Comparative Study of Hydrogen and Carbon Isotopic Composition of Gases Generated from the Pyrolysis of a Peat under Saltwater and Freshwater Conditions

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Abstract: To understand the influence of the diagenetic water medium on the isotopic compositions of thermogenic coalbed gas, both hydrous and anhydrous closed-system pyrolyses were performed at temperatures of 250°C to 650°C on an herbaceous marsh peat. Compared to the results of anhydrous pyrolysis, the hydrocarbon gases generated from hydrous pyrolyses have very different hydrogen isotopic compositions. However, the carbon isotopic compositions of the hydrocarbon gases became only slightly heavier in hydrous pyrolysis, compared to that from anhydrous pyrolysis. With the progress of thermal evolution from peat to a more advanced thermal maturity of vitrinite reflectance values (R_o) of 5.5% during the pyrolysis, the difference in the average δD value increased from 52‰ to 64‰ between the hydrous pyrolysis with saltwater and anhydrous pyrolysis and increased from 18‰ to 29‰ between the hydrous pyrolysis with freshwater and anhydrous pyrolysis, respectively. The difference in the average δ^{13}C value was only 1‰–2‰ between the hydrous and anhydrous pyrolysis. The relationships between the δD values of the generated hydrocarbon gases and R_o values as well as among δD values of the hydrocarbon gas species are established. The close relationships among these parameters suggest that the water medium had a significant effect on the hydrogen isotopic composition and a minimal effect on the carbon isotopic composition of the hydrocarbon gases. The results of these pyrolyses may provide information for the understanding of the genesis of coalbed gas from herbaceous marsh material with the participation of different diagenetic water media.

Key words: simulation experiment, gas product, hydrogen and carbon isotope, diagenetic water medium, influencing factor, Xinjiang

1 Introduction

Coalbed methane (CBM) is the product of coalification that originated from and accumulated in coal measures (Clayton, 1998; Tao Mingxin, 2005). It is a clean energy with huge resource potential. Study of CBM carbon and

hydrogen isotopes can provide insight into the understanding of the sources of CBM (Dai et al., 1986; Dai Jingxing and Qi Houfa, 1989; Rice, 1993; Tao Mingxin, 2005; Song Yan et al., 2012a, b; Rao et al., 2014; Wu et al., 2017) and can add geological information for CBM exploration and development (Kotarba, 1990; Liu et al., 1997; Clayton, 1998; Kotarba and Rice, 2001;

Qin Yong et al., 2000). The coalification process of coal-forming material is generally considered to involve diagenetic water. However, the effect of diagenetic water medium on isotopic compositions of thermogenic CBM, especially hydrogen isotopes, is unclear.

Hydrous thermal simulation is one effective tool to illustrate the influence of the diagenetic water medium on the hydrogen and carbon isotopic compositions of pyrolysis products of organic matter, such as bitumen, oil, biomarkers and gases (Hoering, 1984; Dabbagh et al., 1994; Lewan, 1997, 1998; Schimmelmann et al., 1999, 2001; Lu Shuangfang et al., 2010; Reeves et al., 2012). However, such studies on the isotope geochemistry of hydrocarbon gases are limited (Lu Shuangfang et al., 2010; Reeves et al., 2012). In previous studies, the organic materials used include kerogen, low grade coal, shale, organic compound, and the water used was seawater, oilfield water, distilled water and artificially D-depleted or D-enriched water. The simulation temperature was generally less than 600°C.

The formation of pyrolysis CBM begins with the coalification of peat. The environments of peat formation include both freshwater swamp and saltwater marsh. Therefore, either freshwater or saltwater could have participated in peat coalification. Because of the formation and accumulation of CBM are largely associated with the metamorphism of high grade coal, the pyrolyses in this study were conducted in a closed-system at temperatures ranging from 250°C to 650°C, with, in turn, the freshwater from a swamp, saltwater from a saltwater lake and no water, to simulate better peat coalification in natural environments. The hydrogen and carbon isotopic compositions and the generation of the hydrocarbon gases were studied during the simulations.

The purposes of this work are: (1) to investigate the difference in hydrogen and carbon isotopic compositions and evolution of hydrocarbon gases generated under the participation of different water media; (2) to understand the effects of different types of water on the hydrogen and carbon isotopic compositions of the pyrolysis hydrocarbon gases in the process of peat coalification; and (3) to provide information for the identification of isotopic geochemical characteristics of thermogenic CBM formed

under different diagenetic water media.

2 Samples and Experiments

The peat material used in the simulation experiment was collected from an herbaceous marsh in Halashazi, Altay (48° 06′ 59″ N; 88° 21′ 52″ E) in Xinjiang Autonomous Region, western China. The sample was collected from a depth between 1.5 and 3.0 m. The organic carbon content of the peat was 32.3% (Table 1). The peat material was dried at room temperature and ground to 60 mesh. The crushed peat sample was treated with HCl to remove carbonate minerals. The treated sample was then extracted with chloroform using a Soxhlet apparatus (Duan et al., 2016) to remove soluble organic matter.

Pyrolyses were performed in closed stainless steel vessels (Duan et al., 2011, 2012, 2016). This pyrolysis included five types of samples (Alt, W1, W3, W4 and W5; Fig. 1−7 and Table 1−3). Sample Alt underwent anhydrous pyrolysis (Table 1). Samples W1 and W3 had hydrous pyrolysis (peat to water weight ratio=1:1.5) and were heated for 72 h at temperatures ranging from 250°C to 650°C at 50°C intervals. Waters used in the W1 and W3 pyrolyses were saltwater (with a δD value of 9‰) collected from Qinghai Lake and freshwater (with a δD value of −99‰) collected from Ruoergai freshwater swamp, respectively (Table 2). Samples W4 and W5 also underwent hydrous pyrolysis and the water used was Ruoergai freshwater swamp freshwater, heated for 12 h and 144 h at 450°C, respectively. After pyrolysis, the generated gases from each temperature interval were collected and measured by displacement with saturated salt water.

The carbon isotopic compositions of gases were analyzed with Gas Chromatography-Thermal Conversion-Isotope Ratio Mass Spectrometry (GC-TC-IRMS). The GC was an Agilent 6890 and the IRMS was a Thermo Finnigan Delta plus XP (Bremen, Germany). The GC was equipped with a fused silica capillary column (CP-Carbobond, 25 m×0.53 mm i.d., 10 μm film thickness, Varian) with helium as the carrier gas. The temperature of the GC oven was programmed from 30°C to 240°C at a rate of 15 °C/min, and then held at 240°C for 15 min. The

Table 1 Parameters of peat sample in this study

Region	Sample No.	Sample	Altitude (m)	Climate	TOC (%)	δD of rainwater (‰)	Average annual rainfall (mm)	Average annual evaporation (mm)	Average annual temperature (°C)
Altay	Alt	Herbaceous peat	2560	Cold dry	32.3	−100	350–600	1816	1.8

Table 2 Parameters of the water samples

Pyrolysis sample No.	Added water source	Water type	δD (‰)	pH	Salinity (‰)	Duration at each temperature spot (hour)
W1	Qinghai Lake	Saltwater	9	8.5	14.15	72
W3	Ruoergai swamp	Freshwater	−99	5.0	-	72
W4	Ruoergai swamp	Freshwater	−99	5.0	-	12
W5	Ruoergai swamp	Freshwater	−99	5.0	-	144

thermal combustion was performed in a micro-volume ceramic tube with CuO, NiO and Pt wires at 850°C. The analytical precision of the carbon isotopic composition is about ±0.3‰. The $\delta^{13}C$ values were calculated relative to pulses of CO_2 standard and normalized to the PDB (belemnite carbonate from the Cretaceous Peedee formation, South Carolina, USA) standard (Chikaraishi et al., 2012). The hydrogen isotopic compositions of the collected gases were analyzed with a GC (Ultra trace GC, Thermo Fisher, Milan, Italy) coupled to an isotope ratio mass spectrometer (MAT 253, Thermo Fisher Scientific Corp., Bremen, Germany) via a high temperature furnace (1450°C) (GC-pyrolysis-IRMS). The GC was equipped with a fused silica capillary column (HP-Al$_2$O$_3$, 50 m × 0.53 mm; Agilent Technologies, USA) with helium as the carrier gas. The temperature of the GC oven was programmed from 40°C to 250°C at a rate of 15°C/min, and then held at 250°C for 10 min.

The H$_3^+$ factor was measured daily with reference H$_2$ gas pulses at different signal levels. The measured H$_3^+$ values were 6.9 ppm/nA with the daily standard variation less than 0.2 ppm/nA. The average reproducibility of the hydrogen isotope values was better than ±3‰. All the values are reported relative to V-SMOW. The solid residues were analyzed for vitrinite reflectance using a Leitz MVP III microscopic photometer system with a standard deviation of less than ±0.07%.

3 Results and Discussion

3.1 Yields of all gases and hydrocarbon gas
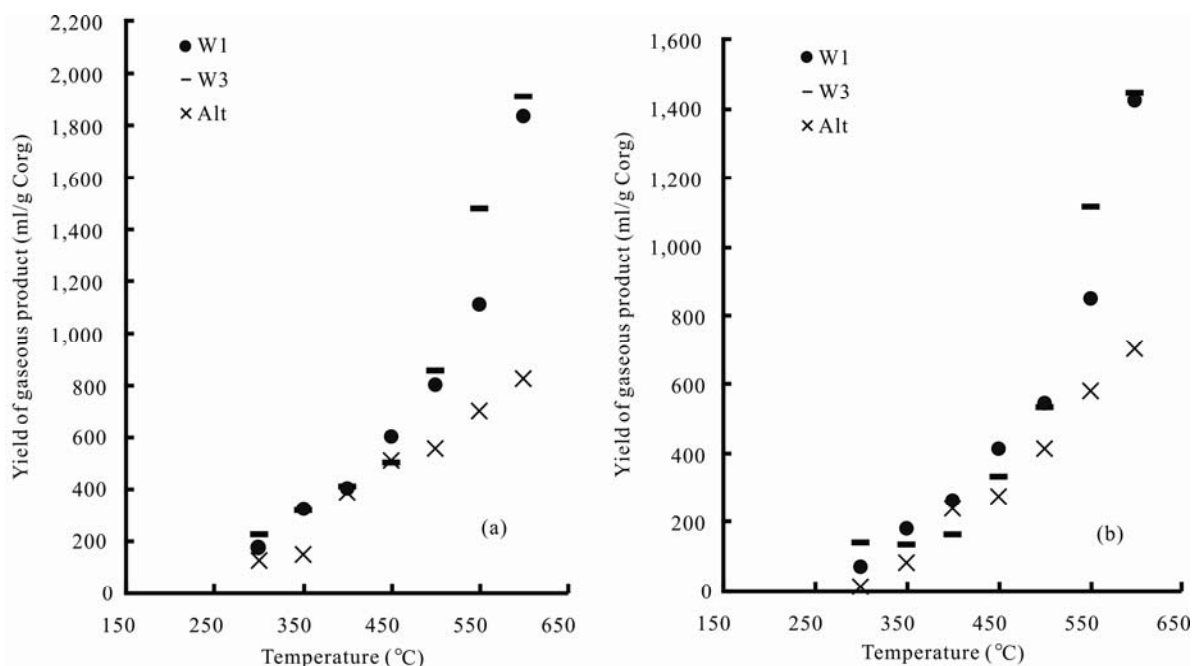
The yields of gaseous products are shown in Fig. 1.

Under the same pyrolysis conditions, the total yield of all gases and the yield of hydrocarbon gas are much higher in the presence of water than those under anhydrous pyrolysis conditions. This observation shows that water might be involved in the chemical reactions responsible for gas generation, resulting in the high gas yield (Lewan, 1997; Lewan and Roy, 2011; Sun Lina et al., 2015). It can be also observed that the total yield of gas generated during the freshwater pyrolyses was higher than that in the saltwater pyrolysis, except for the 350 and 450 temperature points. However, the yield of hydrocarbon gas was initially higher in the saltwater pyrolysis than that in freshwater pyrolyses at temperatures up to 500°C except for the 300 temperature point, and was lower in the saltwater pyrolysis than that in the freshwater pyrolyses at 500°C to 650°C. The reason for the changes in the total yield of gases and the yield of the hydrocarbon gas during saltwater and freshwater pyrolyses is unclear. With increasing pyrolysis temperature, the yields of all gases and hydrocarbon gas increased and these yields accelerated especially after 400°C.

3.2 Hydrogen isotopic composition of hydrocarbon gas generated under hydrous pyrolysis conditions

As shown in Fig. 2, the δD values of methane generated under anhydrous, saltwater and freshwater pyrolysis conditions were from −363‰ to −122‰, −346‰ to −40‰ and −319‰ to −135‰, with average δD values of −258‰, −193‰ and −275‰, respectively. The respective δD values of ethane were from −291‰ to −104‰, −238‰ to −94‰ and −293‰ to −250‰, with average δD values of −206‰, −157‰ and −277‰, respectively. The δD

Fig. 1. Total yield of gas (a) and yield of the pyrolysis hydrocarbon gas (b) as a function of pyrolysis temperature.
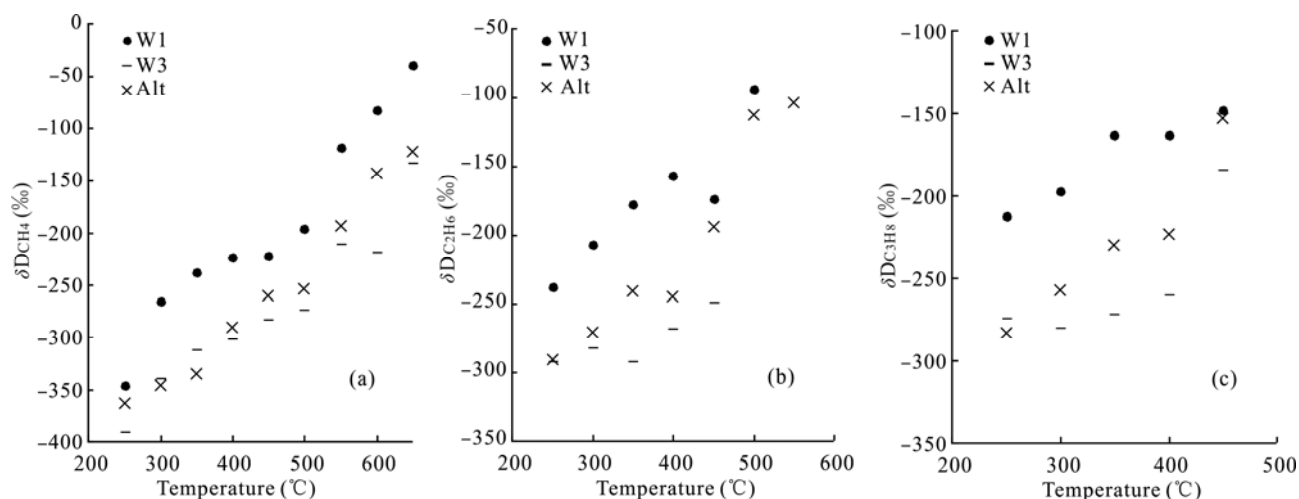
Fig. 2. δD value of methane (a), ethane (b) and propane (c) of the 2 hydrous and 1 anhydrous pyrolyses as a function of pyrolysis temperature.

values of propane were from −84‰ to −153‰, −212‰ to −149‰ and −257‰ to −184‰, with average δD values of −229‰, −177‰ and −255‰, respectively, under these same conditions. The δD values of methane, ethane and propane appeared to have a distribution of saltwater pyrolysis > the anhydrous pyrolysis > freshwater pyrolysis except for the 300 and 350 temperature points (Fig. 2a) and the 250 temperature point (Fig. 2c). This is consistent with the heavy hydrogen isotopic composition of the saltwater and light hydrogen isotopic composition of the freshwater. The δD values of methane, ethane and propane are positively correlated with the increase of pyrolysis temperature. These show that water medium and pyrolysis temperature have a significant effect on the hydrogen

isotopic composition of the pyrolysis hydrocarbon gas.

The time of thermal simulation also has a significant effect on the hydrogen isotopic composition of the hydrocarbon gas (Fig. 3a). With the increase of the experiment duration, the hydrogen isotopic compositions of methane, ethane and propane generated in the experiments with freshwater at 450°C became heavier. It is observed that the rate of change in δD value of ethane slowed with time. The difference in δD values between 12 h and 144 h pyrolyses was 79‰ for methane and 98‰ for ethane. These results show that the experiment time had a significant influence on the hydrogen isotopic composition of hydrocarbon gas in hydrous pyrolysis.

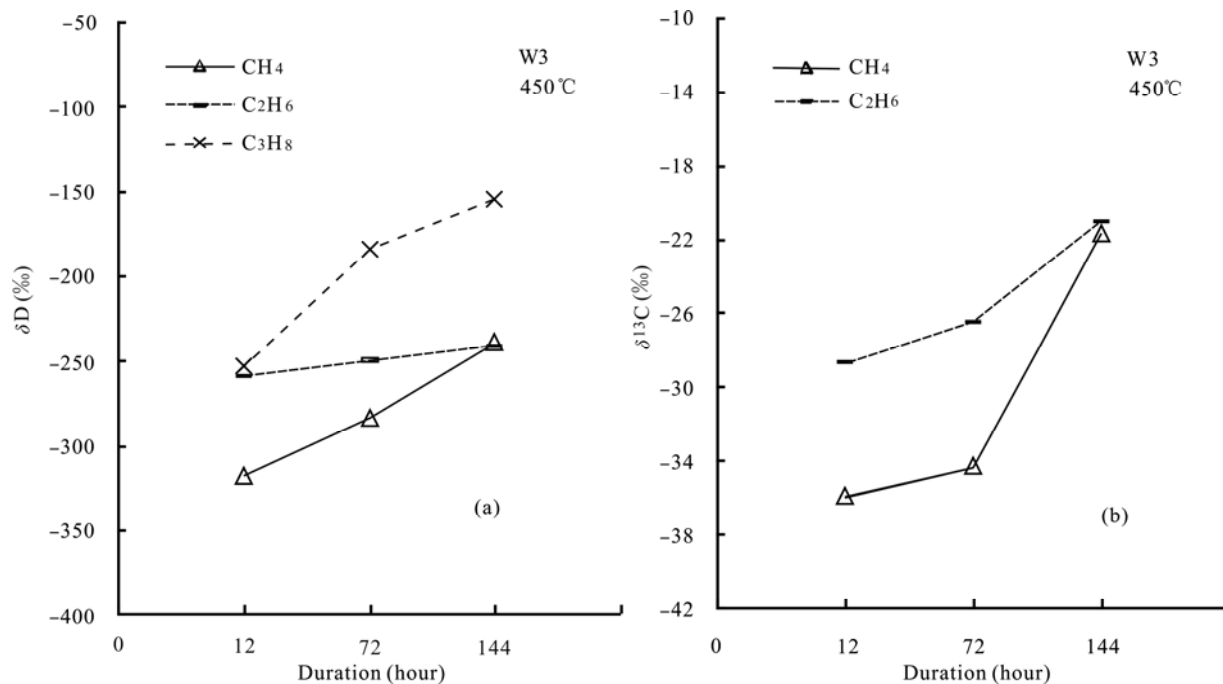In general, the rate of chemical reaction processes

Fig. 3. δD (a) and δ^{13}C (b) of the pyrolysis hydrocarbon gases as a function of pyrolysis duration.

involved in organic matter maturation is governed by a first order Arrhenius law, such that pyrolysis temperature and heating time have a complementary relationship (Waples, 1982). Therefore, the hydrocarbon gas generated from the pyrolyses performed at a certain temperature for long durations had a heavy hydrogen isotopic composition. These results show that the geological time factor should be considered in the interpretation of hydrogen isotopic compositions of CBM generated under natural conditions when diagenetic water was involved.

3.3 Carbon isotopic composition of hydrocarbon gas generated under hydrous pyrolysis conditions

The δ^{13}C values of methane generated under anhydrous and hydrous conditions with saltwater and freshwater ranged from −43.7‰ to −29.4‰, −44.8‰ to −28.1‰ and −45.8‰ to −28.9‰, with average δ^{13}C values of −36.2‰, −34.1‰ and −35.4‰, respectively (Fig. 4). The δ^{13}C values of ethane were from −36.7‰ to −24.8‰, −30.5‰ to −22.0‰ and −33.0‰ to −24.7‰, with average δ^{13}C values of −20.1‰, −18.5‰ and −19.0‰, respectively, under these three different conditions. These results show that the difference in δ^{13}C values of the generated methane and ethane was very small among anhydrous and the two different hydrous pyrolyses with a difference of only 1‰ to 2‰, on average. The order of the increase in the δ^{13}C values of methane and ethane was the added saltwater pyrolysis > the added freshwater pyrolysis > the anhydrous pyrolysis. The δ^{13}C values of the generated methane and ethane increased with increasing pyrolysis

temperature. The effect of the time of thermal simulation on the carbon isotopic composition of the generated hydrocarbon gas during the hydrous pyrolysis, however, was more apparent (Fig. 3b). As shown in Fig. 3b, with the increase of pyrolysis duration from 12 h to 144 h, the δ^{13}C values of methane and ethane increased from −25.9‰ to −21.7‰ and from −28.6‰ to −21.1‰, respectively, an increase of 4.2‰ and 7.5‰ for methane and ethane respectively.

3.4 Influence of diagenetic water media on hydrogen and carbon isotopic compositions of thermogenic CBM

The thermogenic CBM accumulated in coal measures is formed from peat in the process of coalification, which is generally thought to involve diagenetic water. However, the influence of diagenetic water on the hydrogen isotopic composition of CBM is poorly understood. The water involved in the coalification process includes acidic freshwater with a low δD value and alkaline saltwater medium with a high δD value.

The pyrolyses of this study on an herbaceous marsh peat were conducted to simulate the involvement of these two types of water medium. The results show that these water media had a significant effect on the hydrogen isotopic composition of the hydrocarbon gas. The average δD value of methane, ethane and propane produced by the simulation experiments in the marsh freshwater medium decreased by 82‰, 86‰ and 78‰, respectively, compared with that from the experiments in the saltwater medium (Table 3). Compared with the anhydrous
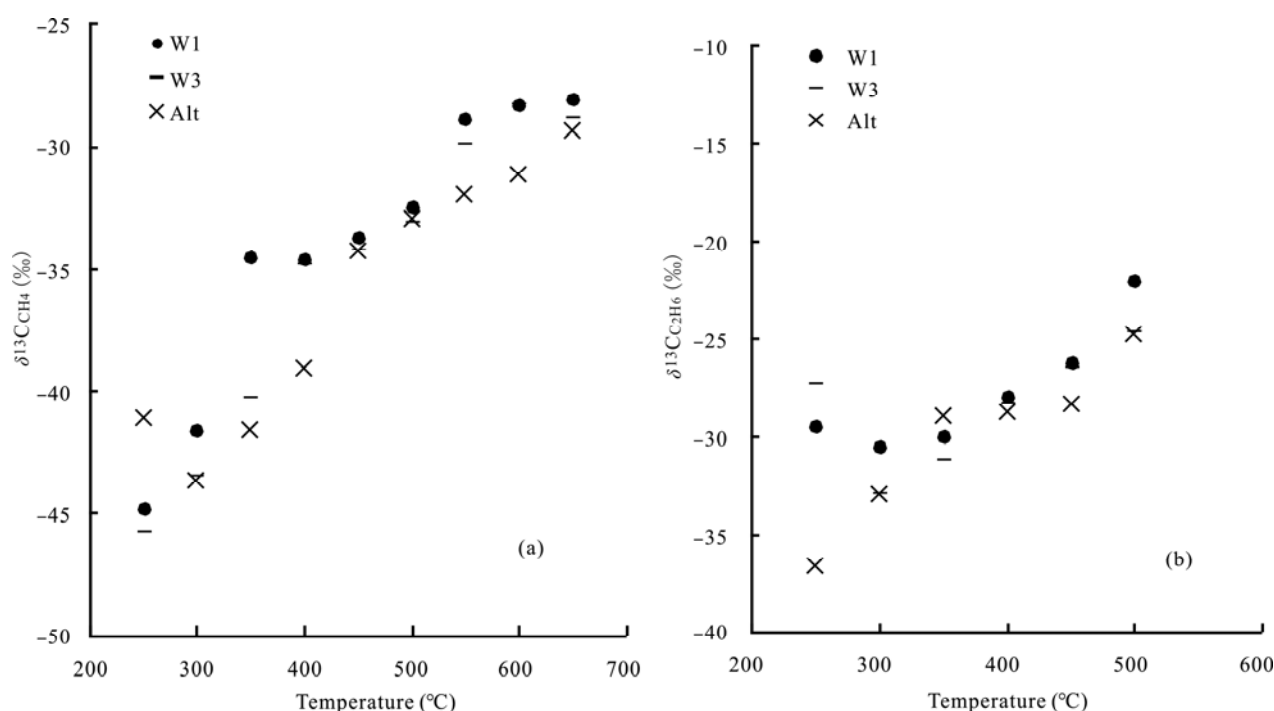

Fig. 4. δ^{13}C value of methane (a) and ethane (b) of the 2 hydrous and 1 anhydrous pyrolyses as a function of pyrolysis temperature.

Table 3 Average δD value of methane, ethane and propane generated during the 2 hydrous and 1 anhydrous pyrolyses at different evolution stages

Pyrolysis temperature (^{o}C)	R_o (%)	δD_{CH4} (‰)	δD_{CH4} (‰)	δD_{CH4} (‰)	$\triangle_{CH4}$ (‰)	$\triangle_{CH4}$ (‰)	$\triangle_{CH4}$ (‰)
		W1	W3	Alt	W3-W1	W1-Alt	W3-Alt
250	0.7	−346	−391	−363	−45	17	−29
300−400	1.2−2.5	−243	−325	−324	−82	82	−1
300−500	1.2−3.5	−229	−303	−297	−73	68	−5
300−650	1.2−5.5	−174	−260	−243	−86	70	−17
250−650	0.7−5.5	−193	−275	−257	−82	64	−18
Pyrolysis temperature (^{o}C)	R_o (%)	δD_{C2H6} (‰)	δD_{C2H6} (‰)	δD_{C2H6} (‰)	$\triangle_{C2H6}$ (‰)	$\triangle_{C2H6}$ (‰)	$\triangle_{C2H6}$ (‰)
		W1	W3	Alt	W3-W1	W1-Alt	W3-Alt
250	0.7	−238	−293	−291	−55	53	−2
300−400	1.2−2.5	−181	−281	−252	−101	71	−29
300−450	1.2−3.1	−179	−273	−238	−94	58	−36
250−450	0.7−3.1	−191	−277	−248	−86	57	−29
Pyrolysis temperature (^{o}C)	R_o (%)	δD_{C3H8} (‰)	δD_{C3H8} (‰)	δD_{C3H8} (‰)	$\triangle_{C3H8}$ (‰)	$\triangle_{C3H84}$ (‰)	$\triangle_{C3H8}$ (‰)
		W1	W3	Alt	W3-W1	W1-Alt	W3-Alt
250	0.7	−212	−275	−284	−63	72	9
300−400	1.2−2.5	−175	−271	−237	−97	62	−35
300−450	1.2−3.1	−168	−250	−216	−82	48	−34
250−450	0.7−3.1	−177	−255	−229	−78	52	−26

pyrolyses, the average δD values of the generated methane, ethane and propane increased by 64‰, 57‰ and 52‰ in the saltwater pyrolyses (Table 3). These changes in δD vales are consistent with the fact that the saltwater has a high δD value (9‰) and the freshwater has a low δD value (−99‰). The correlation between the hydrogen isotopic compositions of the hydrocarbon gases and the water media indicate that possible exchange or incorporation of water-derived hydrogen into the organic matter had occurred during the hydrous simulation experiments. This is because the hydrogen isotopic composition of hydrocarbon gas formed in the anhydrous thermal pyrolysis of the peat represents the hydrogen isotopic composition of the original organic material. The participation of D-enriched and D-depleted waters during the hydrous pyrolyses leads to the hydrogen isotopic composition of the generated hydrocarbon gases becoming very different in these two hydrous pyrolyses.

Previous studies had shown that water-derived hydrogen was added to or exchanged with organic hydrogen (in kerogen, bitumen, oil, organic compounds) during thermal maturation (Hoering, 1984; Lewan, 1997, 1998; Weres et al., 1988; Schimmelmann et al., 1999, 2001, 2006; Reeves et al., 2012). In this study, the pyrolysis material (kerogen, bitumen, oil, organic compounds) of the peat may exchange the H with that in the added water. Thus, the hydrocarbon gas generated during the pyrolysis of the organic matters (kerogen, bitumen, oil, organic compounds) should reflect the hydrogen isotopic characteristics after the hydrogen exchange (Table 3). On the other hand, water-derived hydrogen can be incorporated into free radicals of hydrocarbon gas (Lewan, 1997, 1998) and exchange with hydrocarbon gas during the pyrolysis (Junk and Catallo, 1997; Reeves et al., 2012). Such incorporation and

exchange via free radicals can change the hydrogen isotopic composition of the hydrocarbon gas generated in the hydrous pyrolyses. As a result, the hydrogen isotopic compositions of the hydrocarbon gases mirror the hydrogen isotopic composition of the added water in these experiments.

Analysis of the relationships of the hydrocarbon isotopic compositions among the three different pyrolyses at different maturity stages yielded some interesting observations (Table 3). The mathematical models of hydrogen isotope compositions of the hydrocarbon gases with R_o are shown in Fig. 5. In the saltwater pyrolyses, the regression equation between δD values and R_o is $\delta D_{C1}=54.4R_o−358.2$ for methane, $\delta D_{C2}=7.9R_o−255.3$ for ethane and $\delta D_{C3}=25.7R_o−223.6$ for propane, respectively. In the freshwater pyrolyses, the regression equation between δD values and R_o is $\delta D_{C1}=43.5R_o−407.0$ for methane, $\delta D_{C2}=17.3R_o−308.6$ for ethane and $\delta D_{C3}=35.6R_o−319.4$ for propane, respectively. These relations have a good correlation with R^2 values lie between 0.73 to 0.93. The relationships of δD values among methane, ethane and propane are shown in Fig. 6, which clearly separate the hydrocarbon gas samples generated in a freshwater environment from those generated in saltwater. These results clearly provide information on the interpretation of the hydrogen isotopic compositions of hydrocarbon gases regarding their generation and evolution level under different diagenetic conditions.

The presence of diagenetic water may change the chemical reaction process, speed and mechanism in the formation of hydrocarbon gases, thus affecting the carbon isotopic fractionation of hydrocarbon gases of CBM. A possible evidence for this view is that the yields of the total gas and hydrocarbon gas generated in the hydrous
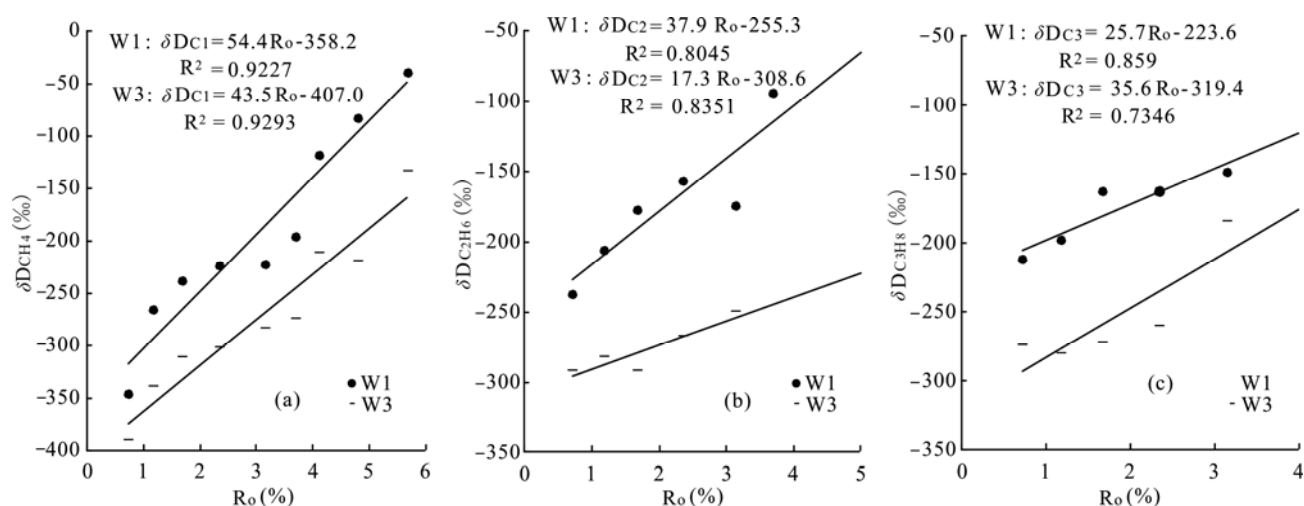
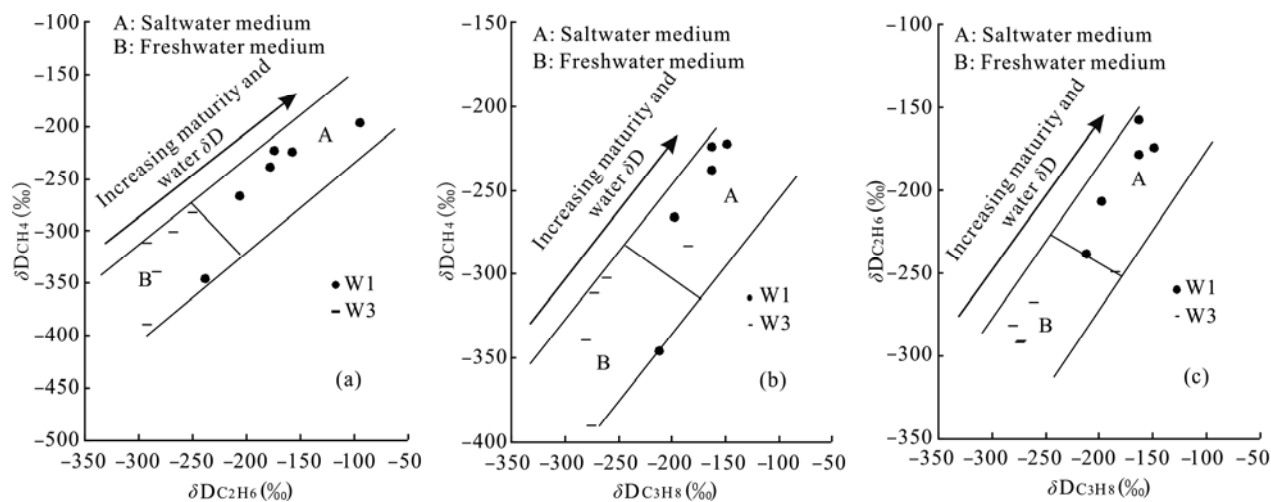Fig. 5. δD value of methane (a), ethane (b) and propane (c) of the 2 hydrous pyrolyses as a function of R_o.

Fig. 6. Correlation diagram of the δD value of methane vs. ethane (a), methane vs. propane (b) and ethane vs. propane (c) of the 2 hydrous pyrolyses.

pyrolyses were higher compared to those in the anhydrous pyrolysis (Fig. 1). Previous studies have shown that water has little effect on carbon isotopes of pyrolysis products of organic matter (Schimmelmann et al., 2001). The results of this study indicate that the carbon isotopic compositions of the methane and ethane generated in the hydrous pyrolyses were, on average, 1‰ to 2‰ heavier than those generated in the anhydrous pyrolyses, which is similar to the difference in the carbon isotopic composition of liquid hydrocarbons between hydrous and anhydrous pyrolyses of organic matter (Schimmelmann et al., 2001). The constructed mathematical relationships between δD and $\delta^{13}C$ values of methane for the saltwater and freshwater environments are $\delta D_{C1}=15.3\delta^{13}C_{C1}+328.7$ and $\delta D_{C1}=10.9\delta^{13}C_{C1}+110.0$, respectively (Fig. 7). The R^2 values are 0.86 and 0.82 for these two correlations, respectively, indicating a strong correlation. These results could be useful in studying on the isotopic geochemistry of thermogenic CBM.

4 Conclusions

The results of the pyrolyses show that hydrocarbon gases generated under the freshwater diagenetic environment have lighter hydrogen isotopic composition than those under the saltwater diagenetic environment. The difference in average δD values between the two types of diagenetic environments is from 78‰ to 86‰, which is consistent with the difference of about 108‰ in δD value between the freshwater and the saltwater. The average δD values of the generated hydrocarbon gases were 52‰ to 64‰ higher in the saltwater pyrolyses and 18‰ to 26‰ lower than those during anhydrous pyrolyses, respectively. The average $\delta^{13}C$ values of the generated hydrocarbon gases were 1‰ to 2‰ higher in the hydrous pyrolyses than those from the anhydrous pyrolyses. Therefore, hydrogen isotope ratios of the generated hydrocarbon gases show a relatively large variation.
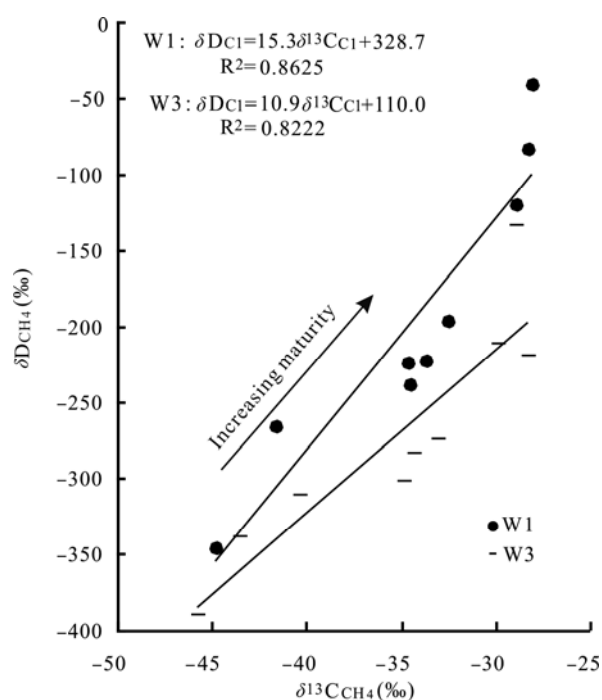
Fig. 7. Correlation diagram between the δD value and the δ^{13}C value of methane of the 2 hydrous pyrolyses.

The hydrogen isotopic compositions and isotopic differences of hydrocarbon gases generated in the pyrolyses of the peat in the presence of different water media at different stages of maturity have been determined. The mathematical relationships between δD and R_o values and between δD values of the pyrolysis hydrocarbon gases in the presence of freshwater and saltwater are established. These results may be used to evaluate the formation of CBM generated from coal-forming material at different maturity stages and the participation of different diagenetic water media.

Acknowledgements

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