

COMBINED USE OF $\delta^{34}\text{S}$ OF DIBENZOTHIOPHENES AND $\delta^{13}\text{C}$ OF METHYL CYCLOHEXANE TO DETERMINE THERMOCHEMICAL SULFATE REDUCTION

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Thermochemical sulfate reduction (TSR) is one of the most important organic-inorganic interactions and widely occurs in hot carbonate petroleum reservoirs and in hydrothermal environments. Basically, two processes are associated with TSR under high temperature. One is the thermochemical reaction of sulfate in petroleum reservoirs to produce H_2S , followed by back-reactions of petroleum hydrocarbons with TSR-derived H_2S to produce organic sulfur compounds. Another is the C-C bond cleavage of hydrocarbons followed by preferential aromatization and weak cyclization, compared to non-TSR-involved degradation. Both reactions occur simultaneously and induce sulfur and carbon isotopic fractionations. The sulfur isotopic fractionation may occur: (1) during H_2S generation from sulfate by TSR, and (2) during the reaction of H_2S with organic compounds, finally leading to the formation of ^{34}S -enriched OSC. The carbon isotopic fractionation benefits from the preferential cleavage of ^{12}C - ^{12}C bond, resulting in ^{13}C -enriched monoaromatics in the gasoline hydrocarbons. The sulfur and carbon isotopes of individual OSC and gasoline hydrocarbons are mainly controlled by the relative rates of formation and destruction of each compounds. This is the theoretical base for sulfur and carbon isotopes as proxies to determine TSR process. Amrani et al (2012) claimed that $\Delta^{34}\text{S}_{\text{BTs-DBTs}}$ is a highly sensitive proxy to assess the TSR process due to different thermal stability of BTs and DBTs. However, no regular trend was found in respect to sulfur isotope fractionation of BTs itself during their and our pyrolysis experiments, which was considered to be induced by the rapid formation and degradation of BTs upon thermal maturation (Amrani et al., 2012; Xiao et al., 2018). This uncertainty probably accounted for some contradictory results presented in their publications (Amrani et al., 2012; Cai et al., 2016). Therefore, the reliable determination of the occurrence and extent of TSR is still ambiguous and requires a comprehensive diagnostic.

In this study, sulfur isotopes of individual OSC in marine oils from the Tarim basin, NW China are determined. Integrated with carbon isotopes of individual gasoline hydrocarbons, a new method is developed to identify TSR. Based on previous studies and field observation (H_2S concentration), the studied oils were derived from Cambrian source rocks and can be divided into three groups: (1) non-TSR involved oils but some of them experienced in-reservoir cracking; (2) slight-TSR altered oils; and (3) severe-TSR altered oils. Although carbon isotopic composition of monoaromatics is more sensitive in respect to preferential aromatization during TSR, $\delta^{13}\text{C}$ of methylcyclohexane (MCH) is measured here due to relatively low concentration of monoaromatics in most non-TSR altered marine oils. Less carbon isotopic fractionation of MCH could be expected because of weak cyclization during TSR process. Therefore, combined use of $\delta^{13}\text{C}_{\text{MCH}}$, and $\delta^{34}\text{S}_{\text{DBT}}$ in crude oils could provide a new way to determine TSR.

Our data and previously published data (Cai et al., 2016) demonstrate that $\delta^{34}\text{S}$ values of DBTs in normal marine oils from the Tarim basin mainly range from 15‰ to 20‰. With increasing thermal stress, $\delta^{13}\text{C}_{\text{MCH}}$ and $\delta^{34}\text{S}_{\text{DBT}}$ values strongly depend on processes involved

and the intensity of alteration experienced (Fig.1a). Although non-TSR-induced oil cracking results in ^{13}C -enriched MCH, no significant ^{34}S enrichment or depletion in DBT occurs, probably suggesting less sulfur isotopic fractionation of DBTs under the temperatures of 100°C to 140°C for the occurrence of TSR. Our further thermal simulation experiments without TSR confirm this speculation. TSR-induced oil destruction is characterized by ^{34}S -enriched DBT, and the sulfur isotope fractionation by TSR is very sensitive and can be detected even in the early stage (slight TSR alteration with little H_2S in reservoir). Although the whole oil gas chromatogram from the severe TSR-altered reservoir shows a remarkable enrichment of aromatic hydrocarbons (Fig.1b), $\delta^{13}\text{C}_{\text{MCH}}$ value is just close to that in the non-TSR, moderate thermal cracking oils (SN1, TZ83, and LS2 in Fig.1a). This is in agreement with preferential aromatization and weak cyclization during TSR process. Thereafter, the magnitude and direction of hydrocarbon destruction in petroleum reservoir with increase temperature in deep earth can be defined in respect to TSR-induced oil cracking and non-TSR-induced oil cracking, and further four stages in respect to TSR alteration can be divided by confirmed TSR-involved reservoirs in the field. This approach should be a powerful tool for identification and assessment of thermochemical sulfate reduction in petroleum exploration in deep buried basins, as well as for understanding the basic reaction mechanisms and kinetics controlling TSR process.

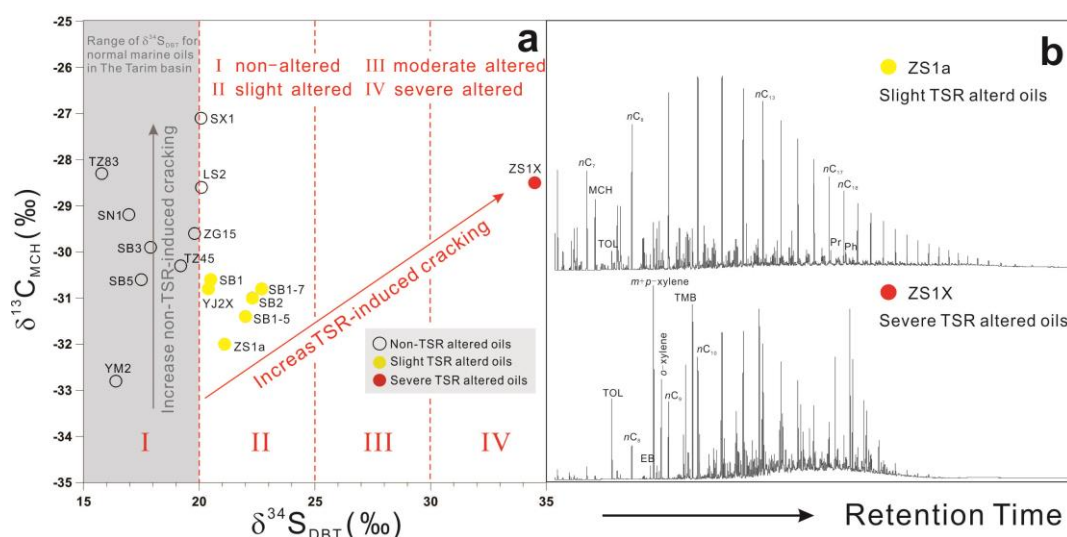


Figure 1 $\delta^{13}\text{C}_{\text{MCH}}$ v.s. $\delta^{34}\text{S}_{\text{DBT}}$ in crude oils showing different trends for non-TSR-involved and TSR-induced oil cracking with increasing temperature (a), and whole oil gas chromatograms from different extent of TSR-altered reservoirs(b).

References

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