

FACTORS CONTROLLING THE OCCURRENCE AND COMPOSITION OF PYRROLIC NITROGEN IN OILS OF THE NORWEGIAN CENTRAL GRABEN

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The Central Graben is one of the most prolific petroleum provinces in the World having been explored since 1969 and contains 3061 mill bbl petroleum in 20 known Jurassic to Paleogene oil and gas fields. Thermally mature Upper Jurassic to basal Cretaceous, oil-prone, marine black shales of the Mandal and locally the Farsund formations are the principal source rocks. The maturity of the source rock plays most likely the greatest role in controlling the bulk petroleum properties (Cornford 1994, Hughes *et al.* 1995), but crude oil composition are further influenced by the depositional environment of the source rock and can be altered after expulsion from the source by phase separation, biodegradation, water washing or in-source thermal maturation. However, produced oils represent a cumulative gathering from kitchens of different thermal maturity and maturity assessment can vary depending on the boiling range and polarity of the compounds evaluated.

Maturation indices are routinely measured on the saturate and aromatic fractions of crude oils. Here we focus on the acidic N-, S-, and O-(hetero) compounds that are readily ionised using Fourier transform ion cyclotron resonance mass spectrometry in ESI negative mode, and relate their occurrence and distribution to maturity with reference to geochemical and isotopic indices based on hydrocarbons. Fourteen non-biodegraded crude oils from both Jurassic siliciclastic and Upper Cretaceous carbonate reservoirs (>2,500 m depth) in different structural settings (marginal and basin-central locations) were investigated. They cover an API range from 29 to 55° API, and thus broadly represent a range of different crude oil maturities.

The ionised components of the polar fraction of the Central Graben crude oils are depicted using pie-diagrams in Fig. 1a. Nitrogen is overall the dominant class, followed by oxygen; sulphur is only present in minor amounts. More specifically, N₁, O₁ and O₂ compounds, representing the carbazoles, phenols and carboxylic acids are most abundant. While the earliest mature oil contains abundant O₁ compounds, all of the more mature oils are dominated by N₁ components; indeed, relative abundances do not vary significantly within a maturity range of 0.9 to 1.1% R_O (%R_O obtained from correlation in Fig. 1b). Though the relative abundance of N₁ does not seem to be maturity-controlled, its aromaticity, however, increases as function of maturity as is reflected by the double bond equivalent (DBE) class distribution. A comparison of the dominant DBE classes shows that N₁ DBE 9 decreases compared to its higher fused homologues (Fig. 1b), irrespective of local influences. Initially presented by Oldenburg *et al.* (2014), the maturity assessment of the polar fraction further

- (1) can be correlated with conventional hydrocarbon biomarker data (best fit for 29 Ts/Tm, but also 27 Ts/Tm),
- (2) shows a higher degree of aromatization and condensation at ~1.1% R_O in different basin locations, and

(3) distinguishes a slightly higher abundance of N_1 DBE 12 compounds (benzocarbazoles) for carbonate reservoirs (triangles in Fig. 1b) and does not fall within a range defined by Oldenburg *et al.* (2014).

To what degree these contrasting compositions are controlled by reservoir rock-crude oil interactions, whereby the N_1 fraction of the carbonate reservoir displays retarded aromatization as compared to that seen in clastic reservoirs, will be discussed in this contribution.

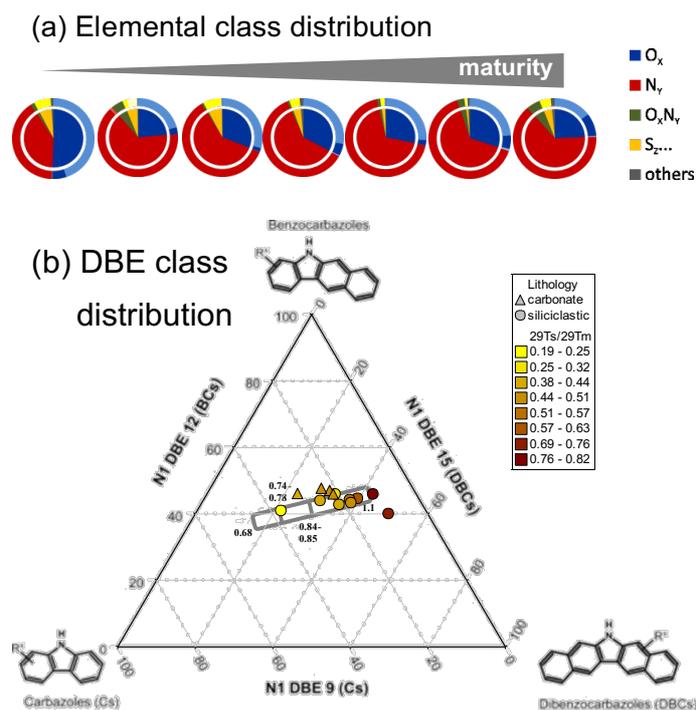


Figure 1 Elemental class distribution of the polar fraction of crude oils (a) and maturity assessment on basis of its nitrogen compounds (b) fitting with biomarker data (here: C_{29} Ts/Tm). Increasing maturity is illustrated by a relative decrease of carbazole portions (N_1 DBE 9). Carbonate reservoirs contain a slightly higher proportion of benzocarbazoles (N_1 DBE 12). The grey bar was defined by Oldenburg *et al.* (2014), and confirmed by our in-house database, as representing a maturity suite of oils sourced by the marine Kimmeridge Clay Formation.

References

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