

IMPACT OF THERMAL MATURITY AND EVAPORATIVE LOSSES ON COMPOUND SPECIFIC CARBON ISOTOPE RATIOS OF LIGHT HYDROCARBONS IN WHOLE-OILS

M. A. Mamouni^{1,2}, D. Duclerc¹, R. Elias¹

¹TOTAL S.A., France, ²University of Paris XI, France

Introduction

Compound-specific-isotope-analysis (CSIA) on carbon and hydrogen in petroleum fluid samples (gas, oil & rock extracts) became a standard analytical tool in many geochemical laboratories during the last decades. CSIA data are now routinely used for a great variety of applications including the assessment of genetic relationships between gases, oils and source rocks (e.g., gas-oil, oil-oil & oil-source correlation studies). In addition several studies have shown that CSIA data can be used to assess several individual source rock and reservoir-related processes such as thermal maturation and petroleum biodegradation. Most of the previously published studies focus on the medium-heavy to heavy crude oil fractions (C₁₅+ fraction) detected within the saturated hydrocarbon fraction such as normal alkanes (Barrie et al., 2016). In this presentation however we emphasize the utility of CSIA on light hydrocarbons (C₄-C₉ hydrocarbon range for normal-, branched-, cyclo-alkanes and light aromatic hydrocarbons) directly detected in the whole oil (untreated & undiluted). In this study CSIA was carried-out on a series of six crude oils and various rock extracts from Vaca Muerta Formation in the Neuquén Basin, onshore Argentina. The analysed sample set represents both a source and reservoir rock formation (unconventional play) covering a maturity range from the black oil to gas/condensate window (VR₀ ~ 0.7 – 1.4 %). In this presentation we will propose some new maturity proxies based on CSIA and we will also discuss the effect of evaporative fractionation on the light hydrocarbon carbon isotopic compositions in the selected sample set.

Results

Our compound-specific-carbon-isotope-analyses ($\delta^{13}\text{C}$ CSIA) on light hydrocarbons (C₅-C₉ range) in crude oils from the Vaca Muerta Formation show that a maturity increase from VR₀ ~ 0.7% - 1.4% can go along with an isotopic shift of up to 6 ‰ (towards heavier $\delta^{13}\text{C}$ values) for individual molecules. We will show that the stable carbon isotopic composition ($\delta^{13}\text{C}$) in particular for light normal alkanes, branched alkanes but also for light aromatic hydrocarbons systematically evolve with increasing maturity. On the contrary, cyclic alkanes are apparently less affected by a systematic isotopic fractionation during thermal maturation. We will suggest here some new isotope ratios in the light hydrocarbon range that can be used (after local calibration) as complementary maturity proxies not only in classical black oils but also in condensates samples.

In this study we have also carried-out a systematic comparison between CSIA results for the C₁₅ – C₂₅ hydrocarbon range (normal alkanes) in produced oils and corresponding reservoir rock extracts from the Vaca Muerta Formation. Our results demonstrate that $\delta^{13}\text{C}$ signatures for C₁₅ – C₂₅ paraffin's in dead oils and corresponding reservoir rock extracts are very similar in the lower maturity range from VR₀ = 0.7 – 1.3%. However, for maturities above VR₀ > 1.3% we can observe a clear offset between $\delta^{13}\text{C}$ values (C₁₅ – C₂₅ range) detected in dead oils and reservoir rock extracts with the latter being more depleted in ¹²C. As the higher maturity liquids are obviously also characterised by a more volatile molecular composition we attribute this

depletion in ^{12}C in the rock extracts to an evaporative fractionation effect that is more pronounced in the core extracts than in the produced oils.

However, also for the analysed dead oils representing higher maturities with $\text{VR}_0 > 1.3\%$ we can observe an elevated ^{12}C depletion in the light hydrocarbon range. Our results however demonstrate that the impact from evaporative losses is typically within the range of 1–2‰ ^{12}C depletion (depending on the volatility of the individual molecule) and therefore is typically much less pronounced than the isotopic shift of up 5–6 ‰ that can be attributed to a maturity increase in the analysed sample set.

Conclusions

This study suggests that a maturity increase from $\text{VR}_0 = 0.7 - 1.4\%$ can go along (for the Vaca Muerta fluids) with a systematic and linear $\delta^{13}\text{C}$ isotopic shift of up 6‰ towards heavier carbon isotopic compositions for individual light hydrocarbons. However, our study also showed that the impact of evaporative losses must be taken into account, in particular for the most volatile fluids (here representing relatively highest maturities). Nevertheless, the example of the studied Vaca Muerta sample set suggest that the impact of evaporative losses ($\delta^{13}\text{C}$ shift of 1–2‰) is much less pronounced than the observed maturity effect ($\delta^{13}\text{C}$ shift of 5–6‰). Hence it appears reasonable that, under consideration of the evaporative fractionation effect, CSIA on light hydrocarbons can be considered as a complementary tool to define thermal maturity even for light fluids such as condensates where typical molecular maturity proxies are often difficult to define (e.g., low abundance of biomarkers).

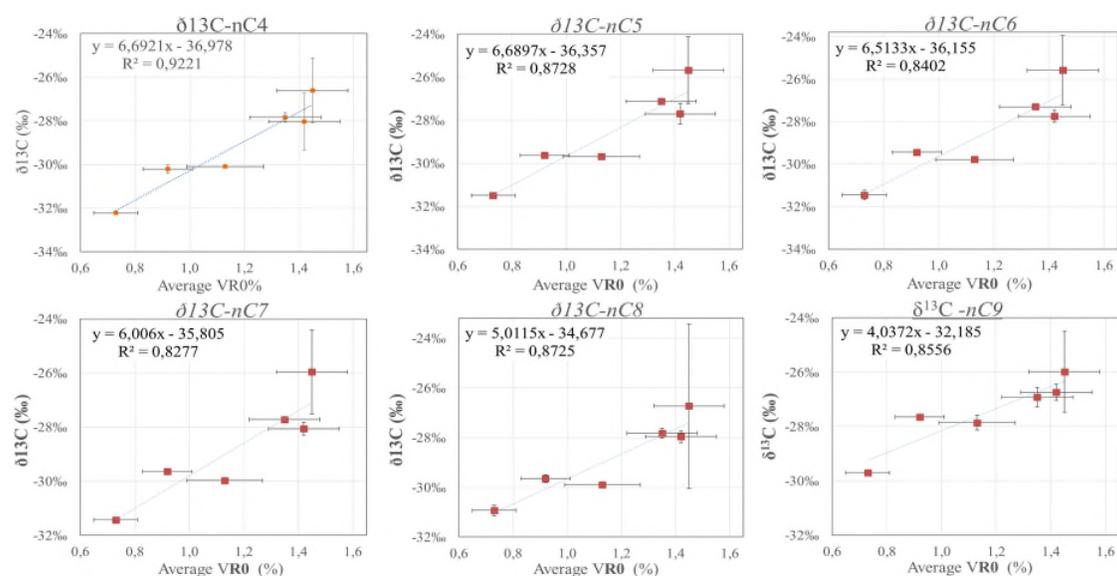


Figure 1 Correlation of compound-specific-carbon-isotope analysis ($\delta^{13}\text{C}$) results for light hydrocarbons (C4 - C₉ normal alkanes) in dead oils produced from the unconventional Vaca Muerta Formation (Argentina) with corresponding average thermal maturities ($\text{VR}_0\%$).

References

Barrie, C.D., Taylor, K.W.R., Zumberge, J. (2016): Measurement of compound-specific carbon isotope ratios ($\delta^{13}\text{C}$ values) via direct injection of whole crude oil samples. Rapid Commun. Mass Spectrom. 2016, 30, 843–853