

MATURATION PROCESSES USING COMPOUND SPECIFIC SULFUR ISOTOPES ANALYSIS IN PYROLYTIC AND NATURAL OILS

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Sulfur has a unique role in the organic matter (OM) cycle through its diagenetic and catagenetic processes. As the OM comprises of multiple sulfur-moieties (e.g., in isoprenoid or branched carbon skeletons), the sulfur isotope ratio ($^{34}\text{S}/^{32}\text{S}$) of specific compounds generated from the OM hold the promise to gather better understanding on the OM cycle.

This work studied the structural and sulfur isotope ratio changes in specific organic sulfur compounds (OSCs, short compounds and biomarkers) as well as in bulk sulfur phases (H_2S , kerogen, oil) during thermal maturation and oil formation. Semi-open pyrolysis experiments were conducted on a thermally immature, organic and sulfur-rich source rock (Ghareb formation, Israel). Oil and gas samples were collected sequentially in several points along the maturation path and were analyzed. In addition, four natural crude oils from Israel were analyzed and the results were compared to the pyrolytic oils.

The composition of short OSCs in the oil phase (thiolanes, alkyl thiophenes, benzo-thiophenes (BTs) and dibenzo-thiophenes (DBTs)) showed a clear increase in the degree of aromatization with the increase in maturation. The $\delta^{34}\text{S}$ of those compounds showed relatively large variability ($\sim 10\%$) in the immature bitumen and first pyrolytic oil. At later stages of thermal maturation, the variability of the sulfur isotopic values in the kerogen gradually decreased ($\sim 2\%$). The decrease in the variability follows the thermal stability of the OSCs, where the less stable alkyl thiophenes were the first to lose their variability, followed by the more stable BTs.

The trends in the $\delta^{34}\text{S}$ of the OSCs suggests three mechanisms to explain the structural changes and isotopic fractionations of OSCs in the kerogen and generated oils: (A) Cleavage of weak S-S and C-S bonds which releases large amounts of H_2S followed by cyclization of the precursors in the kerogen with small fractionations. (B) Re-reaction of the released S species with hydrocarbons and generation of new OSCs within the kerogen matrix. (C) Cleavage of stronger C-C bonds and transformation of OSCs create more stable compounds (e.g. DBT) from multiple sulfur sources. Compared to mechanism B and C, mechanism A preserves the distinct $\delta^{34}\text{S}$ values of the precursors.

The overall outcome of the maturation process yields OSCs with $\delta^{34}\text{S}$ values that closely reflect the kerogen and can be used as a fingerprint for oil-oil and oil-source rock correlation in wide ranges of thermal maturities. The applicability of such correlation is demonstrated by comparing the compound specific $\delta^{34}\text{S}$ values of 4 natural oil samples to that of the pyrolytic oil on a spider diagram (Fig. 1). The shaded polygon shows the maximum and minimum isotopic values for each compound in the pyrolytic oil, while the 4 natural oils are shown by the different symbols. As can be seen the Tzuk Tamror, Gurim and Emuna oils are very close

to the pyrolytic oil suggesting a similar source rock. The considerable differences in the $\delta^{34}\text{S}$ values obtained for the Yam-2 oil compared to the pyrolytic and the other 3 natural oil samples attest for its origin from a different source rock.

The relatively high variability in the $\delta^{34}\text{S}$ of the short OSCs in the immature rock ($\sim 10\%$) is probably a remnant of the original $\delta^{34}\text{S}$ acquired during the sulfurization of the OM in the early diagenetic process. The $\delta^{34}\text{S}$ in sulfurized biomarkers shows a higher variability ($\sim 14\%$, Shawar et al., (2015)). Compared to the short OSCs the larger biomarkers better represent the kerogen structure, and so the use of their $\delta^{34}\text{S}$ in paleo-environmental studies has great potential. Studies done on recent sediments shows even a higher variability in the $\delta^{34}\text{S}$ ($\sim 20\%$, Raven et al., (2015)). The overall trend is a continuous homogenization of the sulfur isotope variability along the diagenetic and catagenetic processes of sediments and source rock. Understanding the processes responsible to the homogenization of the $\delta^{34}\text{S}$ can unravel the chemical and structural changes that the OM experiences through its cycle.

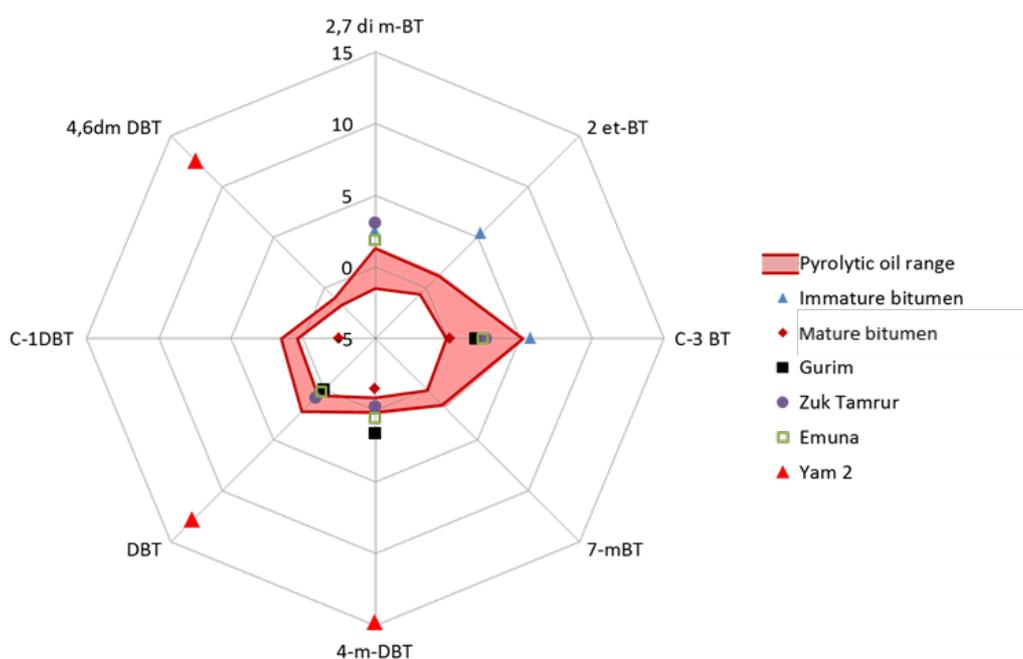


Figure 1. Spider diagram for oil-oil correlation between the pyrolytic oil and 4 natural oil samples

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