

Molecular and stable isotopic evidence for the mechanism of thermochemical sulphate reduction

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Thermochemical sulfate reduction (TSR) is the abiotic reduction of sulfate to hydrogen sulfide coupled with the oxidation of organic compounds to carbon dioxide, and is one of the most important organic-inorganic interactions that occur in high-temperature carbonate environments. TSR is of great concern to the petroleum industry because of its potential to significantly reduce amounts of recoverable resource and increase costs of production due to sour gas. It is also thought to play a role in the formation of Mississippi Valley Type massive sulfide ore deposits. TSR requires the stepwise reduction of S^{6+} to S^{2-} , and is thought to involve a complex series of chemical reactions. However, the details of these reaction mechanisms are not well understood. These uncertainties make it extremely difficult to predict the potential for TSR occurrence in natural environments.

In the past decade, a number of theoretical and experimental studies have provided important insights into the reaction mechanisms of TSR. Quantum chemistry molecular modeling has shown that S-O bonds in free sulphate ions (SO_4^{2-}) require more energy to break than S-O bonds in bisulfate (HSO_4^-) or magnesium sulphate contact-ion-pairs ($MgSO_{4aq}$) [1]. Gold-tube pyrolysis experiments have shown that TSR involves an initial uncatalyzed reaction phase and a later catalyzed phase [2]. Recent compound-specific sulfur isotopic analysis of organosulfur compounds generated during TSR experiments have confirmed this two-stage reaction mechanism. Furthermore, a theoretical model based on field observations of the stable carbon isotopic composition of hydrocarbon gases from TSR fields has shown the importance of partially oxidized hydrocarbons in controlling the rate of TSR [3]. This work has suggested that there may be a third, late stage of TSR that is hydrocarbon limited and slower than the catalyzed phase.

The collective results from these studies provide a more in depth understanding of the reaction mechanisms of TSR and allow for better predictive models. This highlights the utility of molecular and stable isotopic techniques for probing the details of complex geochemical problems such as TSR.

[1] Ma et al. (2008), *Geochimica et Cosmochimica Acta* **72**, 4565-4576. [2] Zhang, T. et al. (2012), *Geochimica et Cosmochimica Acta* **96**, 1-17. [3] Xia, X., et al. (2014), *Geochimica et Cosmochimica Acta* **139**, 472-486.