Hydrous pyrolysis of kerogens with FeS: insights into the carbon and hydrogen isotope fractionation of hydrocarbon gases in deep formation

KUN HE*, SHUICHANG ZHANG, JINGKUI MI

Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083, China
(*correpondence: hekun1@petrochina.com.cn)

As ubiquitous substance in sedimentary basins, water was suggested to involve in the maturation of organic matters and and provide H for the generation of petroleum. In this study, isothermal hydrous pyrolysis of four kerogens with and without FeS were conducted by a gold-tube system to address the effects of water-mineral interactions on the generation and isotope fractionation of hydrocarbon gases.

The yields of hydrocarbon gases (C_{1-5}) in hydrous pyrolysis of kerogens with FeS are nearly 1~1.5 times higher than those in anhydrous pyrolysis and hydrous pyrolysis without FeS. These results implied that the indirect hydrogenation by mediate H_2 should be more important for the generation of C_{1-5} than the direct reactions between water and organic matters. In addition, the yields of C_{2-5} are much higher in hydrous pyrolysis with FeS. Surprisingly, the H_2S and CO_2 yields evidently decreased with the presence of FeS. This may be attributed to the reactions between H_2S/CO_2 and FeS, which can form pyrite (FeS_2) and siderite ($FeCO_3$). As another possibility, CO_2 may be reduced by H2 to generated hydrocarbon gases.

The carbon ($\delta^{13}C$) and hydrogen (δD) isotopic ratios of C_{1-5} during pyrolysis were apparently affected by the presence of water and FeS. The evolution of the difference of $\delta^{13}C$ between ethane and methane ($\delta^{13}C_2$-$\delta^{13}C_1$) with Easy%R_o, is apparently different in anhydrous and hydrous pyrolysis with and without FeS. For hydrous pyrolysis with FeS, there is a negative correlation between $\delta^{13}C_2$-$\delta^{13}C_1$ and Easy%R_o, which is essentially consistent with that for natural gases in the subsurface. Moreover, a reversal of $\delta^{13}C$ for methane and ethane (i.e. $\delta^{13}C_1 > \delta^{13}C_2$) was observed for hydrocarbon gases generated in hydrous pyrolysis of pure graphite or methyl-aromatics with FeS. Meanwhile, the presence of water apparently resulted in depletion of D for C_{1-5}. In hydrous pyrolysis with FeS, δD values of C_{1-5} are much lower. Hence, the hydrogenation by water or H_2 may be responsible for the rollover of δD_1 for shale gas as well as carbonate reservoir gas at extremely high maturity.