

Carbon and hydrogen isotopes fractionation of TSR-altered gas products of thermal simulation experiment

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Thermochemical sulfate reduction (TSR) in marine carbonate gas reservoirs can produce different carbon and hydrogen isotopic compositions from those of conventional gas reservoirs. This study aims to better understand how TSR can affect geochemical and isotopic compositions of gas reservoirs. Laboratory simulation of TSR was conducted with crude oil in the presence of MgSO₄ at temperatures of 350°C, 360°C, and 370°C for different durations of 4~219 h in a closed system. Results show that isotope compositions of alkane gas resulted from the TSR became heavier with increasing carbon number, i.e., $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$ and $\delta^2\text{H-C}_1 < \delta^2\text{H-C}_2 < \delta^2\text{H-C}_3$. However, at the same temperature, $\delta^{13}\text{C}_1$ decreased at first and then became larger with increasing heating time within a certain range. Compared with the $\delta^{13}\text{C}_1$, $\delta^{13}\text{C}_2$ and $\delta^{13}\text{C}_3$ increased in a much wider range as heating continued. Specifically, the $\delta^{13}\text{C}_2$ varied in a range slightly smaller than the $\delta^{13}\text{C}_3$. The narrower variation range of $\delta^{13}\text{C}_1$ was because of rapid oxidation of hydrocarbons by TSR which produced CH₄ with similar isotope compositions to the source material. Furthermore, carbon and hydrogen isotopes of alkane from TSR became larger with increasing gas souring index (GSI), i.e., $\text{H}_2\text{S}/(\text{H}_2\text{S} + \sum \text{C}_{1-5})$, and the CH₄ had a smaller variation range than the C₂H₆. $\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2$ and $\delta^2\text{H-C}_1 - \delta^2\text{H-C}_2$ normally decreased as oil underwent thermal cracking. However, they may show an increasing trend because TSR can reduce the variation range of isotopes of CH₄. The isotope compositions of C₂H₆ were more heavily affected by thermal cracking before oxidization by TSR, which resulted in their short variation range. The rapid oxidation of hydrocarbons by TSR resulted in the series of $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$, which is similar to the isotopic composition of source materials. ¹³C was gradually enriched in the residual heavy alkanes during the TSR process, which increased the $\delta^{13}\text{C}_2$ value and changed the partially reversed isotope sequence to positive isotope sequence.