

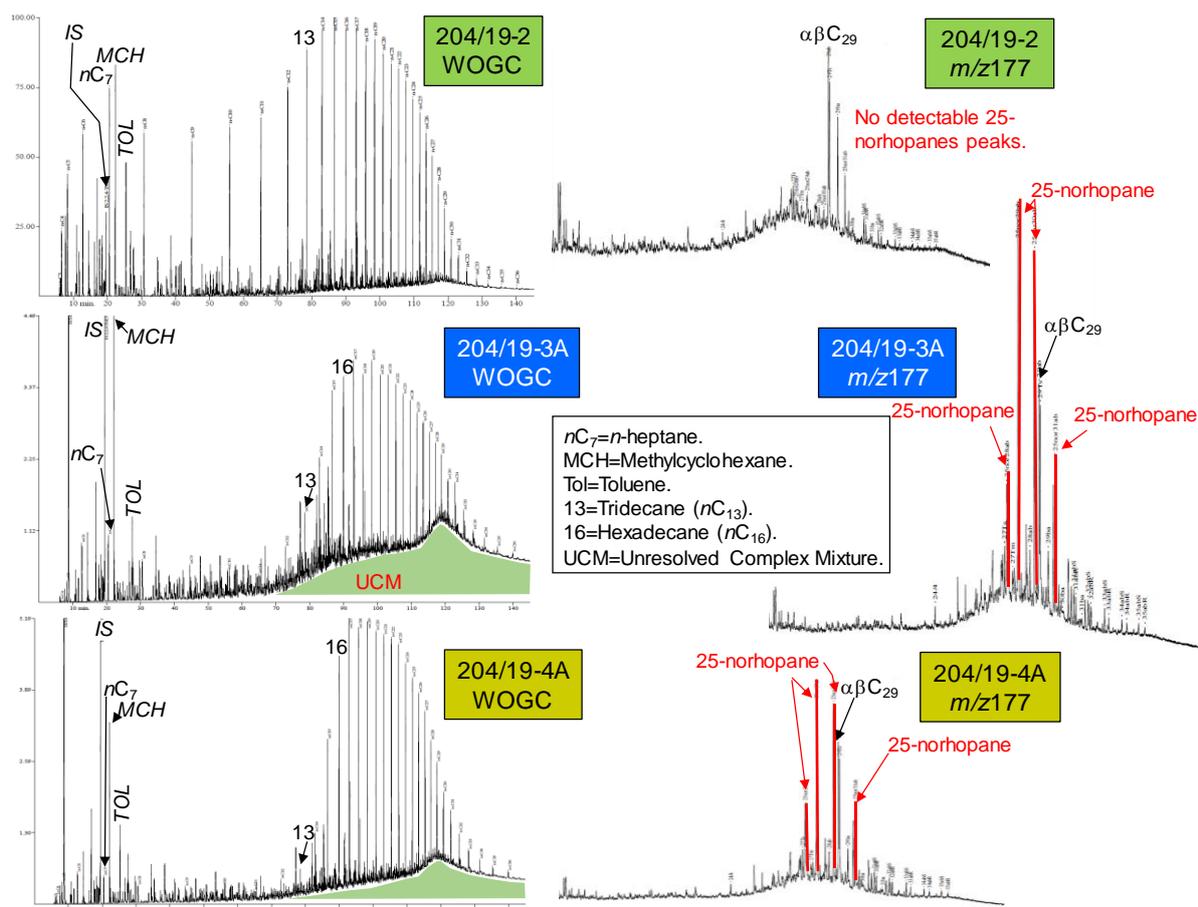
## Distinguishing evaporative fractionation and biodegradation of petroleum – An example from West of Shetland (UK)

by Marianne Nuzzo

The effects of the alteration of petroleum in subsurface reservoirs due to microbial biodegradation or to physical evaporative fractionation processes are sometimes difficult to distinguish. Biodegradation is the degradation of petroleum compounds by aerobic or anaerobic microbes at the Oil-Water Contact (OWC) (e.g., Head *et al.*, 2003). Microbes degrade some classes of compounds more readily than others, resulting in the removal of the former before the latter become significantly depleted (e.g., Huang & Larter, 2005). Characteristically, light hydrocarbons are removed at lower biodegradation levels than are heavier ones (e.g. Peters, Walters & Moldowan, 2005), with gasoline-range hydrocarbons (C<sub>6</sub> to C<sub>10</sub>) being typically affected first. Similarly, *n*-alkanes are more readily degraded than branched, cyclic or aromatic compounds. Evaporative fractionation refers to “the complex of phenomena involved in the separation of gas from oil in the subsurface” (Thompson, 1987), with the removal of the gas fraction evolved from the liquid, and its migration to other traps (or no trap). This results in characteristic alteration of the compositions of both migrated (gas) and residual (liquid) phases. As a gas phase forms in the reservoir, hydrocarbon compounds will partition variably between the gaseous and the liquid phase, depending on their molecular weight (lighter compounds are more volatile). Additionally, C<sub>3</sub>-C<sub>10</sub> range hydrocarbons have variable affinities for gas or liquid phases (*i.e.*, different vapor-liquid equilibrium constants), depending on their molecular configuration (normal, aromatic, branched and/or cyclic). Within C<sub>7</sub> hydrocarbon compounds, for example, *n*-heptane (*n*C<sub>7</sub>) or methyl-hexanes tend to partition more favourably in the gaseous phase compared to methylcyclohexane (MCH) and the aromatic toluene which become enriched in the residual liquid (Thompson, 1987, 1988).

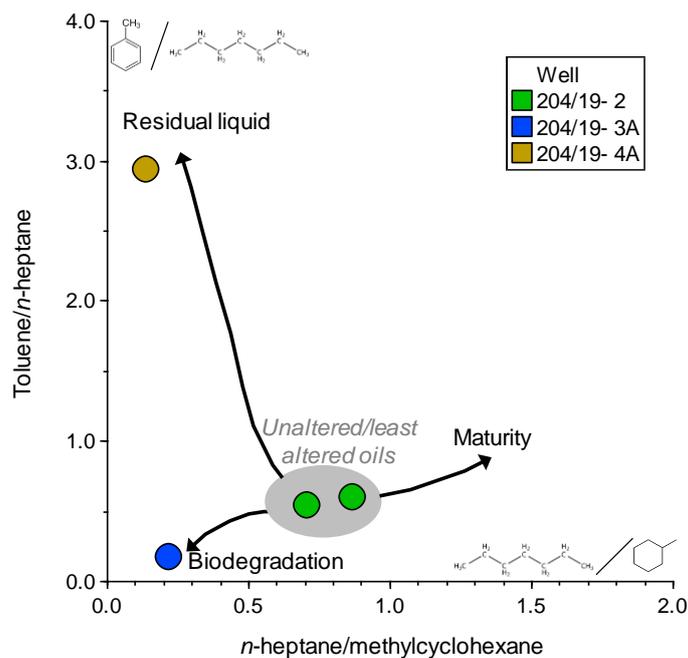
As a result, fractionated residual liquids and moderately biodegraded oils are sometimes difficult to distinguish. Furthermore, both processes are not necessarily mutually exclusive, and the compositions of biodegraded and of fractionated fluids are strongly dependent on charging patterns (Larter *et al.*, 2006; Thompson, 1991), as illustrated here by an example from West of Shetland (WoS) oils.

The Whole Oil Gas Chromatograms (WOGCs) from three oils from Block 204 are shown in **Figure 1**. The uppermost sample (204/19-2) is very moderately altered, with part of the hydrocarbons of the gas (C<sub>3</sub>-C<sub>5</sub>), gasoline (C<sub>6</sub>-C<sub>10</sub>) and diesel (C<sub>11</sub>-C<sub>13</sub>) fractions having been removed. By contrast, the middle sample (204/19-3A) is more severely altered, and hydrocarbons in the C<sub>3</sub>-C<sub>16</sub> range have been extensively removed. Heavier *n*-alkanes have probably also been degraded significantly, leading to the rise of the baseline (Unresolved Complex Mixture or UCM, the “hump” in green). The lowermost sample (204/19-4A) is also highly altered (C<sub>3</sub>-C<sub>16</sub> largely missing), but the removal of the heavier hydrocarbons is not as significant as in the 204/19-3A oil (hence the lower UCM). The presence of a UCM is very characteristic of biodegraded oils (e.g., Head *et al.*, 2003). In addition, the occurrence of 25-norhopanes (terpane biomarker compounds diagnostic of alteration of hopanes which only occurs under severe biodegradation; Bennett *et al.*, 2006), indicates that the three fluids contain a severely biodegraded charge (**Figure 1**). However, the presence of more easily degradable hydrocarbon compounds (the *n*-alkane peaks in the WOGCs) shows that the extensively biodegraded oil has received later charges. The composition of C<sub>7</sub> hydrocarbons provides insight into the emplacement and alteration of these later charges (**Figure 2**).



**Figure 1: Left: Whole Oil Gas Chromatograms (WOGCs) for oils from wells 204/19-2, 204/19-3A and 204/19-4A in the West of Shetland (UK). Right: GC-Mass Spectrometry  $m/z$  177 traces showing the presence of 25-norhopane homologues that are diagnostic of very severely biodegraded oils. Data source: Oil & Gas Authority, UK.**

The plot of toluene/ $nC_7$  versus  $nC_7$ /MCH ratios (**Figure 2**) is based on differences in relative levels of  $nC_7$ , MCH and toluene in pristine and altered fluids (Thompson, 1987). The composition of  $C_7$  gasolines of the 204/19-2 fluid is very comparable to that of pristine oils, indicating that the most recent charge(s) is only very moderately altered. By comparison, the 204/19-4A fluid is depleted in  $nC_7$  compared to both MCH and toluene, typical of residual liquids in fractionated reservoir fluids. The alteration of the oil from 204/19-3A compared to the most pristine 204/19-2 fluid is slightly different, because both  $nC_7$ /MCH and toluene/ $nC_7$  ratios are decreased. In this case,  $nC_7$  has been preferentially biodegraded and toluene, which is more soluble in water than other  $C_7$  hydrocarbons, extensively removed by dissolution at the OWC. Hence, after receiving later charges, the reservoir oil in 204/19-3A has experienced further moderate to high biodegradation. By contrast, in 204/19-4A it has been fractionated, leading to the removal of part of the gas-soluble and volatile hydrocarbons from the residual liquid. These three oils from Block 204 in the WoS show the complex interplay of charging and alteration events in the formation of petroleum accumulations, and highlight the value of gasoline geochemistry in unravelling these intricate processes.



(Modified after Thompson, 1987)

**Figure 2: Plot of the ratios of toluene/*n*-heptane versus *n*-heptane/methylcyclohexane (modified after Thompson, 1987) for three oils from Block 204 in the West of Shetland (UK). Data source: Oil & Gas Authority, UK.**

#### References

- Bennett, B., Fustic, M., Farrimond, P., Haiping Huang, Larter, S.R., 2006. 25-Norhopanes: Formation during biodegradation of petroleum in the subsurface. *Organic Geochemistry* 37, 787-797
- Head, I.M., Jones, D.M., Larter, S.R., 2003. Biological activity in the deep subsurface and the origin of heavy oil. *Nature* 426, 344-352.
- Huang, H., Larter, S., 2005. Biodegradation of Petroleum in Subsurface Geological Reservoirs, in: Ollivier, B., Magot, M. (Eds.), *Petroleum Microbiology*. ASM Press, pp. 91-121.
- Larter, S., Haiping Huang, Adams, J.M., Bennett, B., Jokanola, O., Oldenburg, T., Jones, M., Head, I., Riediger, C.L., Fowler, M., 2006. The controls on the composition of biodegraded oils in the deep subsurface: Part II - Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction. *AAPG Bulletin* 90, 921-938.
- Oil and Gas Authority, UK. Open data available at: (<http://data-ogauthority.opendata.arcgis.com/datasets?t=Geochemistry>)
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *Biomarkers and Isotopes in Petroleum Exploration and Earth History*, Second edition ed. Cambridge University Press, Cambridge
- Thompson, K.F.M., 1987. Fractionated aromatic petroleums and the generation of gas-condensates. *Organic Geochemistry* 11, 573-590.
- Thompson, K.F.M., 1988. Gas-condensate migration and oil-fractionation in deltaic systems. *Marine and Petroleum Geology* 5, 237-246.
- Thompson, K.F.M., 1991. Contrasting characteristics attributed to migration observed in petroleum reservoirs in clastic and carbonate sequences in the Gulf of Mexico, in: England, W.A., Fleet, A.J. (Eds.), *Petroleum Migration*. Geol. Soc. Special Publication No. 59. Geological Society, London, pp. 191-207.