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**Assessment and Quantification of Petroleum Alteration Processes on the Reservoir Scale
Using Oil Compositional Variability and Compound Specific Isotope Ratios**

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Petroleum is the cumulative result of numerous sequential and parallel processes occurring in the system source-carrier-reservoir-cap rock over geological time. The initial control of its composition is from the source rock, namely by the organofacies and maturity level of the kitchen area(s), and is therefore a basin scale phenomenon (tens to hundreds of kilometers). The pressure and temperature conditions of the source-carrier-reservoir system during expulsion, migration and accumulation, again at the basin scale, are the next stage of potential change. Under subsurface reservoir conditions the petroleum may be in a single vapor phase, in which case it is termed a gas accumulation, a single liquid phase, as exemplified by crude oils which are undersaturated with respect to gas, or a two-phase system comprising a gas cap in equilibrium with an underlying crude oil accumulation. Petroleum in reservoirs is then subjected to different degrees of abiotic and biotic “attack”, which often reduces oil quality, including evaporative fractionation, gravity segregation, gas deasphalting, gas stripping, water washing, cap rock leakage, biodegradation and biosynthesis. Among these, biodegradation is a main control in shallow prospects which may lead to a significant reduction of volumes in place as well as compositional changes which are the basis of quality deterioration in particular during the early stages of alteration. The majority of the global petroleum reserves are more or less significantly biodegraded (Head et al., 2003). Main goals of our research on in reservoir alteration processes are to understand the mechanisms of hydrocarbon degradation and to quantify the effects on oil composition and properties.

Considering molecular level alteration, various classification systems characterizing different degradation stages were proposed; the most commonly applied schemes were suggested by Peters and Moldowan (1993) and Wenger et al. (2001). These widely employed biodegradation models focus on qualitative alterations mainly occurring at advanced biodegradation levels, although much of the significant deterioration of petroleum quality goes along with the depletion of volumetrically relevant compounds during the rather early stages of biodegradation. In an earlier study we have used sample sets of crude oils from geographically diverse petroleum systems, where compositional variability was mainly due to microbial activity in the reservoirs, to investigate these effects in detail (Elias et al., 2007). This research showed that conventional molecular biodegradation parameters, such as the Pr/*n*-C₁₇ and Ph/*n*-C₁₈ alkane ratios are not suitable for defining the extent of biodegradation correctly. Thus, we suggested a new molecular biodegradation parameter, the degradative loss that can be used to quantify the depletion of individual crude oil constituents. The approach allows improved assessment of the extent of biodegradation in crude oil samples and also to predict crude oil quality, as assessed from API gravity, directly from the molecular composition. Contrasting conventional assumptions, our findings showed that the degradation patterns of light hydrocarbons and *n*-alkanes differ in different petroleum systems. This suggests that microbial communities are different and therefore generate different molecular degradation patterns which have to be evaluated individually for each system.

In the past decade, compound-specific isotope analysis has become a powerful tool in environmental and petroleum geochemistry to evaluate the biodegradation of hydrocarbons (for reviews see Meckenstock et al., 2004, and Vieth and Wilkes, 2010). Previously, we used carbon isotope ratios of light hydrocarbons to characterize in-reservoir biodegradation in an oil field (the Gullfaks field) offshore Norway. Increasing biodegradation of light hydrocarbons was assessed by decreasing concentrations which were correlated to enrichment in ^{13}C . This study for the first time showed that carbon isotope fractionation caused by biodegradation of light hydrocarbons in a petroleum reservoir can be described using the Rayleigh equation (Vieth and Wilkes, 2006). Subsequently, we proposed that the Rayleigh model can be used to quantify biodegradation of light hydrocarbons in petroleum reservoirs and discussed the geochemical implications for processes such as charging and mixing as well as the limitations of the method (Wilkes et al., 2008). An important aspect is that carbon isotopic compositions of petroleum constituents comprising more than ca. 10 carbon atoms will not be changed even at advanced stages of alteration. Thus, their isotopic heterogeneity which is mainly due to primary controls may be regarded as a meaningful tool for correlation purposes even at moderate levels of biodegradation.

Hydrogen isotopic compositions of individual crude oil constituents also show a significant variability which, however, seems to be less straightforward to be interpreted than the carbon isotopes. Apparently, maturity is a main control on δD values (e.g., Dawson et al., 2005; Schimmelmann et al., 2001). The hydrogen isotopic composition of isoprenoids like pristane and phytane seems to be influenced more strongly by hydrogen exchange processes than the hydrogen isotopic composition of the *n*-alkanes of similar GC retention behavior. Therefore, the difference in δD of these isoprenoids to δD of the “surrounding” *n*-alkanes might be useful as a proxy to evaluate the residence time of the oil in the reservoir assuming that with increasing residence time the difference in δD between isoprenoids and “surrounding” *n*-alkanes should decrease.

The concepts outlined above have been applied towards a case study investigated within our Industry-Partnership-Program project “BioPetS Flux” whose main goal is to develop integrated models for quantifying and predicting the extent of post-filling alteration processes. Within this project the vertical and lateral variability of petroleum composition in a compartmentalized oil field offshore Norway, which contains crude oils of different levels of alteration in the different reservoir compartments, is characterized and interpreted at high resolution. To account for different filling scenarios, selected crude oil samples from surrounding fields have also been analyzed. Aliphatic and aromatic hydrocarbons including biomarkers are used to characterize organic facies, the depositional environment and the maturity. In addition, polar compounds have been investigated using advanced tools such as electrospray mass spectrometry.

For the detection of compositional heterogeneities constituents of both oils and reservoir core extracts were quantified and different parameters were applied to indicate the variability of the molecular composition with respect to different levels of alteration. Application of the “mean degradative loss” (Fig. 1a; Elias et al., 2007; see above) revealed significant lateral and vertical differences in the alteration level of the oils. Furthermore, there was evidence for mixing of altered and fresh oil, as for example the co-occurrence of 25-norhopane and *n*-alkanes indicates recharging processes. Similarly, the stable carbon and hydrogen isotopic compositions of light hydrocarbons, *n*-alkanes, pristane and phytane of oil samples have been evaluated and several new isotope parameters have been developed to assess and differentiate primary and secondary processes that occurred and influenced the molecular and isotopic composition of the oils on the reservoir scale. We observed good correlations between concentrations and $\delta^{13}\text{C}$ values of *i*C5, *n*C5 and *n*C6 that fitted to the Rayleigh equation indicating that biodegradation takes (took) place (Fig. 1b). We then were able to establish a regional scheme for this petroleum system mapping the charging and alteration effects occurring on the reservoir scale. These results are in accordance with the basic organic geochemical characterization and lead to a more precise assessment of the reservoir alteration processes. This presentation will discuss the benefits and limitations of the outlined concepts

towards an improved evaluation of reservoir scale processes based on the results obtained for this North Sea petroleum system.

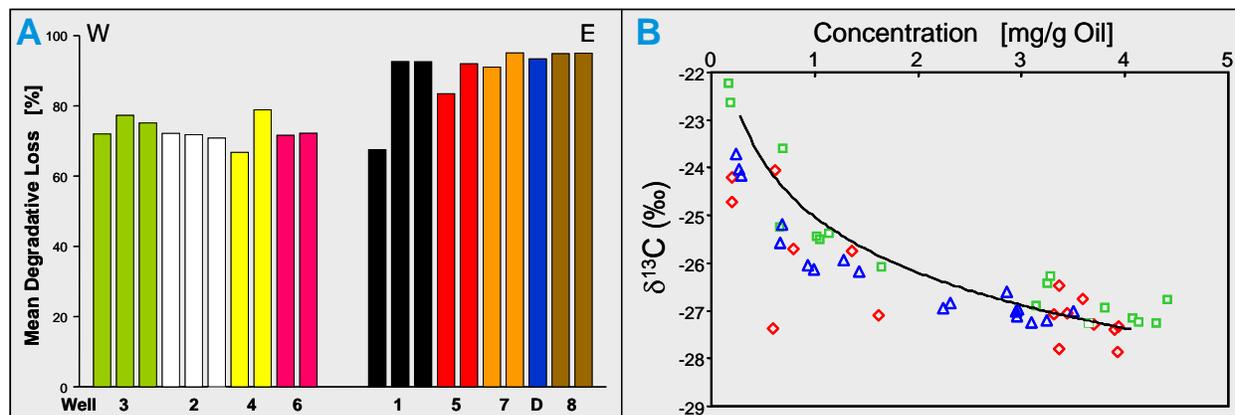


Fig. 1. Indications of biodegradation in a North Sea oil field. A) Mean degradative losses were calculated according to Elias et al (2007) using an oil from a neighboring oil field as the reference. Wells are ordered from West to East. The data document a lateral as well as a vertical variability of the oil composition and different levels of alteration. B) Carbon isotopic compositions of *i*C₅ (blue triangles), *n*C₅ (green squares) and *n*C₆ (red diamonds) versus concentration. The logarithmic correlation indicates that the data fit the Rayleigh equation.

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