

## **Influence of sulfate on S.A.R.A. fraction of soluble organic product from thermal degradation of kerogen**

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Sulfates can increase, and result in earlier peaking of, hydrocarbon generation from kerogen. There has been speculation that sulfates might act as catalysts to facilitate the thermal degradation of kerogen, but no definitive experimental evidence has so far been obtained. In this study, we investigated the influence of sulfates on the thermal decomposition of kerogen by conducting two groups of simulation experiments in gold tubes, one with kerogen only and the other consisting of well-mixed kerogen and sulfates.

Consistent with previous studies, our data demonstrated that the sulfate-bearing kerogen samples generated more hydrocarbons with lower peak production temperatures compared to their sulfate-free counterparts. However, the hydrocarbon yields of the sulfate-bearing samples declined sharply at  $T > 350$  °C, suggesting that the products were consumed by thermochemical sulfate reduction (TSR) reaction. Quantitative analysis of different S.A.R.A. fractions implied that the presence of sulfates improved the yields of resins and asphaltenes at the early stage of petroleum generation. Based on the mechanism of TSR, we hypothesized that a redox reaction between sulfate and  $-H_2C-CH_2-$  moieties significantly facilitated the breakdown of various molecular components in kerogen, leading to the formation of resins and asphaltenes.

The novel chemical process that we discovered in our current study reveals a new reaction paradigm between aqueous sulfate and organic macromolecules, which have three geochemical implications: 1) the redox activity of sulfates plays a more significant role than temperature elevation in promoting the thermal decomposition of kerogen during the early stage of oil window. 2) the increase in resin and asphaltene contents conduces to petroleum expulsion. 3) sulfate-stimulated destruction of geological organic polymers, such as kerogen and asphaltenes, might influence the geochemical behaviors of underground organophilic trace elements.