

## Study of the first stage of TSR in controlled laboratory experiments and ab initio calculations

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The term “Thermo chemical Sulfate reduction” (TSR) refers to the non-biogenic reduction of sulfate to H<sub>2</sub>S coupled to the oxidation of hydrocarbons in hot petroleum reservoirs (>120 °C). In this work, the sulfur isotopic fractionation associated with the formation of organic sulfur compounds (OSCs) during thermochemical sulfate reduction (TSR) was studied using gold-tube pyrolysis experiments to simulate TSR (Meshoulam et al. 2016). The observed S-isotopic fractionations between sulfate and BT, DBT, and H<sub>2</sub>S in experimental simulations of TSR correlate well with a multi-stage model of the overall TSR process (Zhang et al. 2012). Large kinetic isotope fractionations occur during the first, uncatalyzed stage of TSR, 12.4‰ for H<sub>2</sub>S and as much as 22.2‰ for Benzothiophene (BT). The fractionations decrease as the H<sub>2</sub>S concentration increases and the reaction enters the second, catalyzed stage. Once all of the oxidizable hydrocarbons have been consumed, sulfate reduction ceases and equilibrium partitioning then dictates the fractionation between H<sub>2</sub>S and sulfate (~17‰).

In order to study the initial stage of TSR, we conducted similar reactions using sulfite as the sulfur source (Meshoulam et al. 2016). The fractionation between the sulfite and OSC reached ~10‰ indicating that the product of the initial stage of sulfate can be sulfite. The initial stage of TSR was addressed previously by several authors. One of the proposed mechanisms is the formation of sulfate esters via the reaction of the sulfate with thiols which were shown to increase the reaction rate (Amrani et al. 2008). Other proposed mechanism is the concentric reduction of sulfate by alkanes to sulfite (Ma et al. 2008). However, none of the mechanisms describe above was tested under controlled laboratory experiments. A recent work published by Pirzadeh et al. (2015) showed that the sodium dodecyl sulfate (SDS) can undergo TSR at temperature of 150<sup>0</sup> - 200<sup>0</sup>C and at a time of a few days. Because TSR probably occurs at the interface between the water and the organic matter sulfate ester may play a significant role in the initial stages of TSR (Amrani et al. 2008).

In order to test the possibility of sulfate ester as the initial sulfate specie being reduced, we will present data about the S isotopic fractionation related to the reduction of sulfate esters under controlled laboratory conditions. We compare the experimental data with ab initio calculations of sulfate ester formation and reduction in conditions similar to those prevail in the laboratory experiments and natural reservoirs. This data is correlated to the data of Meshoulam et al. (2016) in order to estimate the contribution of this sulfate reduction pathway to the net S fractionation between the initial S source to the organic and inorganic reduced S species during the initial TSR stage. The possibility of sulfate ester formations under laboratory conditions similar to the natural reservoirs due to the presence of thiols will be discussed as well.

## References

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