

## Novel geochemical tools based on light hydrocarbons from different petroleum settings

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### Introduction

Many important petroleum assets currently being exploited in basins around the world are composed of light oil and gas/condensate accumulations. This is the case for well-known gas provinces such as the North-West Shelf of Australia (NWS) and the Western Canadian Sedimentary Basin (WCSB) [1,2], where current development focuses on conventional and unconventional petroleum reservoirs, respectively. Low-molecular-weight hydrocarbons represent a challenge in petroleum system definition because fluid-to-source correlations are limited. Molecular parameters typically employed for correlations cannot be used due to the low concentration of biomarkers in condensates and light oils (often absent or below detection limits). Additionally, many of these accumulations correspond to high thermal maturity products where key biomarker ratios have already reached equilibrium and thus their application becomes ambiguous. It is therefore necessary to continue to explore geochemical tools based on other compounds and properties of light petroleum fluids in order to accurately estimate hydrocarbon charges, their origin and migration pathways. This is not only relevant in Australia where certain Triassic-Jurassic petroleum fluids are yet to be discriminated [1,3], but also in low-permeability reservoirs from Canada as these often contain in-situ fluids mixed with other hydrocarbons that migrated and charged the reservoirs before the plays became tight [4]. We present novel geochemical tools based on low-molecular-weight hydrocarbons in the C<sub>7</sub>-C<sub>11</sub> range, with special focus on the molecular distribution and isotope ratios of aromatic compounds and how these relate to the source of organic matter, thermal stress, mineral catalysis, and/or alteration in the reservoir. Light aromatic hydrocarbons are also the most water-soluble hydrocarbon fraction. Hence, their geochemical fingerprinting is fundamental for forensic studies in determining the source and fate of these compounds in water bodies due to oil spills, hydraulic fracturing and oil sand mining practices.

### Methods

A total of 45 samples of petroleum condensates and light oils from the North-West Shelf of Australia, the Western Canada Sedimentary Basin, and the Maracaibo sub-Basin of Venezuela were analyzed. Whole-oil analysis was conducted using standard methods for gas chromatography – mass spectrometry (GC-MS). The condensate and light oil samples were also fractionated into aliphatic and aromatic hydrocarbons using small-scale silica - liquid chromatography; both fractions were also analyzed via GC-MS. The stable carbon compound specific isotope analysis (CSIA) of the aliphatic and aromatic fractions was performed using gas chromatography – isotope ratio mass spectrometry (GC-irMS), under the same GC conditions implemented for GC-MS analysis.

## Results

The most abundant light aromatic compounds identified in the samples include xylenes ethyltoluenes, dimethyl-ethylbenzenes, tri- and tetra-methylbenzenes. Minor compound classes include cymenes, diethylbenzenes and other *iso*-aklylbenzenes. The presence of these compounds is ubiquitous and thus they are shown to be generated in both siliciclastic and carbonate source rocks. However, certain compounds are favored with increasing thermal maturity such as (i) *para*-isomers (1,4-substituted) over *ortho*-isomers (1,2-substituted), and (ii) dimethyl-ethylbenzenes over tetramethylbenzenes. The 1,3-substituted compounds (*meta*-isomers) are also more prominent in claystones compared to carbonates, and their abundance increases with thermal stress. The  $\delta^{13}\text{C}$  values of alkylbenzenes can vary by up to 11 ‰ for the same compound in different samples, and variations of up to 6 ‰ between isomers (e.g. ethyltoluenes) from the same sample are also observed. Increasing methylation does not have a consistent effect on the  $\delta^{13}\text{C}$  values, and isotope differences between compound classes can be almost negligible in highly mature fluids. Geochemical tools based on the molecular distribution and isotopic composition of light aromatic hydrocarbons have been applied to establish fluid families in hydrocarbon reserves originating from terrigenous and mixed marine-terrigenous organic matter (e.g. the Northern Carnarvon Basin, Browse Basin and the Bonaparte Basin, Australia), and marine organic matter (in the WCSB, and Maracaibo sub-Basin) [5,6]. Molecular ratios based on alkylbenzenes have also been used to discriminate producing intervals at a semi-regional scale in low-permeability reservoirs from the Montney Formation, WCSB.

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