

## COMPOUND SPECIFIC ISOTOPE ANALYSES OF ALKYL BENZENES IN OILS

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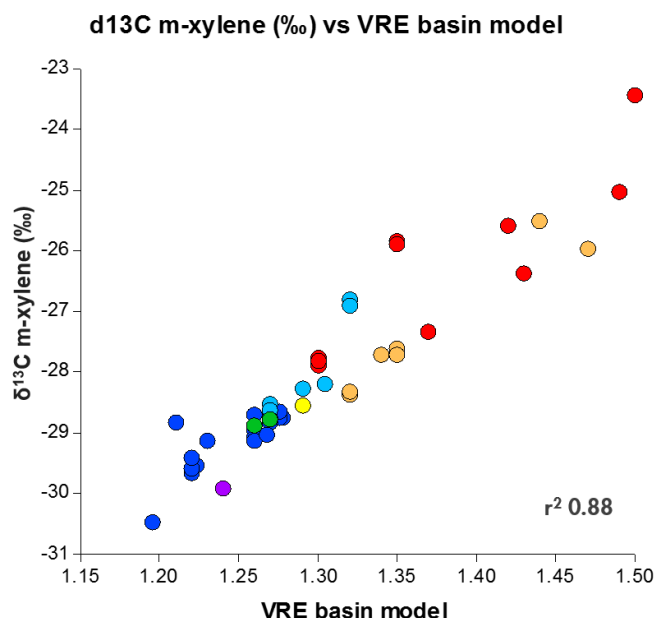
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Geochemical fingerprinting is widely applied for reservoir surveillance and compartmentalization, fluid movement and production allocation (van Bergen and Gordon, 2018, and references therein). Within Shell, geochemical fingerprinting is primarily undertaken using multidimensional gas chromatography (MDGC), which allows for highly accurate determination of C<sub>2</sub>- and C<sub>3</sub>-alkylbenzene concentrations. The relative distributions of alkylbenzenes can be used to determine small variations between different fluids that are otherwise very similar. For instance, fluids derived from the same source rock but contained in multiple stacked reservoirs can be differentiated. There are a range of causes that influence the alkylbenzene distributions: different source rocks yield different (relative) concentrations (Hartgers et al., 1994) and maturity also strongly influences the relative distributions. In addition, fluids may be altered due to migration and various in-reservoir processes. Isotope ratios for the individual alkylbenzenes provide an additional dimension of information, which may provide insights into the processes causing the aforementioned variation in alkylbenzene distributions.

Analyses of compound specific stable isotopes (expressed as  $\delta^{13}\text{C}$ ) of alkylbenzenes on whole oil dilutions was achieved by coupling of an MDGC with an isotope ratio-mass spectrometer (IRMS). The system was tested and showed good reproducibility with standard deviations of 0.1-0.2 ‰. The first set analyzed consisted of 73 samples from an unconventional play in Canada. A large variation in compound specific carbon isotope ratios was observed within the sample set, with  $\delta^{13}\text{C}$  values ranging from -31 to -22‰. The  $\delta^{13}\text{C}$  values of individual alkylbenzenes correlated generally well with bulk aromatic  $\delta^{13}\text{C}$  values but showed a significantly larger range of isotope values (1.5-2x). Principal component analyses showed that almost all variation within this sample set is explained by maturity, where loadings and orientation of the compound specific isotope values correlate with those of vitrinite reflectance equivalent (VRE), the prime parameter for maturity. VRE values were derived from a regional basin model that was calibrated using organic petrography analyses. *Meta*- and *para*-xylene (*m*- and *p*-xylene) showed the strongest correlation with VRE, being more enriched in  $^{13}\text{C}$  at higher maturity due to the stronger  $^{13}\text{C}$ - $^{12}\text{C}$  bonds breaking at higher temperatures. For example, carbon isotope values of *m*-xylene show an increase of 8‰ over a VRE range of 1.2 to 1.5 with a  $r^2$  of 0.88 (see Fig. 1). This shows not only a very good correlation with maturity but also a high sensitivity of alkylbenzene  $\delta^{13}\text{C}$  values, as shown here for *m*-xylene, towards VRE.

The advantage of CSIA on alkylbenzenes over isotopes of other compounds is that this information can be directly linked to the compounds that are used to understand and monitor the reservoir. In addition, this technology may show isotope differentiation for fluids that have otherwise a very similar fingerprint. Moreover, different types of alkylbenzenes show different isotope ratios related to different original source compounds (Holman and Grice, 2018) and/or a different extent of fractionation. Therefore, a more diverse isotope fingerprint is obtained relative to, for instance, *n*-alkane CSIA. Additional sample sets are currently being analyzed

showing that, apart from maturity, other processes can be deduced, examples of which will also be presented. Overall, CSIA of alkylbenzenes provides a new and different dimension of information and additional resolution for production geochemistry as well as basin-wide petroleum system understanding.



**Figure 1** Compound specific carbon isotope ratios ( $\delta^{13}\text{C}$  ‰) of *m*-xylene plotted against the basin model-derived VRE. Samples are from one formation of an unconventional play in Canada. Different colours indicate different license blocks.

## References

- van Bergen, P.F., Gordon, M., 2018. Production geochemistry: fluids don't lie and the devil is in the detail. Geological Society, London, Special Publications 484, <https://doi.org/10.1144/SP484.1>
- Hartgers, W.A., Sinninghe Damsté, J.S. De Leeuw, J.W., 1994. Geochemical significance of alkylbenzene distributions in flash pyrolysates of kerogens, coals, and asphaltenes. *Geochimica et Cosmochimica Acta* 58, 1759-1775.
- Holman, A.I., Grice, K., 2018.  $\delta^{13}\text{C}$  of aromatic compounds in sediments, oils and atmospheric emissions: A review. *Organic Geochemistry* 123, 27-37.