The influence of elemental sulfur and sulfur bearing minerals on the evolution of biomarkers

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Introduction

Sulfur is widely occurred in sedimentary rock in both organic and inorganic forms (elemental sulfur and sulfur-bearing minerals), especially in marine sediments. Though sulfur and sulfur-bearing minerals are not the main constituents of sedimentary rock, they are very important for the generation and evolution of hydrocarbons (Song et al., 1998; 2005). The aim of this study is investigating the influence of sulfur and three sulfur-bearing minerals (ferrous bisulfide, ferrous sulfate, and ferric sulfate) on the evolution of biomarkers. In order to only discuss the influence of sulfur and three sulfur-bearing minerals on the evolution of biomarkers, the bitumen extracted from the Dalong Formation source rock was chosen for pyrolysis experiments. Different simulation temperature and different sulfur content were also conducted in the pyrolysis experiments.

Results

The absolute concentrations for individual saturate biomarkers were calculated and plotted to investigate the changes in biomarker concentrations under different pyrolysis conditions. At 300^{o}C, the absolute concentrations of individual terpanes (Fig 1) in the pyrolysates of all six experiments are very similar. However, the absolute concentrations of individual hopanes have significant differences among the pyrolysis products (pyrolysates) of different kinds of additives used. Meanwhile, the absolute concentrations of individual steranes also vary with different additives. This phenomenon is consistent with the terpanes having high resistance to both biodegradation and thermal alteration compared to other kinds of saturate biomarkers (Seifert and Moldowan, 1979; Peters et al., 2005). For hopanes, their absolute concentrations of individuals in the bitumen pyrolysates with FeS_2 are similar to those in pyrolysate of neat bitumen, while those in the pyrolysates of bitumen with $FeSO_4$ and $Fe_2(SO_4)_3$ are lower than pyrolysate of neat bitumen. It is probably because the thermochemical sulfate reduction (TSR) occur when $Fe_2(SO_4)_3$ and $FeSO_4$ were present in pyrolysis system. Meanwhile, the influence of $Fe_2(SO_4)_3$ on biomarkers is higher than $FeSO_4$. It can be explained by high oxidation ability of ferric iron compared to ferrous iron. The absolute concentrations of individual hopanes in the bitumen pyrolysate with S and the combination of S plus Fe are the lowest in all six experiments. When temperature is up to 330 ^{o}C, the influences of different kinds of additives on the absolute concentrations of saturate biomarkers are also similar to those at 300 ^{o}C. The only difference is the extent of influence of S on saturate biomarkers at 330 ^{o}C is higher than that at 300 ^{o}C.

The values of source-related biomarker parameters for pyrolysates with different additives are also compared. When temperature is lower than 330^{o}C, the presences of sulfur-bearing minerals do not significantly change the source related biomarker parameters. When S or the combination of S plus Fe existed, most of the source-related biomarker parameters based on hopanes are still stable. However, the parameters based on steranes including the distribution of C_{27-29} ααα20R steranes and S21/S22 ratio are changed. Meanwhile, TT23/H30 ratio also varies with the kinds of additives used, especially for the use of S and S plus Fe together. Our recent work also suggest that the source-related biomarker parameters based on hopanes are more stable than those based on steranes in both free and bound fraction, due to the different

chemical structure and mode of incorporation of their precursors into kerogen (Wu and Geng, 2016).

Conclusions

Different forms of sulfur in the chemical states have different influences on the evolution of biomarkers in geologic sample. Based on this study, it indicated that the influence of FeS_2 on both the concentration and the distribution of biomarkers is very limited. $FeSO_4$ and $Fe_2(SO_4)_3$ will slightly change the concentration and the distribution of biomarkers, due to the thermochemical sulfate reduction (TSR). Moreover, the influence of $Fe_2(SO_4)_3$ on biomarkers is higher than that of $FeSO_4$, because of high oxidation ability of ferric iron compared to ferrous iron. While the influence of elemental sulfur on both the concentration and the distribution of biomarkers is very significant.

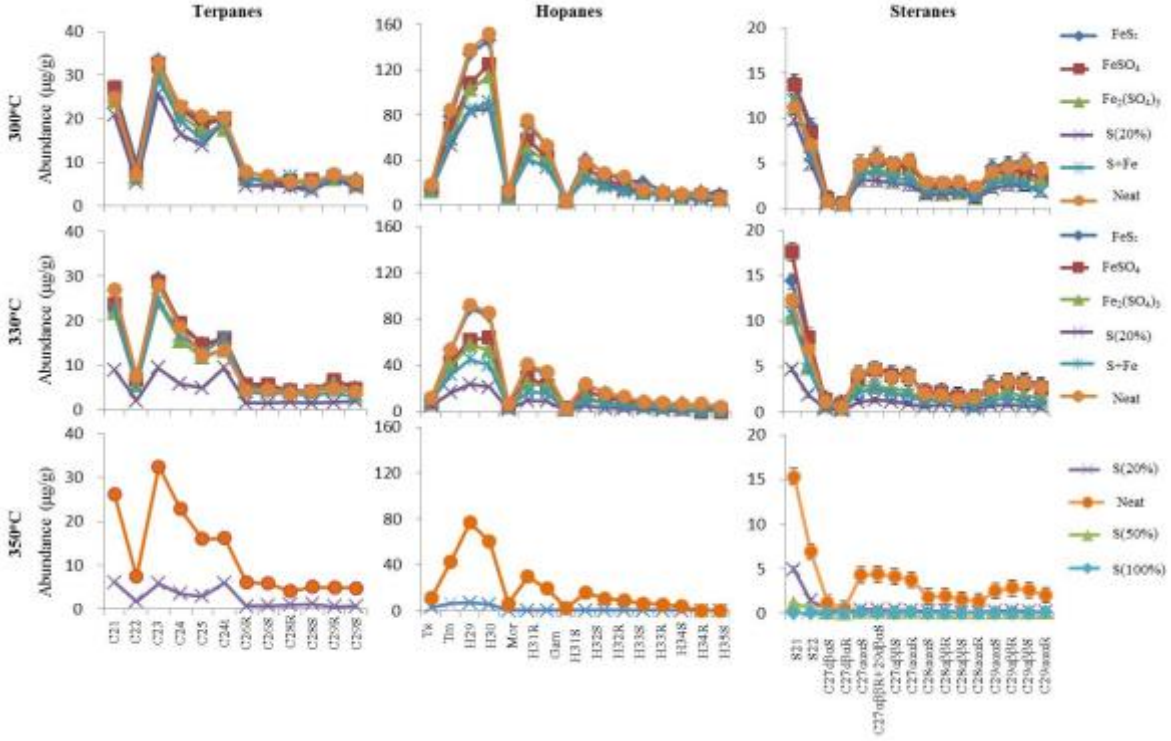

Figure 1 *The variations of absolute abundances of saturate biomarkers in pyrolysate of bitumen with different additives at various temperatures.*

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