

## 3.1.P02

### Predicting petroleum formation and composition: Insights from petroleum asphaltene pyrolysis

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Kinetic studies on source rock kerogens have been established as the key method for predicting the timing of oil and gas formation. However, the availability of source rock samples, especially in new exploration or venture areas is becoming more and more restricted. This has direct implications on risk assessment during exploration. The macromolecular fraction, the asphaltenes, of reservoir oils may aid in bridging this gap as similarities between asphaltene and source rock pyrolysates have been observed (Pelet, Behar et al. 1986). Moreover bulk kinetic concepts have successfully been applied to asphaltenes, with certain limitations (di Primio et al. 2000; Dieckmann et al. 2002). For this reason, a set of Norwegian source rocks and corresponding oil asphaltenes have been investigated in terms of petroleum formation and composition. The type II source rock is of Late Jurassic age and belongs to the Viking Group of the Norwegian North Sea. Bulk petroleum formation from source rocks and asphaltenes resulted in similar kinetic parameters of 54-55 kcal/mol for the main activation energies and a frequency factor around  $1E+14$  s<sup>-1</sup>. Bulk petroleum formation from both sample types was predicted to be very similar, with onset temperatures of around 130–140°C and Tmax temperatures of 150-155°C, respectively.

Artificial maturation experiments have been performed under closed system conditions on a selected source rock and a corresponding petroleum asphaltene sample. In the present case, bulk petroleum compositions (C1-5, C6-14 and C15+) are very similar for both during the main phase of petroleum formation. This is not the case, however, when tracing compositional changes on a molecular level. Alkylated thiophenes and aromatic hydrocarbons are depleted relative to alkyl-chains within the petroleum formed from the petroleum asphaltene sample. For that reason the products from the asphaltenes generally have a hydrogen richer character than products formed from their related source rock.

Moreover, for slow heating rates the gas to oil ratio during the initial stage of petroleum formation from asphaltenes is characterized by slightly higher values, while lower GOR values can be found at overmature levels of thermal alteration. Compositional kinetic calculations have shown an earlier onset of oil to gas cracking in the presence of source rock kerogen at a vitrinite reflectance of around 1.3 %Ro. Asphaltene products however show higher thermal stabilities, resulting in a later onset of oil to gas cracking at maturities of around 2.1 %Ro. These as well as the molecular compositional differences might have a strong effect on the phase behaviour during petroleum migration when using these data as input in numerical models.

## 3.1.P03

### Thermochemical sulfate reduction by hydrocarbons in an evaporate-carbonate reservoir, Ørn Formation, Upper Palaeozoic, Barents Sea

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Thermochemical sulfate reduction (TSR) may result in reaction products which, especially at low vitrinite reflectance values, might be difficult to distinguish from microbial products without advanced microscopy and stable isotope analyses. Such products are investigated from the shallow-marine warm-water evaporate-carbonates in the Ørn Formation (Upper Carboniferous - Lower Permian), Barents Sea. We show that the elemental sulfur and blocky calcite replacement of anhydrite nodules were formed due to TSR by hydrocarbons.

Oil staining and hydrocarbon inclusions in the late diagenetic cements have been recognised by the authors, [1] and [2]. The hydrocarbons were emplaced after formation of secondary porosity and stylolitization, but emplaced prior to or contemporaneously with the blocky calcite and sulfur infilling vugs after anhydrite. Chert, chalcedony and mega-quartz are the latest diagenetic phases to precipitate.

S-isotope analyses of the sulfur nodules reflect the composition of the anhydrite dehydrated from gypsum originally derived from seawater [3]. Size distribution of the sulfur and/or calcite nodules (several centimeters in diameter) is similar to the abundant anhydrite nodules recorded in the reference section of the Ørn Formation, well 7128/6-1.

Pyrites that are associated with the sulfur and/or calcite nodules are enriched in <sup>34</sup>S ( $\delta^{34}\text{S}$  8.5 to 19.2‰ V-CDT) relative to sulfate. This extent of fractionation is typical of TSR, and too small to be typical of bacterial sulfate reduction. Furthermore, isotope analyses of the blocky calcite cement adjacent to the sulfur show  $\delta^{13}\text{C}$  (-16.6 to 2.0‰) corroborative of organic matter decomposition related to TSR.

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#### References

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