

CONTROLS ON THE COMPOSITIONAL ALTERATION OF CRUDE OIL DURING IN RESERVOIR BIODEGRADATION

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Biodegradation of crude oil in reservoirs leads to both a significant reduction of volumes in place as well as a strong quality deterioration of the residual oil (e.g. Head et al., 2003; Wenger et al., 2001). The latter is a direct consequence of compositional alteration as the molecular basis for changing physicochemical properties such as the API gravity. Compositional alteration results from the preferential loss of certain compound types believed to be more susceptible to biodegradation than others which appear to be more recalcitrant. However, recent research in our group has shown that oil constituents generally assumed to be relatively recalcitrant to biodegradation including but not limited to the isoprenoids pristane and phytane may be substantially affected even within very initial stages of alteration (Elias et al., 2007). This indicates that most oil constituents are degraded simultaneously, and the important but yet unanswered question thus is: Why does biodegradation of different oil constituents proceed at different rates? This presentation will discuss degradative capabilities of the involved microorganisms and bioavailability of different petroleum constituents as two key controls on compositional alteration using the results from laboratory experiments as well as data from field studies on biodegraded oil reservoirs.

Our work is based on the assumption that biodegradation of hydrocarbons in petroleum reservoirs proceeds under anoxic conditions. Importantly, free energy changes associated with hydrocarbon oxidation depend mainly on the utilised electron acceptor but are largely independent from the type of oxidised hydrocarbon (Spormann and Widdel, 2000). Therefore, thermodynamic differences can be ruled out as a main reason for the preferential removal of certain types of petroleum constituents. With this in mind, model experiments were performed with 16 pure cultures of denitrifying and sulphate-reducing hydrocarbon-utilising bacteria and individual hydrocarbons as pure substrates or crude oil as a complex mixture of organic substrates. These investigations provide a detailed insight into the degradative capabilities of anaerobic hydrocarbon-oxidising bacteria. Importantly, all these organisms exhibit pronounced substrate specificities. For example, all *n*-alkane degraders have their own characteristic range of *n*-alkane chain length that can be utilised. It therefore

must be concluded that either concomitant or successive activity of different types of hydrocarbon-oxidising bacteria is required to achieve the complex alteration patterns observed in petroleum reservoirs. Different patterns of hydrocarbon degradation in different oil fields most likely reflect differences in the respective microbial consortia. Our experiments with crude oil also reveal co-metabolism of hydrocarbons that do not support growth if supplied as pure substrates as a relevant mechanism of compositional alteration of crude oil.

A further result of these experiments is that the relative degradation rates of individual hydrocarbons depend on their variable bioavailability in terms of factors and processes influencing their concentration in the water phase. Microorganisms need liquid water to exist and biodegradation takes mainly place at or near the oil water contact. As a consequence petroleum constituents are available for microbes only when they are dissolved in water. Therefore, bioavailability and hence degradation rates of individual petroleum constituents in oil reservoirs are to a large extent controlled by the physicochemical processes controlling their transport to and into the water phase such as diffusion and partitioning. For example, there is a clear and systematic relationship between decreasing relative degradation rates and increasing chain length of *n*-alkanes. Such effects are observed in laboratory experiments as well as in petroleum reservoirs and are not restricted to *n*-alkanes but also true for other types of petroleum constituents including aromatic hydrocarbons and certain NSO compounds such as carbazoles or xanthenes. Our results from various petroleum systems indicate that concomitant biodegradation of different types of oil constituents is rather the rule than the exception. This has strong implications with respect to the validity of the conventional perception of biodegradation as a process removing different compound classes sequentially resulting in more or less similar patterns of compositional alteration in any biodegraded oil reservoir.

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