CONTROLLING FACTORS OF CARBAZOLE RATIOS: GENERATION, MIGRATION AND EXPULSION BEHAVIOUR

M. Stockhausen[1], L. Di Paolo[2], S. Castellani[2], R. Galimberti[2], U. Berner[3], M. Erdmann[3], R. Elias[4], F. Gelin[4], J. H. Pedersen[5], R. Di Primio[5], L. Schwark[1]

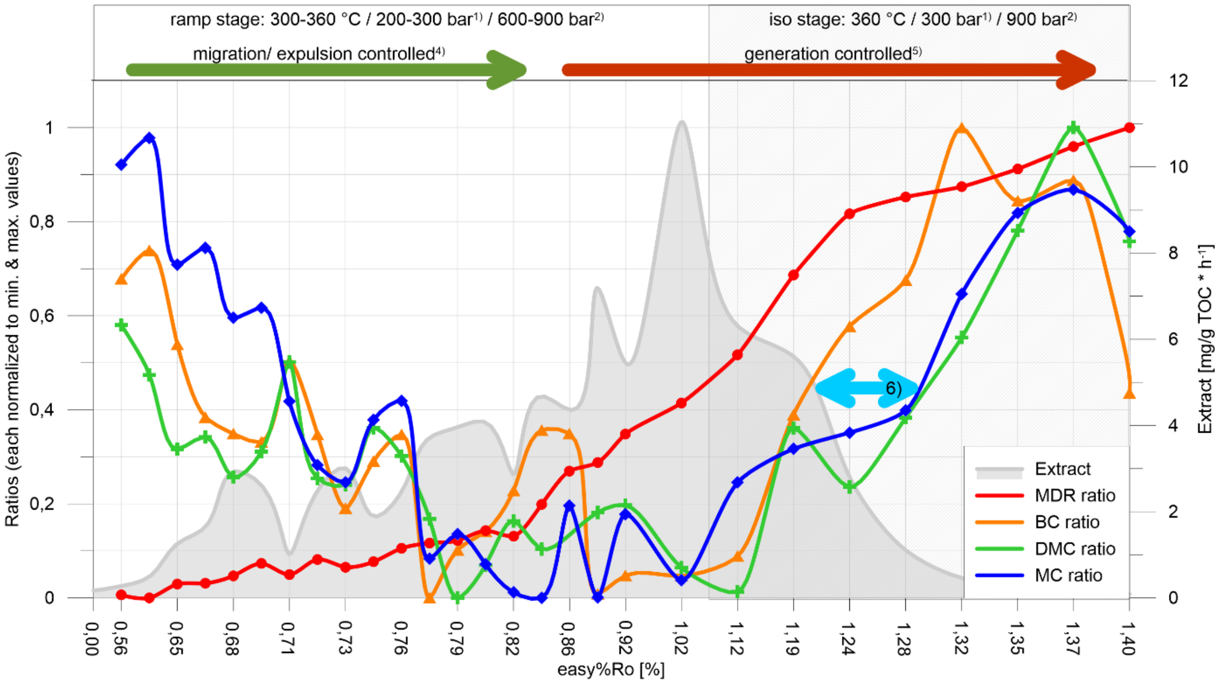
[1]Kiel University, Germany; [2]Eni S.p.A., Italy; [3]Equinor, Norway; [4]Total, France; [5]Lundin, Norway

Knowing the migration history of petroleum within an oil play is essential for oil accumulation prediction and assessment of exploration economics. For this purpose, carbazole ratios were established as simple-to-use evaluation tools for secondary migration distances (e.g. Larter et al., 1996). Carbazoles are particularly qualified for migration studies due to their high polarity, induced by the pyrrolic nitrogen functionality, which interacts with mineral and organic phases. Preferential removal of specific components from migrating oils here forms the basis of the migration proxies: The benzocarbazole ratio (BC) for example is attributed by preferential adsorption of benzo[a]carbazole over benzo[c]carbazole (Larter et al., 1996). Other studies suggested higher affinity of pyrrol-exposed alkylcarbazoles to active sides of clay minerals and organic phases along the migration way, increasing the relative amount of pyrrol-shielded alkylcarbazoles with travel distance (Li et al., 1997).

Investigation of the secondary migration effect onto carbazole ratios were mainly based on observations in natural systems (e.g. Larter et al., 1996, Li et al. 1997) and flow experiments conducted in the laboratory, assuming constant start conditions and composition. This left out of consideration that increasing maturity could impact the carbazole composition. In addition, primary migration through the source rock and expulsion into the carrier bed will affect the carbazole composition and influence the starting conditions prior to secondary migration. Lab-scaled generation and expulsion simulations, carried out with the “Expulsinator”-device, facilitate the investigation of both the impact of generation but also of primary migration and expulsion onto carbazole compositions. The Expulsinator conducts semi-open hydrous pyrolysis of an intact source rock (i.e. with intact mineral matrix and kerogen network) under near-natural lithostatic and hydrostatic pressure regimes (Stockhausen et al., 2013). Thus, the Expulsinator provides a generation and expulsion sequence of oils obtained from an artificially matured source rock. Prior to product recovery the oil and gas generated must migrate through the pore network of the source rock. Hereby it is affected by geochromatography and adsorption/desorption, resulting in product fractionation.

Results delivered by Expulsinator experiments suggest that both migration and increasing maturity affects carbazole ratios. All carbazole ratios, i.e. the BC ratio (benzo[a]carbazole/(benzo[a]carbazole + benzo[c]carbazole)), the DMC ratio (shielded dimethylcarbazoles/exposed dimethylcarbazoles) and the MC ratio (1-methylcarbazole/4-methylcarbazole) decrease in the low maturity range up to ~ 0.8 % Ro (Fig.). The MDR ratio (4-methyldibenzotiophene/1-methyldibenzotiophene), a well-established maturity indicator, shows a moderate increase in the same interval. This suggests that here generation related effects were not in control of the carbazole ratios, but fractionation upon primary migration took place. Especially, the different behaviour of the MC and the MDR ratio is worth mentioning, as both components are structurally very similar. However, results indicate primary migration rates as follows: benzo[a]carbazole > benzo[c]carbazole, shielded dimethylcarbazoles > exposed dimethylcarbazoles and 1-methylcarbazole > 4-

methylcarbazole. With onset of the main generation phase (~ 0.8 % Ro) the BC, MC, and DMC ratio parallels the trend of the MDR ratio, indicating that expulsion effects were superimposed by generation. However, the MC and DMC ratio increased delayed to the BC ratio, indicating a less pronounced impact of generation for the methylated carbazoles. Furthermore, general expulsion characteristics of different source rocks had major impacts onto the behaviour of carbazole ratios: "Bad expellers" showed opposing trends compared to good and excellent expellers (Fig. shows only trends of a good expeller). This was observed, among others, for the BC ratio: In case of a bad expeller the ratio first increased until a maturity of ~ 0.8 % Ro was reached, followed by a decreasing trend. Here, timing of generation and expulsion was crucial for the trends observed: Early generation combined with low expulsion rates diminish generation effects while fractionation due to different migration rates predominated.



Generation & expulsion profile of an Expulsinator experiment (source rock: Posidonia Shale). Pressures ([1)]hydrostatic, [2)]lithostatic) and temperature were increased ramp-wise, followed by constant values. Symbols represent sampling points. Ratios were normalized to their respective lowest and highest values to ensure comparability.
Carbazole ratios were controlled either by [4)]migration & expulsion (green arrow; low maturity range < 0.8 % Ro), or [5)]generation at higher maturity (red arrow; > 0.8 % Ro).
[6)]Offset between the BC ratio and the MC and DMC ratio due to different response to generation effects (blue arrow).

References

Larter, S. R., B. Bowler, M. Li, M. Chen, D. Brincat, B. Bennett, K. Noke, e al. „Molecular Indicators of Secondary Oil Migration Distances". Nature 383, Nr. 6601 (1996): 593–97.
Li, M., H. Yao, L. D. Stasiuk, M. G. Fowler, und S. R. Larter. „Effect of maturity and petroleum expulsion on pyrrolic nitrogen compound yields and distributions in Duvernay Formation petroleum source rocks in central Alberta, Canada". *Organic Geochemistry* 26, Nr. 11 (1997): 731–44.
Stockhausen, M., R. Galimberti, R. Elias, und L Schwark. „Experimental simulation of hydrocarbon expulsion". In Book of Abstracts, 26th International Meeting on Organic Geochemistry. Costa Adeje, Tenerife – Spain, 2013.