



Compound-specific carbon isotope analysis of instantaneous gas generated from shaly coal during hydrous pyrolysis

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Isotopes of natural gases have provided important information for indicating their maturation, origins and influencing factors during the generation processes. In order to distinguish compositions of gas generated at different intervals of maturities, the present study investigates the variation of compound-specific carbon isotope (CSI) ratios of hydrocarbon gases from a shaly coal by instantaneous hydrous pyrolysis, during which the earlier generated gas was evacuated before the start of next maturation stage. The experiments were conducted at ten different maturity stages (0.65 to 2.02 % Ro) from a terrestrial shaly coal with 0.48 % Ro. The gas products were analyzed by GC-IR-MS.

The results show that, in general, the $\delta^{13}\text{C}$ values of methane (C_1), ethane (C_2), propane (C_3) slightly increase, then decrease and finally increase with increasing maturities. This reverse phenomenon indicates the heterogeneous and complex compositions of the kerogen. The isotope compositions of gases exhibit three distinct clusters in natural gas plot of $\delta^{13}\text{C}$ values versus $1/n$ (where n is carbon number of the gaseous molecule), corresponding to three different groups of maturity stages. By linking the same maturity stage of $\delta^{13}\text{C}$ values, all lines show nearly parallel in each group with consistently reverse trend of $\delta^{13}\text{C}_3 < \delta^{13}\text{C}_2 > \delta^{13}\text{C}_1$. These three distinct clusters were also observed in the cross plotting of $i\text{C}_4/n\text{C}_4$ versus $i\text{C}_5/n\text{C}_5$ isomer ratios. This may imply that the kerogen is composed of three discrete structural domains which were progressively cracked at three major groups of maturity stages. The reverse trend was inconsistent with data for gas collected cumulatively in most prior pyrolysis experiments and the linear relationship predicted from kinetic isotope effect (KIE) model. Although the non-linear relationship or reverse trend, $\delta^{13}\text{C}_3 < \delta^{13}\text{C}_2$, was also reported for some natural gases, it was interpreted as a result of mixing from different source rocks or other processes. Our results, however, suggest that this non-linear relationship or reverse phenomenon can also be attributed to the mixing of gases generated from different maturity stages solely from a single source formation. Therefore, our results provide a new interpretation for the variation of isotope data of the cumulative and instantaneous gases in hydrous pyrolysis experiments and isotope variation in natural gas.