

Hydrous pyrolysis of organic matters with the presence of FeS: insights into the carbon and hydrogen isotopic fractionation of hydrocarbon gases in deep formation

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Introduction

As ubiquitous substance in sedimentary basins, water was suggested to involve in the maturation of organic matters and the generation of petroleum (Seewald, 2003). Hydrous pyrolysis experiments demonstrated that water can provide hydrogen for hydrocarbon generation (Lewan, 1997). On this consideration, Seewald (2003) implied a greater gas generation potential in sedimentary basins. Meanwhile, some researchers have implied that the potential interaction between water and organic matters may be responsible for the rollover of carbon and hydrogen isotope in shale gas at high maturity. Generally, the hydrogenation of water can be summarized as two pathways according to previous literature. One is the direct reaction between water and organic compounds either by radical or carbocation mechanisms. The other one is the indirect hydrogenation by H_2 generated by redox reaction between H_2O and reducing minerals. Though reducing Fe-bearing sulfide (i.e. FeS or FeS_2) are usually recognized as important minerals in source rocks, their effects on the maturation of organic matters and the generation of hydrocarbon gases remains uncertain.

In this study, isothermal hydrous pyrolysis of four kerogens with and without the presence of FeS were conducted by a gold-tube system to address the effects of water-mineral interactions on the generation and isotopic fractionation of hydrocarbon gases. The original virinite reflectance (R_o) of four kerogens are 0.70, 1.16, 1.65 and 3.5% respectively. The pyrolysis temperatures are between 330 and 420 °C with pyrolysis time from 120 to 264 hours, the pressures are all set as 50 MPa. At such experimental conditions, the equivalent vitrinite reflectance ($EasyR_o$) is in the range of 1.05~2.5%. Anhydrous pyrolysis of kerogens and hydrous pyrolysis with only FeS were also carried out as control experiments.

Results

For kerogen with low maturity and little sulfur (S) content, the presence of water resulted in the increase of yields of hydrocarbon gases (C_{1-5}) and carbon dioxide (CO_2). However, the presence of water did not promote the hydrocarbon generation potential for type-IIIS kerogens. The evident increase of the H_2S yields in hydrous pyrolysis indicated that the reactions between water and S-bearing groups in kerogens occurred at elevated temperatures. Theoretical calculations demonstrated that the reactions between water and organic sulfo compounds are more thermodynamic favourable than those between water and saturated hydrocarbons. The direct hydrogenation in hydrous pyrolysis may proceed by reactions between water and alkenes or unsaturated groups in kerogens, which have the lowest activation energies (35~40 kcal/mol). Meanwhile, considerable amount of hydrogen (H_2) were generated in hydrous pyrolysis with the presence FeS. The yields of 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 heavy hydrocarbon gases (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 $\text{H}_2\text{S}/\text{CO}_2$ and FeS, which can form pyrite (FeS_2) and siderite (FeCO_3). As another possibility, CO_2 may be reduced by H_2 to generated hydrocarbon gases.

The carbon ($\delta^{13}\text{C}$) and hydrogen (δD) isotopic ratios of C_{1-5} during pyrolysis were apparently affected by the presence of water and FeS. Relatively, the ^{13}C of C_{1-5} (especially for ethane) were somehow depleted in hydrous pyrolysis. The evolution of the difference of $\delta^{13}\text{C}$ between ethane and methane ($\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1$) with EasyR_o , is apparently different in anhydrous and hydrous pyrolysis with and without FeS (Fig. 1). For hydrocarbon gases generated in hydrous pyrolysis with FeS, there is a negative correlation between $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1$ and EasyR_o , which is essentially consistent with that for natural gases in the subsurface. Moreover, a reversal of $\delta^{13}\text{C}$ for methane and ethane (i.e. $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$) was observed for hydrocarbon gases generated in hydrous pyrolysis of pure graphite with FeS. It is noticed that ^{13}C of CO_2 in hydrous pyrolysis with FeS are more enriched than those in anhydrous and hydrous pyrolysis. 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. The hydrogenation of water may be responsible for the rollover of δD_1 for shale gas as well as carbonate reservoir gas at extremely high maturity.

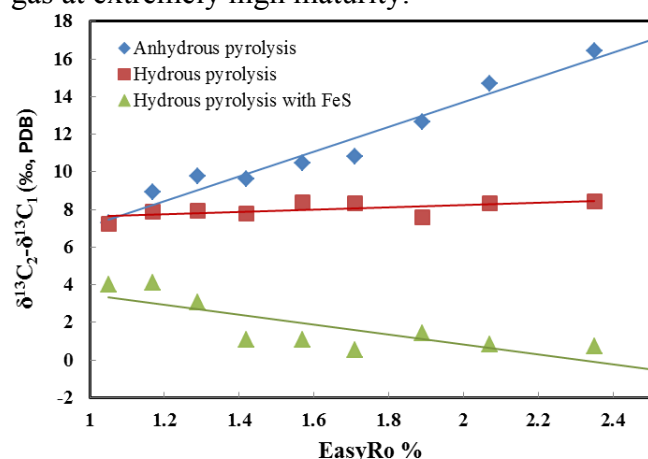


Figure 1 Plotting of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1$ versus EasyR_o during anhydrous and hydrous pyrolysis of Collingwood kerogen (R_o , 1.16%) with and without FeS.

Conclusions

The indirect hydrogenation by H_2 occurred and resulted in the increase of C_{1-5} yields in hydrous pyrolysis with FeS. In addition, the hydrogenation of water can lead to the depletion of ^{13}C and D for hydrocarbon gases. These results can be applied to interpret the carbon isotopic reversal and hydrogen isotopic rollover of natural gases. It is implied that water-minerals-organic matters interactions may enhance the hydrocarbon potential and govern the chemical and isotopic compositions of hydrocarbon gases in deep formation.

References

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