

REACTANT SELECTIVITY OF BIOMARKERS IN THERMOCHEMICAL SULPHATE REDUCTION

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Introduction

Thermochemical sulphate reduction (TSR) is the reduction of sulphate by organic compounds in an oil or gas reservoir at elevated temperature, with an onset temperature of above 120 °C normally. Reactant selectivity during TSR reflects the stability of different compounds and indicates chemical mechanisms of TSR reactions.

Reactant selectivity has been reported for some simple compounds during TSR. Generally, labile sulphur compounds are much more reactive than hydrocarbons and may act as initiators in the autocatalytic TSR reactions (Amrani et al., 2008); gaseous hydrocarbons is far less reactive than liquid hydrocarbons. In gaseous hydrocarbons, the reactivity decreases in the order of isobutane > n-butane > propane > ethane >> methane (Xia et al., 2014).

Typical biomarkers are relatively less stable than alkanes during TSR; they are quite likely depleted if the oxidation of normal alkanes becomes noticeable. Therefore, the reactant selectivity of biomarkers during TSR has hardly been investigated. In this work, we will present reactant selectivity of some terpane biomarkers during an early stage of TSR.

Results and Discussion

Oil samples from a Devonian formation in the Zama sub-basin, Canada, and from a Jurassic formation in the Gulf Coast Basin, USA, were analysed. The oils have API gravity of 40 to 48. Sulphur content is around 1wt% from both places. H₂S content is over 1 vol% in separated gas phase.

The oils have unique biomarker distribution (Figure 1). Well preserved polycyclic terpanes are dominantly C₂₄ tetracyclic terpane, Ts and C₂₉Ts. C₁₉ and C₂₀ components are dominant in tricyclic terpanes; Ts/(Ts+Tm) ratio is close to 1. Hopanes are basically non-existent. Similar terpane distribution appeared in oil samples from the Rainbow Basin (Fowler et al., 2001) and from the Tarim Basin (ZG44C, with API = 48) (Huang et al., 2015).

The variation of terpane distribution is usually contributed to difference of oil sources. The increase of Ts/(Ts+Tm) and the depletion of hopanes depend mainly on thermal maturity. But the pattern in the above samples are different from oils of different sources and of different thermal maturities. The existence of H₂S infers TSR occurred in the region, and terpane distribution may result from selective oxidation of organic compounds at an early stage of TSR.

Molecular structures indicate that tertiary carbon atoms on the side carbon chains of terpane compounds are preferably attacked by sulphate, therefore, most C₂₁₊ terpane molecules are converted. Because a C₁₉, C₂₀ tricyclic terpane or a C₂₄ tetracyclic terpane molecule does not contain a tertiary carbon atom on the side C-C chain, these terpanes are more resistant to

sulphate oxidation. Hopanes are unstable due to the tertiary carbon atom at the 22 position on the side C-C chain. This is consistent to the reactant selectivity during TSR by gaseous hydrocarbon: isobutane is much more reactive than n-butane (Xia et al., 2014).

For the C-C rings in a hopanes molecule, the tertiary carbon atom at the 17(α) position on the five-member ring (ring “E”) is vulnerable to react with a sulphate ion. But this position becomes a stable quaternary carbon for Ts and C₂₉Ts. The tertiary carbon atom at the 18(α) position in a Ts or a C₂₉Ts molecule is hindered by the six-member ring “C”. Therefore, Ts and C₂₉Ts is much more resistant to TSR than Tm.

Conclusion

The unique biomarker distribution in some oil samples indicates the reactant selectivity of terpanes during the very early stage of thermochemical sulphate reduction. Molecules with tertiary carbon atoms on alkyl groups and on five-member rings in the absence of steric hindrance are the most vulnerable to TSR.

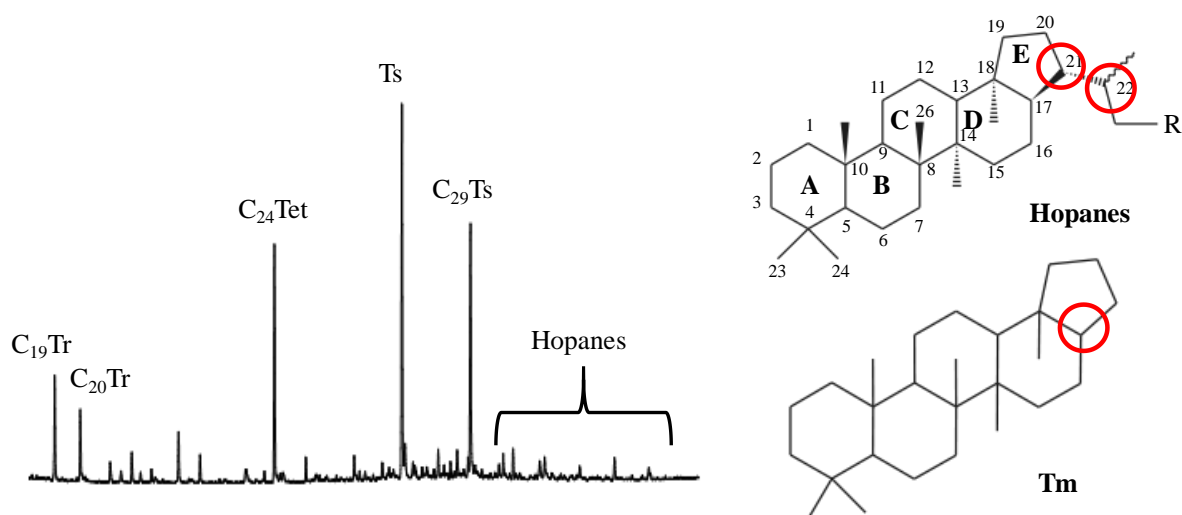


Figure 1 Terpane distribution of an oil sample from the Zama sub-basin, Canada. Circles on the molecular structure scheme mark the tertiary carbon atoms vulnerable to TSR.

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