

## COMBINING FT-ICR MS AND PYROLYSIS TO PREDICT PETROLEUM-TYPE ORGANOFACIES AND EVOLVING FLUID PHYSICAL PROPERTIES

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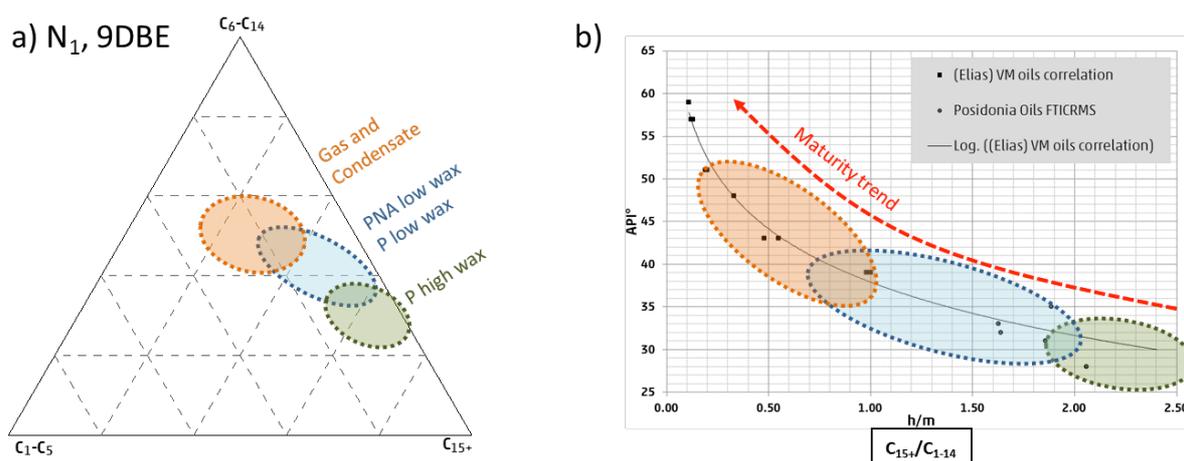
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According to Mullins (2007), deciphering the petroleome, i.e., the complete listing and quantification of all chemical constituents within a given crude oil, will allow the prediction of that fluid's physical properties and thus its behaviour under various PVT conditions (especially during production). Nevertheless, the petroleome changes depending on source rock type, maturity, source or sink environment, biodegradation, etc.. Thus, understanding and being able to predict the petroleum composition as a function of those parameters is more crucial than knowing the petroleome of one specific "ready-to-be produced" oil encountered downhole in an already drilled and tested well.

The bulk composition of first-formed petroleum, or its main chemical building blocks, is of primary importance because it comprises the initial petroleome directly expressed from a specific kerogen, and all subsequent processes occurring in the source-carrier-reservoir system, for instance fluid-rock or fluid-fluid interactions in the matrix/fracture porosity of shales, phase separation during secondary migration or uplift, or fractionation during reservoir leakage, simply act upon this original composition. The role played by source rock kerogen type and maturity in controlling the physical properties of fluids expelled into conventional reservoirs is largely established (e.g. PhaseKinetics approach of di Primio and Horsfield (2006)) and based on genetic relationships between kerogen moieties, deciphered by open-system and closed-system pyrolysis GC-FID, and hydrocarbons in petroleum. Using FT-ICR MS as the detection method but an otherwise similar pyrolysis approach, we aim to improve our understanding of the role played by kerogen type and maturity in controlling the physical properties of fluids in conventional reservoirs and expand this knowledge to fluids retained in their source environment, i.e., in unconventional reservoirs.

Off-line open-system pyrolysis was run for ten immature and early mature source rocks from various depositional environments to provide pyrolysates for ESI(-) FT-ICR MS measurements. One main outcome of the study is that, based on the aliphatic carbon number distribution within, for example, the 9 DBE, N<sub>1</sub> elemental class, petroleum type organofacies fields can be established in a ternary diagram first used in Mahlstedt et al. (2016) that displays carbazoles with alkyl side chains of 1-5 carbon atoms versus carbazoles with alkyl side chains of 6-14 carbon atoms versus carbazoles with alkyl side chains  $\geq 15$  carbon atoms (Figure 1a). These fields roughly correspond to those defined in Horsfield (1989) based on *n*-aliphatic chain length distributions in open-system pyrolysates, but are generally positioned in an area of higher aliphatic carbon numbers/longer chain length within the ternary diagram. Having learned that pyrolysates hold compositions intermediate between retained (extracts) and expelled (oils) fluids (Mahlstedt et al., 2016), pointing to a preferential expulsion of smaller compounds in the crudes and enhanced cyclization and aromatization at the expense of aliphatic carbon within the retained fluids, prediction of the NSO-compounds composition in conventional vs. unconventional oils of a given source rock is possible. Calibration of predicted and encountered compositions in extracts and produced oils is still on-going.

Adapting the approach of Elias and Gelin (2015), who successfully correlated GPC/UV heavy cuts/medium cuts ratios (h/m) of aromatic compounds in oils or extracts to field API, FT-ICR MS derived low and intermediate aliphatic carbon numbers ( $C_{1-14}$ ) of the DBE 9,  $N_1$  elemental class carbazoles as the medium cut and high aliphatic carbon numbers ( $C_{15+}$ ) as the heavy cut can also be used to predict field API (Figure 1b). Plotting aliphatic carbon number based h/m ratios for extracts and oils sourced from siliciclastic rocks on the GPC/UV-API° trend line, meaningful API values could already be assessed indicating the feasibility of this approach to predict physical properties.



**Figure 1** a) ternary diagram displaying the aliphatic carbon number distribution of  $N_1$  compounds of the 9 DBE class in pyrolysates of immature source rocks; b) API° prediction using the heavy over medium cut of  $N_1$  compounds of the 9 DBE class.

## References

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