Influence of thermal maturity on carbon isotopic composition of individual aromatic hydrocarbons

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Anhydrous closed-system pyrolysis experiments were conducted on the pure alkyl naphthalenes, n-alkanes and crude oils in order to investigate the isotopic changes of individual aromatics during laboratory maturation (1.05% to 2.30% Ro). On the whole, aromatic hydrocarbons have better thermal stability than n-alkanes. While the carbon isotopic composition of substituted aromatics exhibits a positive correlation with increasing thermal maturity, there is no significant fractionation in the carbon isotopic composition of unsubstituted aromatics. This finding suggests that the carbon isotopic distribution of unsubstituted aromatics can be used as an effective tool for oil-oil and oil-source correlation, especially for highly-over mature fields. On the basis of those finding, a novel, effective and easy-to-operate method to separate and enrich unsubstituted aromatics directly from crude oil was developed. The pyrolysis at 500 °C for 12 h was found to be sufficient for the purification of unsubstituted aromatics that were free of poly-substituted aromatics and unresolved complex mixture. It allowed further accurate compound specific isotope analysis, and GC-IRMS data showed that the $\delta^{13}C$ values of unsubstituted naphthalene and phenanthrene had no obvious fractionation during the purification process(Table 1). This method laid the foundation for developing new oil-oil correlation indicators.

Crude oil	Naphthalene			Phenanthrene		
	$\delta^{13}C$ (‰)		$\Delta\delta^{13}C$ (‰)[a]	$\delta^{13}C$ (‰)		$\Delta\delta^{13}C$ (‰)[a]
	Before pyrolysis	After pyrolysis		Before pyrolysis	After pyrolysis	
TK258	-33.8	-34.1	-0.3	-33.3	-33.1	0.2
XL4	-32.0	-31.5	0.5	-31.6	-31.7	-0.1
TP17	-31.1	-31.6	-0.5	-32.3	-32.0	0.3
S26	-29.7	-30.0	-0.3	-29.1	-29.8	-0.7
LFP	-	-30.3	-	-28.5	-29.3	-0.8
CX07	-	-24.3	-	-24.7	-25.4	-0.7
CX0642	-23.6	-24.1	-0.5	-23.8	-23.6	-0.2

[a]$\Delta\delta^{13}C$ (‰) $=\delta^{13}C$ (‰) $_{\text{after pyrolysis}}-\delta^{13}C$ (‰) $_{\text{before pyrolysis}}$

Table1: $\delta^{13}C$ values (‰) of unsubstituted naphthalene and phenanthrene of different crude oils before and after pyrolysis.