, especially benzene, toluene, phenols and other aromatics of the light hydrocarbon fraction (Bailey et al., 1973; Palmer, 1984; Palmer, 1993). Acting alone at temperatures >80°C, these processes have only a minor effect on the chemical and physical properties of oil (Peters et al., 2005), and if related to secondary migration they have an insignificant impact (Lafargue and Barker, 1988). However, it must be noted in this context that all oils from the northern and eastern margins of the Central Graben, except the 2/1-9 oil, are depleted in toluene and benzene, independent of reservoir lithology (Fig. 6). Oils from the graben axis (blocks 1/9, 1/6) and western margins (block 2/7) are not depleted in water-soluble aromatic moieties.

However, benzene ratios are comparably elevated in Embla oils and the adjacent 2/7-22 field while the slightly less soluble toluene shows normal ratios to its cycloalkane equivalent. This could represent an effect of mixing with biodegraded Palaeozoic oils (Ohm et al., 2012) that is only observable in the light fraction as benzene and toluene are abundant compounds in crude oils.

4.2. The polar NSO fraction of petroleum

For FT-ICR-MS evaluation the oil sample set was condensed from 24 to 16 oil samples covering the whole maturity and spatial ranges of oils originating from different organofacies within the Central Graben. Putting the focus on samples containing higher rather than lower NSO fraction weights ensures reproducible FT-ICR-MS measurements with overall high signal numbers, a natural Gaussian distribution of signals, and low influence of potential contaminations from drill mud additives. The latter cannot be completely excluded as surface active and bioactive agents used during drilling are rich in cyclic and acyclic sulphur and oxygen constituents that could be ionized using ESI negative mode.

4.2.1. Gross composition

The number of assigned peaks in the mass spectrum of the acidic polar compounds ranges between 489 and 4300 but for the majority of samples it lies between 1200 and 2800 (Table 2). While the number of assigned signals is not necessarily indicative of the absolute concentration of acidic NSO compounds in the oils, a rough trend of decreasing number of signals with increasing API gravity is discernible. Variability is broadest in the range of light oils (32 – 45° API). The number average and the weight average molecular weights (M_n : 320 – 451 Da and M_w : 331 – 484 Da) decrease as a function of

petroleum density and is determined by the relative concentration of individual compounds in the whole oil. Heavier polar compounds become less abundant with increasing API gravity.

4.2.2. Compound class distribution

Table 2 and Fig. 7 show the relative abundances of the major compound classes of Central Graben crude oils being dominated by N₁, O₁ and O₂, thus resembling the elemental class distributions of undegraded crude oils worldwide (e.g. Hughey et al., 2002; Hughey et al., 2004; Li et al., 2010; Oldenburg et al., 2014; Poetz et al., 2014; Liu et al., 2015). In all oils sourced by marine shales N₁-compounds are the major components with 41 to 68% TMIA, and that abundance generally increases with progressive maturity of the oils (see as well Poetz et al., 2014). The O₁ class most likely comprising phenols, sterols, alcohols or indols (Wang et al., 2011; Pan et al., 2013) contributes with 19 to 43% TMIA (1/9-1 DST 8 and 2/2-5) to the total signal, and O₂ compounds comprised of carboxylic acids, range between 2 and 14% TMIA (7/8-3 and 1/9-1). Thus, components with one heteroatom account for 72 – 94% TMIA of the acidic polar fraction, as determined using the ESI (-) ionization mode. Lower mature samples, located in the 2/2 block, contain lower N₁ proportions than higher mature ones, but an influence of the source environment within marine oils could not be ruled out: the 2/2-5 oil was charged from a hypersaline, marine source rock, and the source of the 2/2-1 oil contains a relatively high terrigenous contribution (Pedersen et al., 2006). Significant compositional differences of the Trym condensate (well 3/7-4) containing 86% TMIA of O₁ and O₂ components can be addressed to its origin being coal-sourced from the shallow-marine Lulu Formation.

The maturity effect on compound class distributions has been shown for source rock extracts with the N₁ class increasing in relative abundance as a function of thermal

stress (Poetz et al., 2014). Differently, the relative abundances of the N₁ compound classes in crude oils does not show a consistent behaviour related to maturity (e.g. Oldenburg et al., 2014 for a Viking Graben oil suite; or this communication), but must rather be a result of migration-related effects when source variations can be excluded.

Regional variations in the N₁ and O₁ classes have been documented (Fig. 7). At the outer Steinbit Terrace (block 2/2), oil samples are N₁ dominated but slightly enriched in O₁ compounds. Oils at the Cod Terrace and Jæren High, northwest of the Ula Trend (7/12-6, 7/8-3 and 7/7-2), are strongly dominated by the N₁ compound class and depleted in the O₂ class, ranging between 61 – 64% TMIA N₁, 21 – 31% TMIA O₁ and only 2.0 – 3.6% TMIA O₂ compounds. A clear regional differentiation can be observed between carbonate-reservoired oils from the eastern margin and western basin centre which are most likely not related to maturity (see Fig. 5b). While oils at the Steinbit Terrace (2/5-7, 2/5-11) and the northern Søgne Basin (2/6-5, Fig. 1) contain 46 – 54% TMIA N₁ compounds, 31 – 34% TMIA O₁ and 7 – 10% TMIA O₂ compounds, those in the West in block 1/9 contain higher N₁ portion with 53 – 61% TMIA and lower O₁ with 19 – 25% TMIA.

4.2.3. N₁ compounds & maturity assessment

The DBE class distribution is clearly dominated by DBE 9, 12 and 15 classes (Fig. 8a). Previous studies have shown that these DBE classes belong to the carbazole-family (Hughey et al., 2002; Purcell et al., 2007; Oldenburg et al., 2014; Poetz et al., 2014) consisting of a carbazole-core unit (DBE 9) with one or more *ortho*-fused benzene rings adding 3 DBE to the core unit: DBE 12 = benzocarbazole, DBE 15 = dibenzocarbazole. Higher fused homologues of the DBE 18+ classes can be annelated in *ortho* and *peri* positions (Poetz et al., 2014) and thus the DBE class distribution may vary by ± 2 .

The N_1 class further contains elevated contributions of DBE 10, 13 and 16 (Fig. 8) compounds representing phenylindoles and showing a similar thermal behaviour like carbazoles with increasing abundances from DBE's 9 to 12 / 10 to 13 while DBE's 15 and 16 show lower abundances. Although of different organofacies origin and containing significantly lower N_1 proportions, the 3/7-4 condensate shows a predominance of DBE classes representing carbazole and phenylindol homologues.

Fig. 9 shows a decrease in the relative intensities of carbazoles (DBE 9) with increasing maturity and an increase in relative intensities of benzo- (DBE 12) and dibenzocarbazoles (DBE 15), reflecting annulation and aromatization of core structures as a function of maturity. Oldenburg et al. (2014) have shown that the linear decrease of the DBE 9 class correlates well with vitrinite reflectance data (V_R) of crude oils in the Viking Graben (Fig. 9, inset bar) ranging between 0.68 and 1.1% R_c within their sample set. Further testing with worldwide oil samples of different origin (Mahlstedt et al., 2016) supports this V_R scale. Thus, we can propose that the investigated oils in the Central Graben most likely range between 0.75% R_c for the earliest mature oil (2/2-5) and 1.1% R_c for the most mature oil (2/7-21 S). According to vitrinite reflectances assigned by Oldenburg et al. (2014), the majority of selected Central Graben oils range between 0.8 to 1.0% R_c and are thus in the peak oil window.

4.2.4. Correlating GC-MS maturity and degree of N_1 annulation

Aliphatic and aromatic maturity biomarkers with specificity for the entire maturity range from early to high mature are here correlated with the N_1 annulation of FT-ICR-MS data. As can be observed from relative distributions in Fig. 9, DBE 9 relatively decreases while DBE 15 relatively increases as function of maturity. Fig. 10 shows abundances of DBE classes with $29T_s/(29T_s+NH)$ maturity ratio correlating the best. Although showing similar geochemical behaviour like $T_s/(T_s+T_m)$ due to their same

bacterial origin (Moldowan et al., 1991) and maturity effect (Kolaczowska et al., 1990). 29Ts/(29Ts+NH) might be less influenced by the source rock facies (Peters et al., 2005) but carbazoles might show similar effects (Bakr and Wilkes, 2002). However, elevated 30-NH (nor-hopane) in the 2/2-1 oil could result in an apparently lower maturity level obtained from 29Ts/(29Ts+NH).

Comparing Fig. 9 and Fig. 10, oils charged by the terrigenous-influenced Farsund Formation (2/2-1, Gabrielsen et al., 1985) and the coaly Lulu Formation (Trym, 3/7-4) do not follow the trend of oils described by Oldenburg et al. (2014) and others (e.g. Hughey et al., 2004) that are charged from source rocks containing pure marine organic matter. The Trym condensate is significantly depleted in N₁ compounds (5% TMIA) and cannot be used for maturity assessment. However, the 2/2-1 shows similar N₁ DBE distributions as purely marine oils, thus falling within Oldenburg's trend, but is slightly depleted in DBE 9 compounds (Fig. 10a), when compared to its maturity level from conventional biomarkers (Fig. 5). 29Ts/(29Ts+NH) suggest expulsion at early mature levels, but the N₁ DBE distribution assigns a maturity of 0.95% R_o in the peak oil window (Fig. 9). These outliers could indicate that the proposed maturity-related trend (Oldenburg et al., 2014) is only valid for oils sourced from purely marine source rocks.

Interestingly, lowest mature oils from eastern (2/5-11) and western (1/9-1) carbonate reservoirs show very different DBE distributions with maturity (Fig. 10). While 1/9-1 condensates are enriched in smaller DBE 9 and 12 compounds, the 2/5-11 oil is depleted in bigger and potentially more rod-shaped DBE 12 and 15 compounds for samples of comparable maturity level, with highest variations occurring within the DBE 12 class. Both, a relative enrichment in DBE 9 and relative depletion of DBE 15 classes result in apparently higher relative DBE 12 contribution causing an apparent maturity retardation when using the polar maturity assessment for carbonate oils. Thus, parameters based on the relative stability of hydrocarbon isomers record differently to

that based on annulation and aromatisation of the carbazoles, the latter of which is related to aliphatic chain shortening, as presented below (Fig. 11).

4.2.5. Detailed variations due to reservoir lithology

As alluded to above, the Central Graben crude oils stored in carbonate reservoirs plot above the maturity trend, containing a higher DBE 12 portion by up to 5% at the expense of the DBE 9 and 15 compounds (Fig. 9). Here, carbonate reservoir oils from well 1/9-1 at the western rim of the Central Graben (condensates with API = 46 – 55 °) show a higher deviation from clastic oils than those from the eastern rims near the Mandal High (Fig. 1). Well 1/9-4 from the axial part of the Central Graben is similar to the eastern wells in carbazole abundance distribution. For the eastern wells, 2/5-11 and 2/5-7 at the Steinbit Terrace are most detached from the maturity trend whereas 2/6-5 in the northern Søgne Basin is most similar to oils in clastic reservoirs. The levels of detachment reflect maturity developments within each regional occurrence (Fig. 5, inset) with less mature samples being most detached (1/9-1 and 2/5-11).

Using ternary diagrams to depict chain length distributions of the major N₁ DBE classes related to the carbazole family (12, 15, 18), oils from carbonate and clastic reservoirs fall along the same evolutionary trend, beginning at early mature levels with high C₁₅₊ contribution, followed by intermediate aliphatic carbon numbers dominating peak mature oil compositions and finally short side chains prevailing in late oil window oils. This chain length shortening is exemplified by the benzocarbazoles (DBE 12) in Fig. 11a. Significant compositional differences exist between the oils in the two reservoir lithologies when the individual chain lengths are considered. Fig. 11b shows the carbon number (CN) distribution of DBE class 12 normalized to the individually highest peak for each sample and outlines the differences between regional oil compositions. While oils in clastic reservoirs (solid lines) get more enriched in C₂₋₄ aliphatic side chains and

depleted in higher CN's with increasing maturity, which is most evident for highest mature oil, 2/7-21 S, the oils from eastern carbonate reservoirs are different. Although most deviated from the general trend in Fig. 9, chain length distributions of western 1/9 oils are similar to clastic oils of similar maturity (compare inset of Fig. 5). However, the eastern carbonate reservoirs (2/5-11, 2/5-7, 2/6-5) contain oils with significantly increased C₆₊ side chains apparently resulting from a depletion in the highest abundant, short-chained (C₂₋₃) aliphatic carbon numbers. This relative increase of longer chained, heavier compounds in the major compound class of the polar fraction might affect API gravities with higher densities of eastern oils (Fig. 2).

The intensity of increase in intermediate to long chained homologues (or the loss of short chained compounds) of the oils in the eastern carbonate reservoirs coincides with their ratio of toluene and methylcyclohexane, which is an indicator of the severity of oil-water interactions. Fig. 6 shows that oils in the western carbonate reservoirs are not affected by oil-water interactions. Normally accompanied by biodegradation, the effect of water washing is covered by those bacterial processes, but may occur alone during migration of petroleum through the water-saturated pores of both clastic and carbonate carrier beds and intensifies with longer migration distances (Lafargue and Barker, 1988). Although N₁-containing carbazoles are less polar and thus less water-soluble than oxygen-bearing heterocompounds, water solubility mostly increases with temperature and can be important at higher temperatures prevailing in burial depth of early or main petroleum generation. A more detailed discussion on physicochemical interactions of the particular heterocompounds with polar sites in the carrier-reservoir system is carried out in the following paragraphs after the description of individual distributions.

4.2.6. Other influences on N₁ chain length distributions

Maturity is the major control on crude oil compositions in the Central Graben (Hughes et al., 1985; Cornford, 1994) affecting distributions of carbazole compounds (DBE classes), but not necessarily their chain length distributions. Therefore, we calculated the PEARSON correlation factor R of the relative compound abundances of individual chain lengths in ESI negative FT-ICR-MS mass spectra (Fig. 11b) and the oil's maturity biomarker ratio of 29Ts/(29Ts+NH) (Fig. 9). Such a correlation is exemplified in the appendix (Fig. A.1). A cross plot with the carbon number of aliphatic side chains of each DBE class shows the development with increasing chain length for Central Graben crude oils stored in clastic (Fig. 12a) and in carbonate reservoirs (Fig. 12b). Although charged from a marine source environment (Fig. 4a), 3/7-4, 2/2-1 and 2/2-5 oils have been excluded from correlations due to high facies variations.

In general, chain lengths shortening of aliphatic carbon should result in negative correlations of long chains with maturity, while the relative increase in short aliphatic moieties results in positive correlation. Oils in clastic reservoirs with apparently very short migration distances follow the expected compositional development from cracking of long to shorter chains in the source rock, effective expulsion of all generated and cracked moieties, and show no significant compositional fractionation during secondary migration. DBE classes 9 and 12, carbazoles and benzocarbazoles, show very similar correlation trends (Fig. 12a) with strongly positive R of short aliphatic chains (C₀₋₃), subsequently changing to strongly negative R for intermediate to long chains (C₁₁₊). Larger core molecules of dibenzo- and naphthobenzocarbazoles (DBE 15 and 18) show strongly positive trends for C₀₋₈ and C₀₋₁₂ short to intermediate number of aliphatic carbon atoms. The strongly positive correlation coefficients of DBE 15 and 18 carbazoles for short to intermediate aliphatic chains can be interpreted as a result of maturity-related aromatization of even longer chained, lower-fused carbazole homologues

following reaction mechanisms suggested by Poetz et al. (2014). It is to be expected that carbonate reservoir oils should fall within the same linear trend as clastic oils (Fig. 12b). However, due to their confined range in thermal maturity (Fig. 5), the correlation of compound abundances with $29Ts/(29Ts+NH)$ could indicate different mechanisms than maturity. The maturity-related decrease in DBE 9 carbazoles can be observed, but the relative increase of short alkyl chains as a result of chain shortening is not well developed. Otherwise the formation of higher fused DBE 15 and 18 carbazole homologues by ring annulation as a function of maturity is expressed by a strongly positive R. The inverse correlation trend with increasing carbon number within the DBE 12 class supports the conclusion from chain length distributions that this class is significantly depleted in short chained compounds (chapter 4.2.5). Assuming a homogeneous source and comparing oils of similar maturity, the removal of short-chained benzocarbazoles is a feature of migration fractionation within the carrier-reservoir system.

In that regard, Stoddart et al. (1995) showed that longer migrated oils in the chalk-hosted Eldfisk field, Central Graben are enriched in alkylated carbazoles (equivalent to N_1 DBE 9) relative to benzocarbazoles (equivalent to DBE 12) and that higher methylated C_3 homologues are less hindered in migration than C_1 and C_2 homologues. These migration distance trends based on GC-MS results were confirmed for relative abundances using FT-ICR-MS on the well investigated Duvernay petroleum system, Canada (Liu et al., 2015) and can be related to a higher surface activity of DBE 12 benzocarbazoles (Bennett et al., 2004). Benzocarbazoles were believed to sorb on mineral surfaces (Li et al., 1995; Larter et al., 1996; Larter et al., 1997; Li et al., 1997). Thus, purely water-wet siliciclastic systems might retain/adsorb less surface-active compounds than oil-/mixed-wet carbonate carrier systems. However, carbonate reservoirs might be water-wet prior to oil migration (Abdallah et al., 2007). Even minuscule amounts of polar high-molecular weight (HMW) compounds can sorb to mineral surfaces causing a change

to oil-wetting conditions (Akbarzadeh et al., 2007) and enabling a continuous oil flow without major compositional alterations. Bennett et al. (2004) have shown that low-molecular weight (LMW) C₀₋₃ alkylphenols are able to pre-condition water-wet surfaces to make lipophilic hydrocarbons and lower-polar compounds sorb within the carrier system until saturated. Furthermore, van Duin and Larter (2001) have proved that benzocarbazole distributions are rather altered by oil-water partitioning than by oil-rock partitioning, thus excluding an influence of primary migration within oil-saturated source rocks while promoting migration-related variations within water-filled pore spaces. Following ratios on water-oil partitioning and solubility in Fig. 6, this would suggest that the 7/8-3 oil in a clastic system might have migrated longer than other marginal oils, but this cannot be observed in the DBE 12 CN distribution, due to its lower maturity.

With regard to the solubility context and the negative “maturity” trend in carbonate-reservoired oils (Fig. 12b), it can be said that those are likely related to secondary effects during migration rather than to maturity effects. Such secondary effects are caused by oil-water interactions at the front of the initial oil charge flowing through water-filled pores, fractures and faults. If longer migrated oils contain dominantly alkylated carbazoles over alkylated benzocarbazole species (Li et al., 1995; Stoddart et al., 1995), then oils in carbonate reservoirs at the eastern margin and the 1/9-4 condensate would have migrated shorter distances than the 1/9-1 condensates from the graben axis due to their lower deviation from the general clastic maturity trend and thus higher DBE 12/9 ratios. However, the higher DBE 9 portion of 1/9-1 oils is to be explained with slightly lower maturity (Fig. 5b, inset). While migrating into water-filled pore or fracture systems of carrier rocks, benzocarbazoles with shorter chains (2-3 aliphatic carbon atoms) get removed from the oil phase. This mechanism would explain higher relative DBE 12 compound abundances of intermediate and long aliphatic chains in the eastern oils pointing to longer migration within chalk sequences, when assuming

only one major expulsion charge from a badly expelling source rock (Ziegs et al., 2017). An excellent expeller would rather instantaneously expel multiple smaller increments of oil charges, of which the very first one would be significantly altered by pre-conditioning the migration pathways. Subsequent oil charges of higher maturity are less or not compositionally altered during migration but make up a higher portion of an oil accumulation, thus overprinting migration-related information with the maturity-related chain length distributions. Based on this, the loss of short chained benzocarbazoles and other surface-active compounds in the Central Graben petroleum system, containing a source rock with low expulsion efficiency, might be an indicator for migration distances within different lithologies, thus resulting in different controlling mechanisms.

Following on the above observations, it further needs to be mentioned that for oils in carbonate reservoirs an assignment of biomarker equivalent vitrinite reflectances seems to be difficult, because the maturity assessments based on the hydrocarbon and polar NSO fractions give different results (compare Fig. 5 and Fig. 9). Due to secondary controls other than maturity on DBE 12 class contribution and distribution within the DBE 9/12/15 ternary diagram, Oldenburg's maturity assignment may not be applicable to carbonate oils or an adjustment for migration distances would be necessary.

4.2.7. Factors controlling O₁ compounds

O₁ compounds, being the second most abundant compound class in the Central Graben crude oils, might be even more influenced by secondary processes than N₁ compounds due to higher electron negativity and a stronger dipole moment depending on bonding type. They are dominated by compounds with DBE 4, 5, 6, and 7. O₁ components with much higher aromaticity (up to DBE 22) are also found, but their relative abundances continuously decrease with increasing DBE number (Fig. 13). Possible core

structures for the DBE 4 class could be phenol and its alkylated homologues (Kim et al., 2005; Shi et al., 2010; Liao et al., 2012; Pan et al., 2013), while those with DBE 5 and 6 could refer to indanols and indenols (Liao et al., 2012; Pan et al., 2013). Geng et al. (2012) suggested that DBE classes 7, 9 and 11 correspond to naphthols, fluorenols and phenanthrenols, respectively. DBE 4, 5 and 7 class might also refer to nonaromatic, monoaromatic or triaromatic sterols.

The relative abundances of O₁ DBE classes are principally influenced by facies and thermal maturity and range between 1.3 and 22.1% TMIA for the alkylphenols (DBE 4), 1.5 and 11.9% TMIA for indanols (DBE 5), 2.6 and 8.6% TMIA for DBE 6 and 1.9 and 7.2% TMIA for DBE 7. Early mature oils from the Eastern rim of the Central Graben contain mainly DBE 4 compounds, but only insignificant amounts of species with higher aromaticity. The same feature can be observed for the crude oil 3/7-4 derived from the coaly Lulu Formation and containing the overall highest proportions of O₁ compounds related to a source dominated by terrigenous organic matter. This correlates to high phenol contents in lignocellulosic kerogen pyrolysates (Tissot and Welte, 1984; Horsfield, 1989; Larter, 1990; Rullkötter and Michaelis, 1990; Vandenbroucke and Largeau, 2007). With increasing maturity, the aromaticity and annulation of O₁ compounds increases with increasing abundances of higher DBE classes relative to DBE 4 and 5 classes. However, peak mature oils contain DBE classes 4 – 7 representing a broad chemical inventory. The high-GOR condensates in the graben axis (well 1/9-1) which are peak to late mature are dominated by DBE 4 and show a subsequent decrease for higher DBE classes. Interestingly, other carbonate-reservoired oils (1/9-4 and at the Steinbit Terrace) show several secondary modes at DBE 6, 7 and 11 which is rather a feature of peak mature oils and represents a broad chemical variability. The 2/5-11 oil is slightly depleted in DBE 4 and 5 and dominated by DBE 6 and 7. This is a similar feature as observed in the Mjølner field (2/12-1). Two peak mature oils from the Ula Trend at NE terraces are dominated by DBE 4 compounds and show a second mode at DBE 6 whereas

the northernmost oils from wells 7/7-2 and 7/8-3 show highest abundances of 4 and 5 DBE classes which could be attributed to their slightly lower maturity (see Fig. 5b). The highest maturity oil 2/7-21 S is strongly dominated by higher DBE classes of 6 – 8, whereas DBE classes 4 and 5 (phenols and indanols) are largely absent. A ring annulation as developing within the N₁ class cannot be observed in O₁ DBE distributions. Similar to N₁ DBE 9, 12, 15 and 18 classes, a correlation with 29Ts/(29Ts+NH) was conducted for O₁ DBE 4 and 5 classes showing the same evolutions with increasing number of carbon atoms for oils in different reservoir lithologies, and supporting the surface-active and interphase mechanisms influencing carbazole distributions. An illustration, explanation of the correlation and brief discussion can be found in the appendix (Fig. A.2).

In contrast to the abundance distributions of carbazoles, O₁ DBE 4 and 5 compounds are depleted in their low molecular weight species until C₁₂ (Fig. 14) potentially containing only few aliphatic carbon atoms. This is related to more insensitive compound detection in the ESI negative FT-ICR-MS at $m/z < 200$ Da corresponding to C₁₂₋₁₄ O₁ DBE 4 and 5 compounds. The C# distributions are generally Gaussian distributed with maximum abundances in the range C₂₀ – C₃₀ and outstanding abundances of C₂₃ and C₂₇ compounds. Facies is the dominating control on abundances but not on C# distributions. However, less mature oils are generally more abundant in O₁ DBE 4 and 5 compounds than more mature marine oils in clastic reservoirs. Interestingly, oils in carbonate reservoirs contain a slightly higher portion of shorter chained aliphatic carbon. For the condensates at the western rim of the Central Graben, this phenomenon is more pronounced than for the eastern rim carbonate oils although the latter are more enriched in O₁ compounds. The 2/5-11 oil is more strongly depleted in shorter chained DBE 4 and 5 moieties than 2/5-7 and 2/6-5. The similarity of DBE 4 and 5 compounds (Fig. 14a and b) could hint to similar migration and expulsion mechanisms or a structural relation of both compound classes, either caused by common natural

origin in lignins (Freudenberg, 1966) or due to cyclisation reactions of longer chained alkylphenols (McClennen et al., 1983) similar to the proposed mechanism in Poetz et al. (2014). Therefore, we anticipate that phenolic and indanolic compounds with long aliphatic carbon numbers (C_{25+}) are less influenced by migration-related processes and reflect “true” maturity developments (see as well Fig. A.2 in the appendix). Thus, a ternary plot of both O_1 DBE 4 and 5 with N_1 DBE 15 might be well applicable for maturity assessment (Fig. 15).

Besides carbazoles, phenols and its alkylated homologues have been identified as strong agents in crude oils, altering wetting properties of carrier and reservoir rocks or interacting with non-hydrocarbon phases (Larter and Aplin, 1995; Bennett and Larter, 1997; Larter et al., 1997; Bennett et al., 2004; Bennett et al., 2007b). Similarly to the N_1 compounds, solubility, oil-water partitioning and solid-phase adsorption are controlled by the extent and position of alkylation to the functional group (e.g. Taylor, 1994). Partitioning coefficients of alkylphenols are negatively correlated to temperature, water salinity and the bulk NSO content of crude oils, whereas pressure has no influence (Bennett and Larter, 1997). Oil-water partitioning of phenols and cresols destabilizes the water film around minerals, facilitating apolar sorption on polar surfaces (Bennett et al., 2004) and thus removing these compounds from the migrating oil-phase. Thus, C_{0-1} phenols can rather occur in the water phase, whereas C_{2-3} phenols (Larter et al., 1997) and higher alkylated homologues partition within the oil phase. Due to higher subsurface temperatures during expulsion ($T > 130^\circ\text{C}$, Ziegls et al., 2017), higher alkylated homologues might still interact with the water phase even though water solubility decreases with increasing alkyl chain lengths. Although no change in the relative distributions of phenols was reported, Taylor et al. (1997) observed a systematic decrease in total C_{0-3} phenols in four North Sea oils with migration distance. This process occurs only until saturation in the carrier rocks is reached, because crude oil composition is no longer altered for later charges when using the same migration

pathway. However, these conclusions were drawn from GC-based experiments which are sensitive for lower molecular weights (LMW), but might be extended to high-molecular weight (HMW) homologues measured with FT-ICR-MS in ESI negative mode. Within a DBE class, the chemical behaviour of LMW compounds is rather influenced by its polar, hydrophilic atom than the hydrophobic nature of aliphatic side chains. Consequently, if short chained homologues are strongly removed during migration in water-wet clastic carrier systems or in water-saturated, mixed-wet carbonate systems, long chained phenols relatively increase in abundance with increasing migration distance. This effect might be intensified for a water-saturated carrier system that is water-wet, rather than for an oil-/mixed-wet, water-filled carbonate rock. Observations from carbazole $C\#$ distributions are then confirmed: 1/9-1 carbonate oils have migrated shorter, whereas eastern carbonate oils migrated longer distances.

Carbon number distributions (Fig. 14) and low maturity correlations until C_{27} (Fig. A.2) likewise allow a different interpretation of compounds represented by the O_1 DBE 4 class. C_{23} and C_{27} compounds stand out from the natural CN distribution ranging between C_{14} and C_{45} , and thus could represent other compounds than *n*-alkyl phenol homologues. Zhang et al. (2011) proposed isoprenoidal phenols and Shi et al. (2010) suggested cholesterol and 5,6-dihydrocholesterol as representing C_{27} and C_{28} compounds in Chinese crude oils from Cenozoic source rocks. Cholesterols are precursor structures of diasteranes which are ultimate products of clay-catalysed structural rearrangement via diasterenes (Peters et al., 2005) and are very abundant in the Mandal source rock and Central Graben crude oils. Diasteranes increase as a function of thermal maturity, thus its precursor structures must decrease in abundance which can be observed in Fig. A.2 and Fig. 14 when excluding facies variations from the source rock (inset of Fig. 14). C_{23} compound do as well stand out from the natural distribution. Although no relationship to a distinct steroidal precursor structure has yet been identified, such a structure could be related to most saturated biomarkers containing 21 – 29 carbon

atoms. However, we believe that the gradual, extremely smooth evolution of correlation coefficients R from LMW to HMW DBE 4 and 5 compounds generally represents a homologous series. However, variations for C_{23} , C_{25} and C_{27} compounds in maturity correlation of carbonate and clastic oils suggest other compounds with slightly different thermal stability than n -alkyl-phenols to dominate or influence constituents represented by these O_1 DBE 4 carbon numbers.

5. Conclusion

The present study has investigated 24 crude oil and condensate samples from 16 petroleum accumulations in the Central Graben covering a range in oil qualities of 29 to 55° API and a regional variety from central to marginal basin positions. Major reservoirs in the Central Graben are either Upper Cretaceous to Lower Palaeocene carbonate reservoirs having most likely been vertically charged, or clastic reservoirs of Devonian to Upper Jurassic age. The clastic reservoirs are in direct contact to Upper Jurassic source rocks.

API gravity depth profiles for oils in carbonate reservoirs are different to those in siliciclastic reservoirs. While API gravities of clastic oils increase with depth following depth trends described in the Viking Graben, carbonate oils representing a broad API range are scattered across shallow depth intervals. Whole oils from both reservoir types follow the same compositional trend towards more saturate compositions as a function of maturity. The evaluation of hydrocarbon biomarkers confirmed that the oils are sourced from a homogeneous source rock containing dominantly marine organic matter, sometimes with locally higher oxygenation level and/or terrigenous contribution. They represent a maturity range from peak mature to overmature. Oils are not biodegraded but most marginal oils in clastic reservoirs show indications of oil-water interactions. Importantly, the low petroleum expulsion efficiency of the Mandal Formation (Ziegls et

al., 2017) most likely brings about expulsion in one major charge into carrier and reservoir rocks. This is in contrast to source rocks which are efficient expellers, where multiple oil charges leave the source rock. In this case it can be anticipated that the composition of the earliest oil charge that is altered upon secondary migration is overprinted by the composition of later, more mature and less altered charges.

The polar fraction of crude oils is mainly composed of N₁ and O₁ compounds and although influenced by thermal maturity, basic oil families could be recognised on a regional basis. The thermal maturity assessment based on the carbazole distribution of crude oils in clastic reservoirs of the Viking Graben (Oldenburg et al., 2014) has been compared to several hydrocarbon maturity markers and correlates best with 29Ts/(29Ts+NH). When compared to hydrocarbon maturity biomarkers, its application is limited to clastic reservoir oils charged from a purely marine source rock. An apparent maturity retardation of oils in carbonate reservoirs is caused by a relative increase of N₁ DBE 9 carbazoles and DBE 12 benzocarbazoles accompanied by a partial loss of short aliphatic chained substituents that are attached to the core structure. While the first observation can be related to subtle maturity variations, the latter is here interpreted as a migration effect. Compared to phenol-related, surface-active O₁ DBE 4 and 5 compounds, benzocarbazoles in carbonate reservoirs show a similar relative depletion of their short-chained homologues as compared to oils in clastic reservoirs, as expressed in altered chain length distributions and maturity trends. This is likely a result of physicochemical interactions of petroleum, water and mineral surfaces in the carrier and reservoir systems and can be used to detect differences in carrier lithologies, migration routes and distances.

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6. Appendix

6.1. Maturity correlations: background information

The sample set of 16 crude oils measured using FT-ICR-MS contains oils from different source input and environments, but only oils originating from the principal anoxic facies composed of marine algal organic matter has been used for maturity correlations. As shown in Fig. 9, the compositional evolutions of DBE 9, 12 and 15 compounds are maturity dependent. Hereby, a DBE class combines compounds with short, intermediate and longer saturated chains attached to the core structure (Fig. 11). If a maturity influence of individual compounds cannot be observed, different mechanisms might act upon the distribution of relative abundances of these compounds.

Fig. A.1 illustrates a cross plot of compound abundances (% TMIA) and $29\text{T}s}/(29\text{T}s+\text{NH})$ which is used as indicator of thermal maturity of North Sea crude oils and source rocks. Different developments as function of maturity for crude oils of different reservoir types are represented by correlation coefficients R . R indicates both, strength and direction of a linear correlation (positive or negative) and has been applied to the y-axis of Fig. 12 and Fig. A.2. The figure further illustrates that evolution must not be linearly as assumed for correlation studies, but may develop differently at different maturity levels. It further shows a relative enrichment (% TMIA) of C_{12} -alkylated benzocarbazoles relative to the general inventory of acidic polar NSO compounds for oils in the eastern carbonate reservoirs as compared to clastic oils of the

same maturity level. Contrary, the $29\text{T}_s/(29\text{T}_s+\text{NH})$ ratio might overestimate their maturity but $\text{T}_s/(\text{T}_s+\text{T}_m)$ ratios are in a similar range (Fig. 5).

6.2. Maturity correlations of O₁ DBE 4 and 5 compounds

Compound class distributions (Fig. 7) reveal that O₁ compounds are generally decreasing with increasing maturity relative to N₁ compounds. Having screened the maturity correlations for all dominant O₁ DBE classes for the sub-sample sets, only compounds belonging to the DBE 4 and DBE 5 classes show clear trends with increasing carbon number which can be seen as an indicator for continuous homologous series represented by these DBE classes.

O₁ compounds in oils produced from elastic and carbonate reservoirs behave similar to maturity correlations found in N₁ DBE 12 compounds. While oils from clastic reservoirs show a strongly negative correlation to $29\text{T}_s/(29\text{T}_s+\text{NH})$ for C₂₇₊ compounds, the carbonate-reservoired oils indicate a significant loss of LMW compounds and thus a relative increase in HMW DBE 4 and 5 compounds (Fig. A.2).

Assuming either phenolic or sterolic structures dominantly representing these DBE classes or single C#, the results can be explained coherently in both cases. The strong affinity of LMW phenolic compounds to interact with water-wet surfaces or water phases in migration pathways removes these compounds depending on the distance of migration. Even for short migration distances, clastic pathways need to be wetted making them available for migration of lipophilic compounds. Longer migration distances to eastern carbonate reservoirs containing slightly higher mature oils might result in negative correlations. Similar to steroidal acids representing the O₂ DBE 5 class (Pan et al., 2013), sterolic homologues might represent particular compounds in the O₁ DBE 4 class. Steroidal structures in crude oils ranging between C₂₁ and C₂₈ are not

necessarily maturity dependent, but a chain length shortening might be possible explaining moderately negative correlations in this C# range. The similar reaction to thermal stress of DBE 4 and 5 classes could indicate similar or genetically related core structures and the continuous development with increasing C# to a homologous series of aliphatic chains attached to the same core structures. This might point to phenols and indanols representing DBE 4 and 5 classes.

7. References

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Table 1. Specifications of analysed oil and condensate reservoir samples originating from the Central Graben and ordered according to regional occurrence and structural affiliation within the basin.

Well	DST	TVD (m)		Period	Epoch	Formation	Lithology	Region	Reservoir name	Type	Density (°API)	GOR	BHT (°C)
		Top	Base										
1/3-3	DST 3.3	4211	4214	Jurassic	Malm	Ula Fm	clastic	N' margin	Tambar oil field	black oil	39.2	196	165
2/1-9	DST 1	4078	4108	Jurassic	Malm	Ula Fm	clastic	N' margin	Gyda Sør oil field	light oil	43	548	160
7/12-6	DST 2	3434	3511	Jurassic	Malm	Ula Fm	clastic	N' margin	Ula field	black oil	36.6	66	143
7/12-6	DST 1C	3543	3612	Triassic	Middle Triassic	Skagerrak Fm	clastic	N' margin	Ula field	light oil	43.2	36	149
7/7-2	DST 2	3333	3342	Jurassic	Malm	Ula Fm	clastic	N' margin	Brynhild oil field	black oil	30	20	80
7/8-3	DST 1	3762	3767	Jurassic	Malm	Ula Fm	clastic	N' margin	Krabbe discovery	black oil	29	32	154
1/6-1	DST 4	3153	3159	Paleogene	Paleocene	Ekofisk Fm	carbonate	SW'	Albuskjell gas field	light oil	46	-	-
1/9-1	DST 8	3029	3042	Paleogene	Paleocene	Ekofisk Fm	carbonate	SW'	Tommeliten Alpha gas field	light oil	55	2330-2740	116
1/9-1	DST 6	3079	3083	Cretaceous	Upper Cretaceous	Tor Fm	carbonate	SW'	Tommeliten Alpha gas field	light oil	46	989-1201	118
1/9-1	DST 4	3122	3131	Cretaceous	Upper Cretaceous	Tor Fm	carbonate	SW'	Tommeliten Alpha gas field	black oil	35	365-606	120
1/9-4	DST 4	3137	3127	Paleogene	Paleocene	Ekofisk Fm	carbonate	SW'	Tommeliten Gamma gas field	light oil	50.5	890-2850	90
1/9-4	DST 1	3292	3296	Cretaceous	Upper Cretaceous	Tor Fm	carbonate	SW'	Tommeliten Gamma gas field	light oil	46	890-14000	-
1/9-6 S	DST 4	3115	3123	Paleogene	Paleocene	Ekofisk Fm	carbonate	SW'	Tommeliten Gamma gas field	black oil	29.7	1491	-
2/12-1	DST 1	4598	4610	Jurassic	Malm	Ula Fm	clastic	SW'	Mjølner oil field	light oil	39.4	131	148
2/2-1	DST 1	3715	3730	Jurassic	Malm	Ula Fm	clastic	SW'	Møyfrid discovery	light oil	40.5	70	136
2/2-5	DST 1	3666	3670	Jurassic	Malm	Ula Fm	clastic	SW'	Bumblebee discovery	black oil	32.5	44	141
2/5-11	DST 1	3363	3381	Cretaceous	Upper Cretaceous	Tor Fm	carbonate	SW'	Tjatse discovery	light oil	38.7	-	131
2/5-7	DST 2	3262	3286	Paleogene	Paleocene	Ekofisk Fm	carbonate	SW'	-	black oil	40.7	48	131
2/7-20	DST 1	4099	4258			Palaeozoic	clastic	SW'	Embla oil field	light oil	42.5	375	157
2/7-21 S	DST 1	4314	4347	Devonian		Devonian	clastic	SW'	Embla oil field	light oil	45.4	285	160
2/7-22	DST 1	4489	4496	Permian	Rotliegens	Rotliegend	clastic	SW'	Embla oil field	light oil	47.6	1181	163
2/7-27 S	DST 1	4178	4435			Palaeozoic	clastic	SW'	Embla oil field	light oil	45.4	309	-
2/6-5	DST 1	2927	2953	Cretaceous	Upper Cretaceous	Tor Fm	carbonate	Søgne Basin	-	light oil	38.8	-	117
3/7-4	DST 1A	3470	3537	Jurassic	Dogger	Bryne Fm	clastic	Søgne Basin	Trym gas/condensate field	light oil	44.5	1330	131

Table 2. Relative abundances of compound classes obtained from ESI (-) FT-ICR-MS for 16 oil samples.

Well	DST	TVD (m)	Region	°API	Polars (wt-%)	# of signals	M _n	M _w	Relative Ion Abundance (% TMIA)								
							total	total	O ₁	O ₂	O ₃	N ₁	N ₂	N ₁ S ₁	N ₁ O ₁	N ₁ O ₂	S ₁ O ₃
2/1-9	DST 1	4108	N' margin	43	4.73	2000	362	385	26.07	2.13	0.04	68.14	-	0.31	1.41	-	0.86
7/12-6	DST 1C	3612	N' margin	43	6.14	3237	388	414	28.03	3.55	0.09	62.28	0.09	0.49	4.51	0.01	0.23
7/7-2	DST 2	3342	N' margin	30	14.81	4301	411	438	20.81	2.84	0.02	64.12	1.02	3.96	4.85	0.13	0.05
7/8-3	DST 1	3767	N' margin	29	11.28	3262	402	428	31.11	1.98	0.01	61.21	0.61	1.03	3.13	-	0.11
1/9-1	DST 8	3042	SW'	55	2.00	1292	342	362	19.00	13.80	0.65	53.25	-	0.19	4.40	0.06	3.85
1/9-1	DST 6	3083	SW'	46	3.74	1370	356	376	24.79	7.32	0.05	61.03	-	0.18	3.65	-	1.56
1/9-4	DST 1	3296	SW'	46	3.07	1215	357	378	23.73	5.05	0.12	58.59	-	0.09	1.13	-	7.54
2/12-1	DST 1	4610	SW'	39	6.84	2564	378	401	28.55	4.45	0.06	60.98	0.07	0.30	3.31	0.02	1.64
2/2-1	DST 1	3730	SW'	41	5.18	2833	372	393	41.82	6.28	-	45.32	-	0.16	5.07	-	0.39
2/2-5	DST 1	3670	SW'	33	19.05	3449	451	484	42.44	8.76	0.33	41.35	0.18	0.16	4.45	0.74	0.13
2/5-11	DST 1	3381	SW'	39	6.83	2813	384	409	34.33	10.32	1.42	45.72	0.88	0.25	2.20	-	0.61
2/5-7	DST 2	3286	SW'	41	6.69	1818	380	402	33.81	6.61	0.04	54.40	0.12	0.12	3.85	0.02	0.10
2/7-21 S	DST 1	4347	SW'	45	2.87	2188	371	394	23.79	5.40	0.70	64.97	-	0.47	2.83	0.08	0.16
2/6-5	DST 1	2953	Søgne Basin	39	5.71	2177	375	400	30.84	9.74	0.13	53.87	0.48	0.22	2.23	-	0.86
3/7-4	DST 1A	3537	Søgne Basin	45	1.80	1525	368	387	69.16	16.48	0.37	10.15	-	-	0.08	0.02	0.13

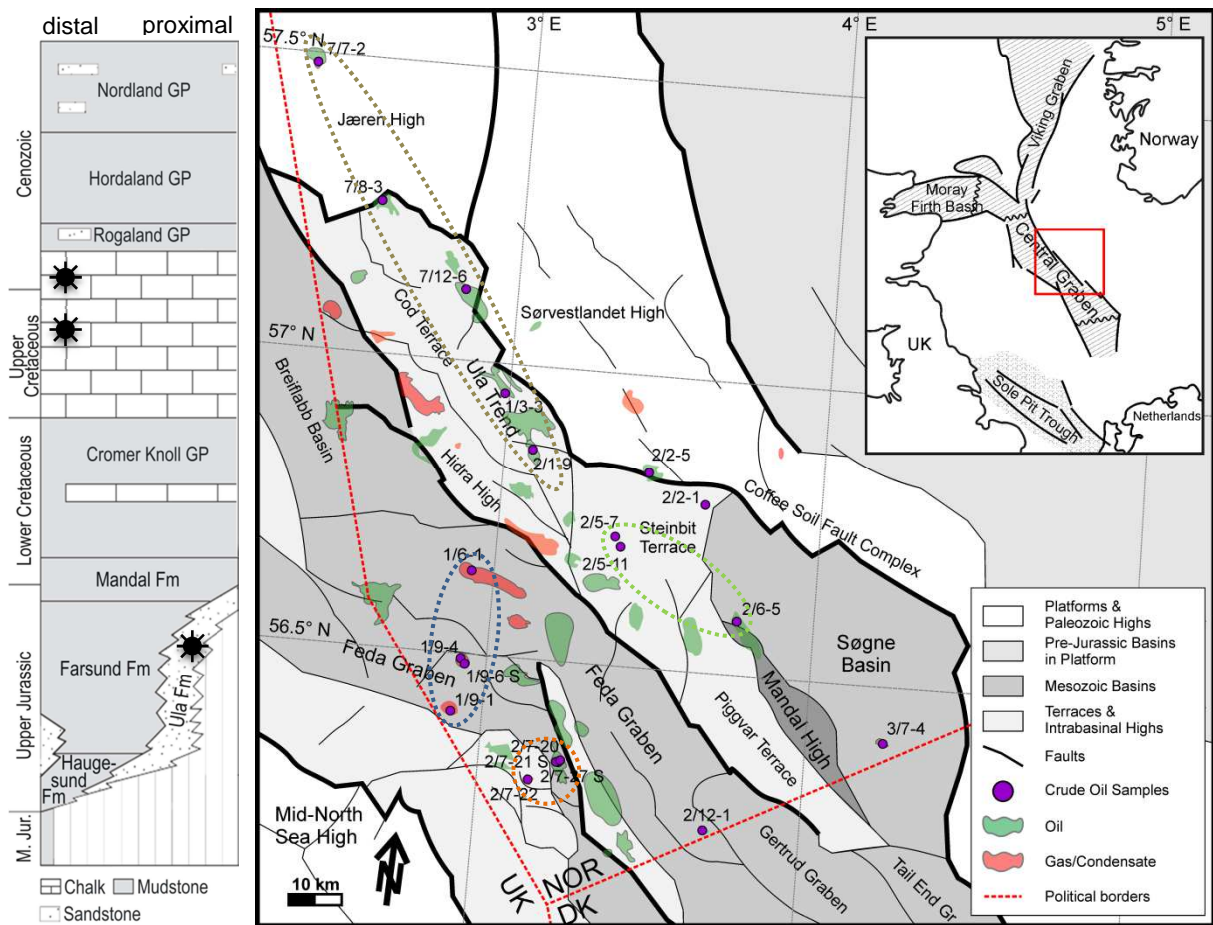


Fig. 1. Investigation area showing the distribution of crude oil samples in the central and marginal area of the Central Graben rift system. Attached is a chronostratigraphic chart of the Mandal-Ekofisk petroleum system (after Cornford, 1994) illustrating oil-bearing reservoir intervals (oil well symbol after PPDM and FGDC). Circles represent oils from different lithologies and groups: green and blue: carbonate reservoirs in eastern and western basin; brownish-green and dark orange: clastic reservoirs of the norther margin (so-called “extended Ula Trend”) and from pre-Jurassic reservoirs, respectively.

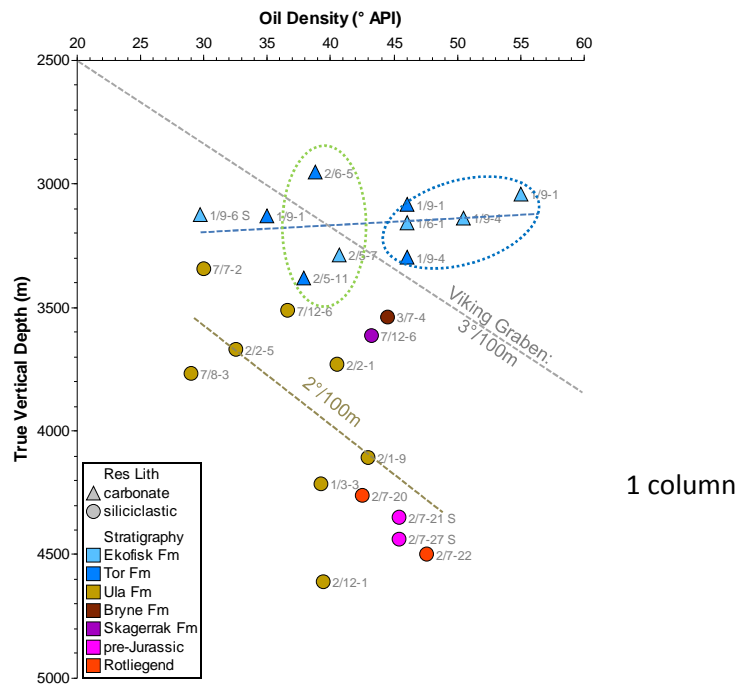


Fig. 2. API gravity variations with depth for different reservoir lithologies and stratigraphic intervals. Crude oils qualities of Cretaceous reservoir rocks are independent of reservoir depth, whereas Jurassic and older reservoirs in clastic strata become gradually lighter with increasing depth with similar gradient as in the southern Viking Graben (Justwan et al., 2006). Circles represent eastern (green) and western (blue) carbonate reservoirs investigated for their polar inventory.

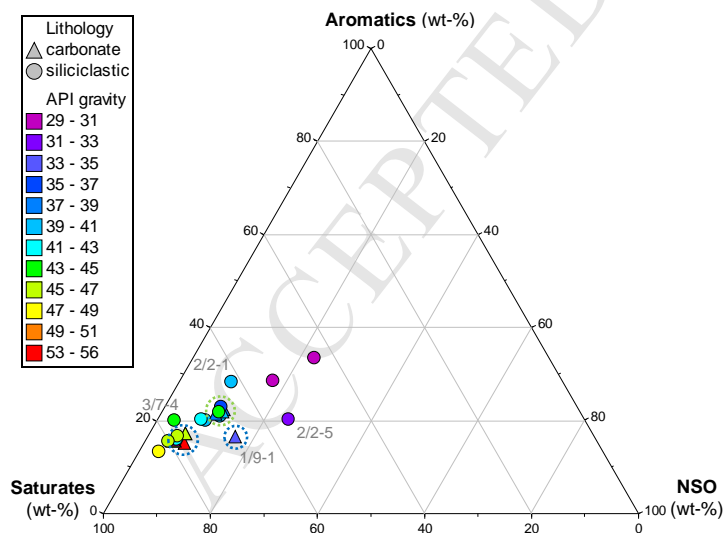


Fig. 3. Gross chemical composition of collected Central Graben crude oils showing common trend towards more saturate composition with increasing API gravity, independent of reservoir lithology. No regional features can be observed; the green circle identifies oils accumulated in the eastern carbonate reservoirs and the blue circles represent oils from the western carbonate reservoirs (Fig. 1).

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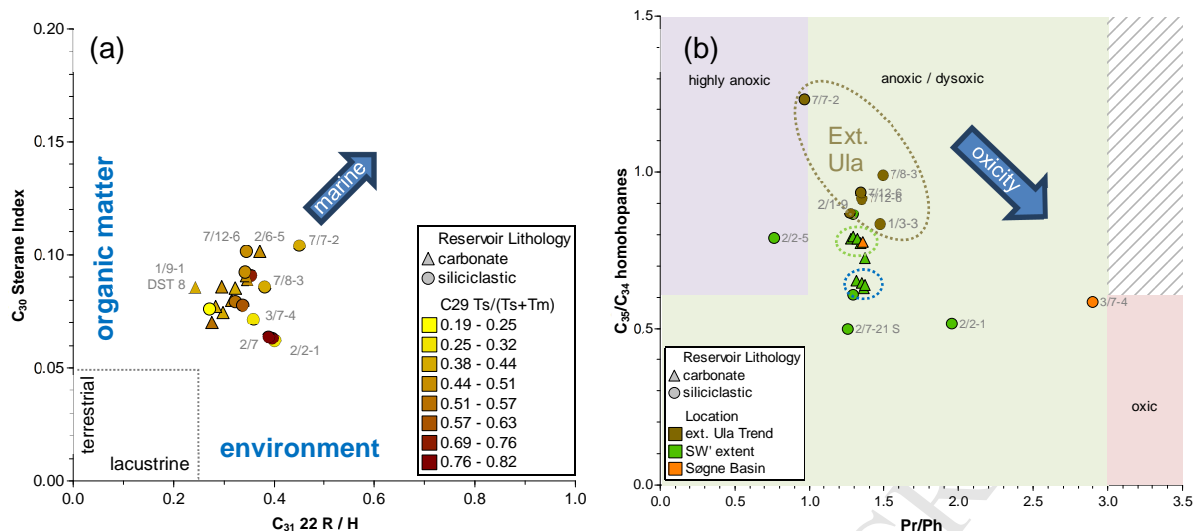


Fig. 4. Biomarker cross plots indicating (a) the organic matter input and (b) the depositional environment with chemical variations in the water column. Colour coding of circles that represent particular basin areas applies as before.

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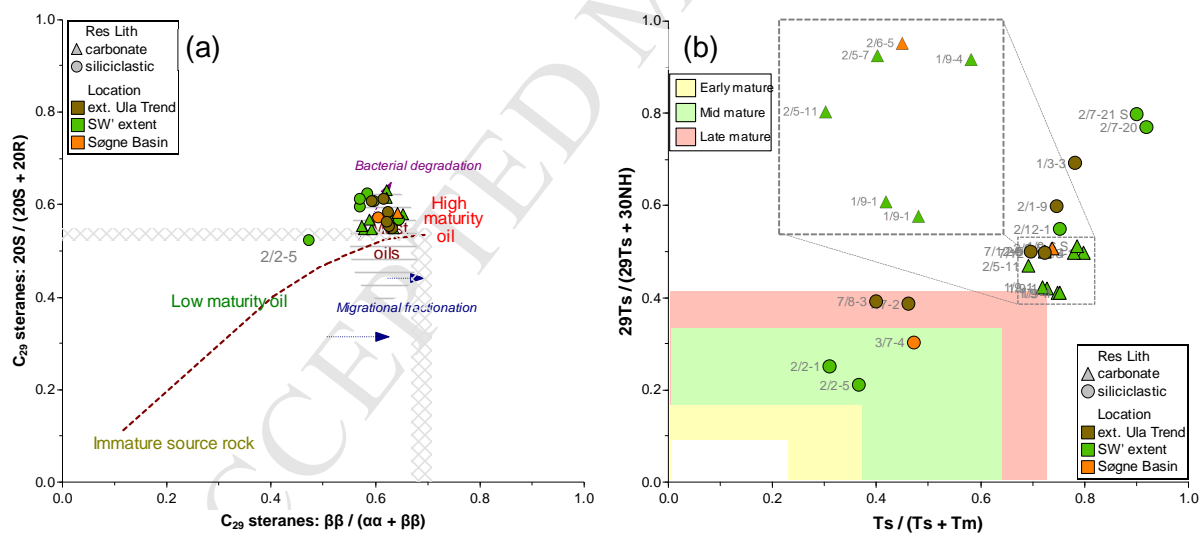


Fig. 5. Thermal maturity of the analysed oil and condensate samples based on (a) sterane isomerization, and (b) C₂₇ vs. C₂₉ Ts/Tm. The inset of (b) shows carbonate oils analysed for their polar, high molecular weight inventory using ESI negative FT-ICR-MS. All of the maturity biomarkers are specific for a distinct maturity range but provide similar results. The vitrinite reflectances for chemical equilibrium of sterane isomerizations are estimated after (Waples and Machihara, 1990) and (Peters et al., 2005).

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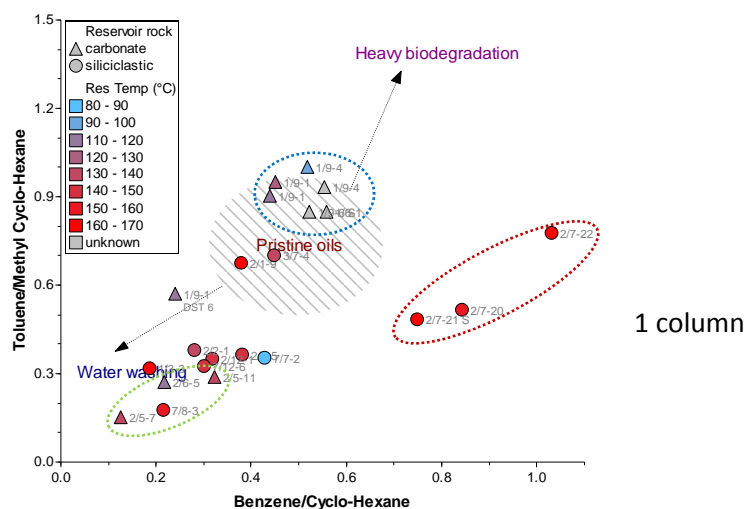


Fig. 6. Cross plot of benzene and toluene ratios against their water-insoluble structural equivalents. Benzene is more hydrophilic than is toluene.

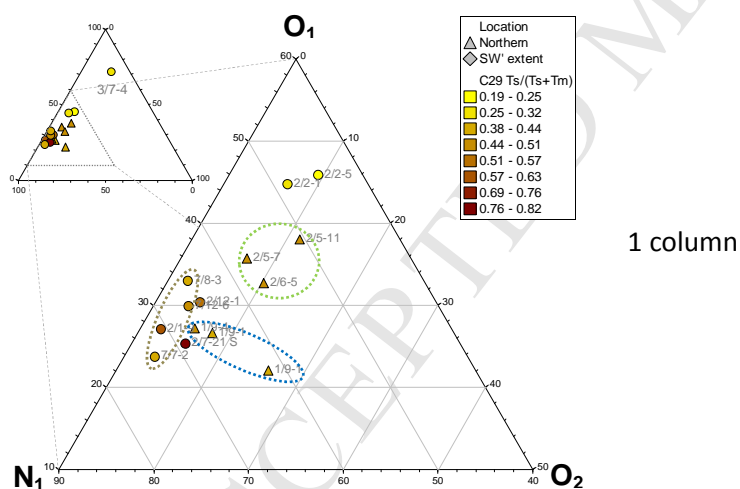
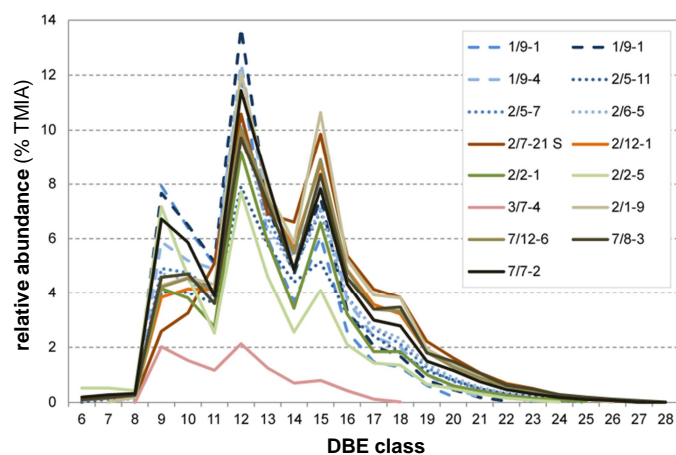
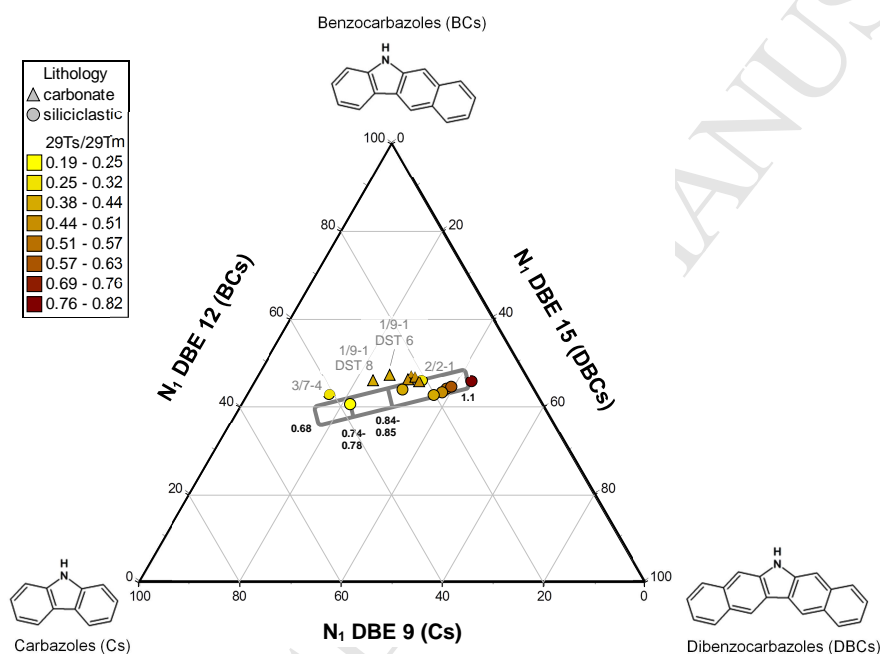


Fig. 7. Rudimentary oil family discrimination using elemental data from FT-ICR-MS. Interferences with maturity can be expected. Combined with maturity assessment, compositional variations within the same maturity stage can be used for classification. Circles represent regions as in previous illustrations.



1 column

Fig. 8. DBE class distribution of the N_1 compound class. Dotted and dashed lines indicate oils from eastern and western carbonate reservoirs, respectively.



1 column

Fig. 9. Maturity assessment based on the distribution of carbazole and its higher fused homologues (Oldenburg et al., 2014). Maturities of the polar and hydrocarbon components of petroleum fit quite well, but show a higher contribution of N_1 DBE 12 benzocarbazoles for carbonate oils and thus an apparent maturity retardation of those oils.

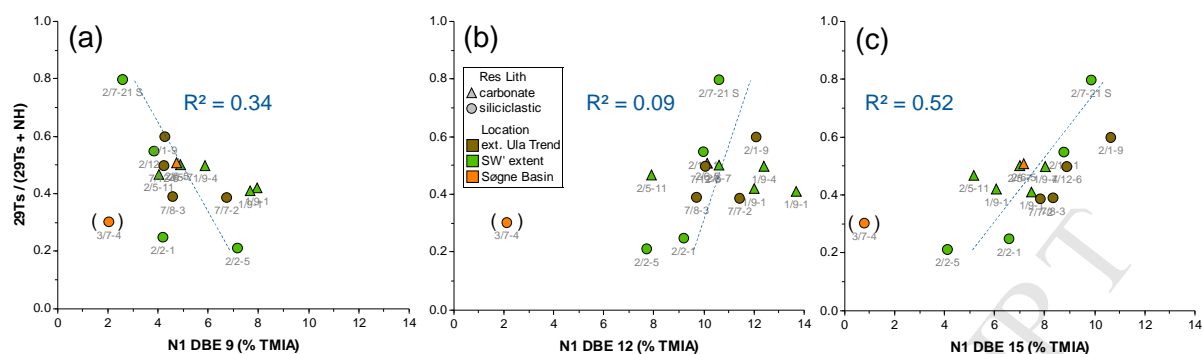


Fig. 10. Correlation of maturity indicator $29\text{Ts}/(29\text{Ts}+\text{NH})$ to the total monoisotopic abundances of N_1 DBE 9, 12 and 15 compounds illustrating that individual abundances (TMIA) react in the same manner as their relative TMIA's in a ternary plot. R^2 has been calculated, excluding 3/7-4 because of too strong facies variations.

2 columns

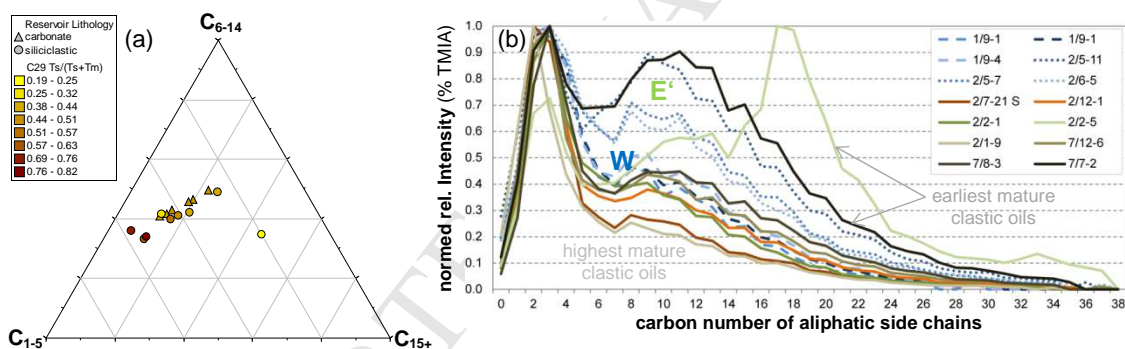


Fig. 11. Chain length distribution of aliphatic carbon attached to benzocarbazole core structures (N_1 DBE 12). Earliest mature oils contain longest side chains (a). Peak oil window mature oils stored in Upper Cretaceous carbonate reservoirs (dashed) contain aliphatic chains with higher contribution of intermediate carbon numbers than clastic oils, depending on regional occurrence (b). Crude oils at the eastern rim contain N_1 components with significantly longer chained substituents than at the western margin (compare Fig. 1).

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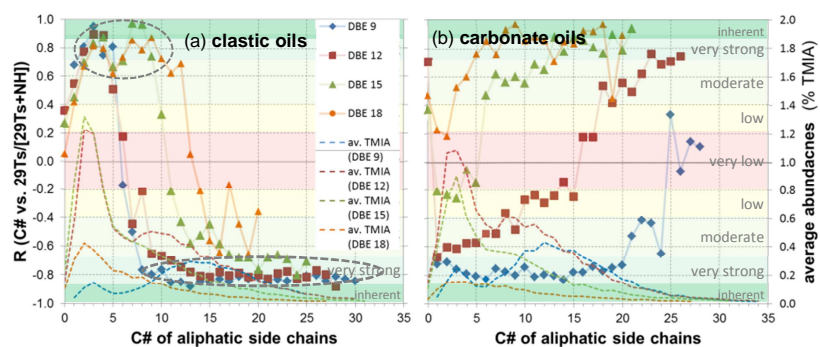


Fig. 12. Maturity correlation of relative abundances of individual N₁ DBE 9, 12, 15 and 18 compound classes representing carbazoles and its higher-fused homologues. Correlation (a) shows oils produced from clastic intervals interbedded with Upper Jurassic OM-rich, marine black shales, and (b) illustrates oils from carbonate reservoirs that lie stratigraphically higher than the principal source rocks. 29Ts / (29Ts + NH) is used as maturity indicator. Colours indicate the strength of the correlation as used in natural sciences. Dotted lines represent the average relative abundances (% TMIA) of the particular compounds in the data set to illustrate the significance of correlations.

1.5 columns

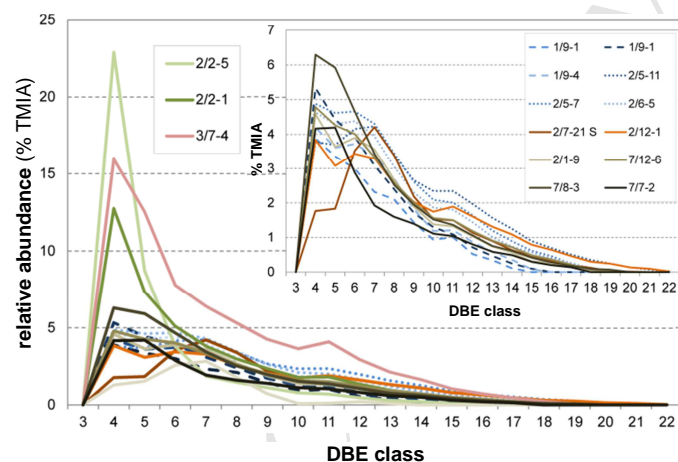
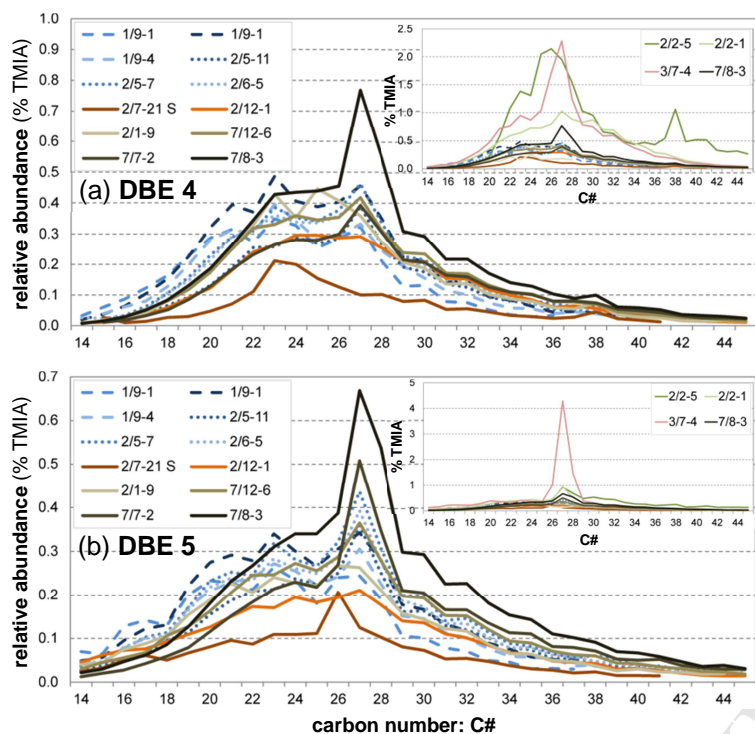


Fig. 13. DBE class distribution of the O₁ compound class. Dashed lines indicate oils from carbonate reservoirs. Inset shows oils with lower O₁ contribution (cf. Fig. 7).

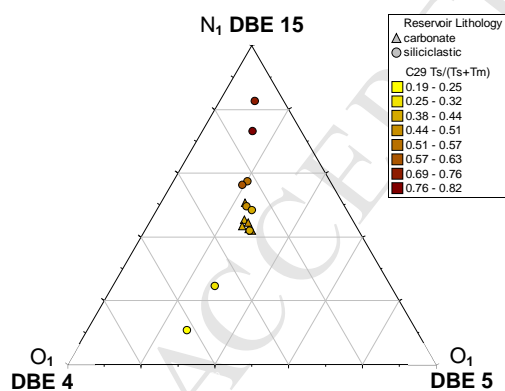
1 column



1 column

Fig. 14. Carbon number distribution of O₁ DBE 4 (a)

and DBE 5 (b) compounds of marine oils. Oils in carbonate reservoirs are represented by dashed lines with 1/9 oils belong to the western basin centre and 2/5 and 2/6 oils are structurally related to the Steinbit Terrace and Søgne Basin. The insets show samples with increased O₁ contribution due to variations in depositional environment.



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Fig. 15. Ternary plot of three DBE classes correlating linearly with 29Ts/(29Ts+NH) maturity indicator. Using different compound classes excludes the influence of rock-fluid interactions.

Appendix

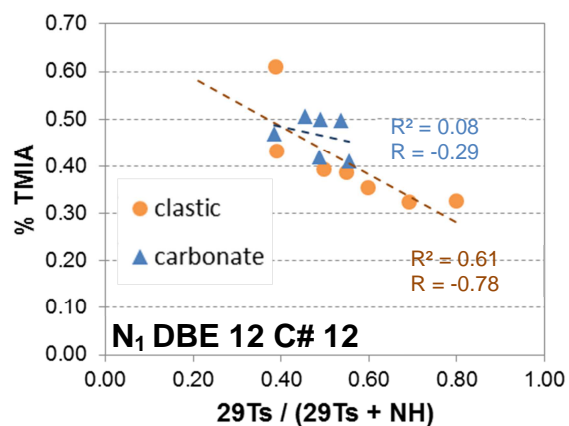


Fig. A.1. Cross plot of compound abundance and biomarker ratio indicating thermal maturity serving for calculation of maturity correlations of N_1 and O_1 compounds; here exemplified for C_{12} -alkylated benzocarbazoles from clastic and carbonate rocks. The strengths of correlations are given by the determination factor R^2 and PEARSON coefficient R .

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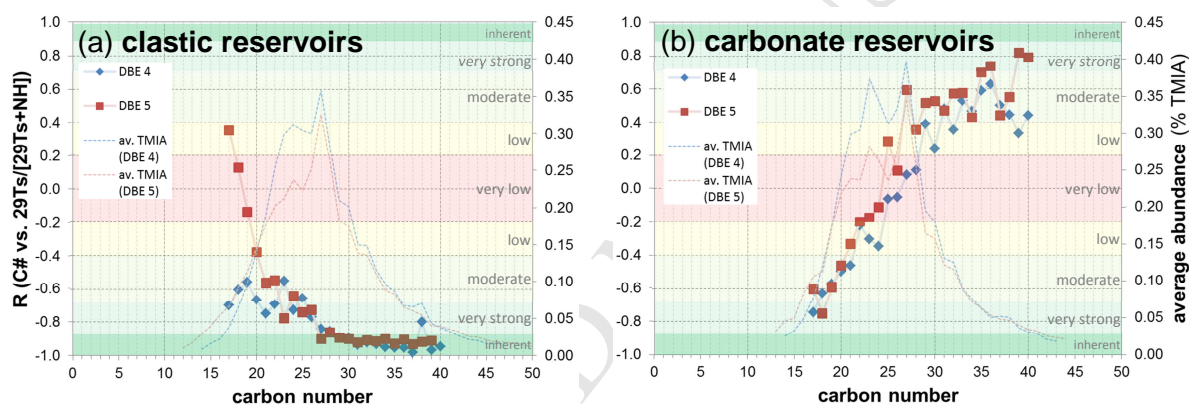


Fig. A.2. Maturity correlation of relative abundances of individual O_1 DBE 4 and 5 compound homologues. Correlation (a) represents these of oil suite produced from clastic intervals interbedded with Upper Jurassic OM-rich, marine black shales, and (b) represents oils from carbonate reservoirs that lie stratigraphically higher than the principal source rocks. $29Ts/(29Ts+NH)$ is used as maturity indicator.

1.5 columns

- Variations in polar NSO's between clastic and carbonate reservoirs
- Maturity assessment based on polar NSO's and hydrocarbons correlate well
- Maturity assessment based on carbazoles only for marine oils in clastic reservoirs
- Migration fractionation in carbonate systems influences maturity assessment
- Short-chained benzocarbazoles (N₁ DBE 12 C₂₋₃) strongly removed during migration