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Original research paper

Hydrogen isotopic characteristic of hydrocarbon gas pyrolyzed by herbaceous swamp peat in hydrous and anhydrous thermal simulation experiments☆

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Abstract

In order to understand the influence of diagenetic water medium on hydrogen isotope of thermogenic coalbed gas, the hydrous and anhydrous pyrolytic simulation experiments have been carried out on herbaceous peat. We studied hydrogen isotope composition and its difference and evolution pattern of the pyrolysis hydrocarbon gases It was observed that diagenetic water medium exerts a significant influence on hydrogen isotope composition of pyrolysis hydrocarbon gases. The experiment added water with heavier hydrogen isotopic composition-than peat-formed environmental water generated hydrocarbon gases with heavier hydrogen isotope compositions. When peat was subject to continuous pyrolysis until 5.5%R_o, average δD values of the generated methane, ethane and propane were increased by 74‰ and 42‰ and 66‰, respectively. It is considered that the reason for hydrous simulation experiment to increase hydrogen isotopic value of pyrolytic hydrocarbon gases is due to isotopic exchange between water-derived hydrogen and organic hydrogen. Mathematical models between the δD values of the hydrocarbon gases generated under the participation of freshwater with higher δD values and Ro values as well as between δD values of the generated hydrocarbon gases were established. These research results provide a scientific basis for the genetic study of thermogenic coalbed methane pyrolyzated by coal-forming materials formed in herbaceous marsh under the participation of diagenetic water media.

Keywords: Simulation experiment; Gas product; Hydrogen isotope; Diagenetic water medium; Influencing factor

1. Introduction

Coalbed gas is the product of coalification, being self-generated and self-accumulated natural gas in coalbed [1,2]. Hydrogen isotope composition of coalbed gas is available to research of coalbed gas genesis [2−5]. During the coalification of coal-forming materials, the hydrogen isotopic composition of the produced coalbed gas is controlled by hydrogen exchange and kinetic fractionation. However, the influence of

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hydrogen exchange between diagenetic water medium and coal-forming materials as well astheir products on hydrogen isotope of thermogenic coalbed gas is still unclear, which restricts the genetic interpretation of hydrogen isotope of thermogenic coalbed gas. Hydrous pyrolytic simulation experiment on organic matter is an effective geochemical method to determine the influence of the water on isotope of the product in thermal evolution process. Previous researchers [6−9] have done some research works in this area, and the organic substances adopted in these works are kerogen, low rank coal, shale, organic compounds, with simulated temperature of lower than 600 °C on the whole.

Peat is the coal with the lowest degree of coalification and is also the most primitive state of coal. Thermogenic coalbed gas in nature is started from coalification of peat, and therefore, simulation experiment of peat is able to better simulate formation and evolution process of thermogenic coalbed gas. In general, original coal-forming material includes herbaceous peat and wood peat and property and hydrogen isotope composition of diagenetic water in swamp is likely to change in coalification of peat, which give rise to isotope exchange between organic hydrogen in coal-forming material and its pyrolysis product and inorganic hydrogen in water. This can result in change of hydrogen isotope composition of coal-forming material and its pyrolysis product. Accordingly, we selected herbaceous swamp peat to carry out thermal simulation experiment under the high temperature from 250 °C to 650 °C with the participation of freshwater which hydrogen isotopic composition is different from that of environmental water formed in the swamp. The difference in hydrogen isotope composition and evolution of hydrocarbon gases generated by herbaceous swamp peat under hydrous and anhydrous conditions were researched. This study aims to understand the influence of freshwater medium with hydrogen isotopic composition different from that in environmental water on hydrogen isotope of hydrocarbon gases generated in coalification process of herbaceous swamp peat, and offer reference basis for the identification of of hydrogen isotopic geochemistry of thermogenic coalbed gas as a thermal pyrolysis result of coal-forming material under the action of diagenetic water medium.

2. Samples and experiment

Peat sample (No. Alt) for simulation experiment were collected from herbaceous swamp in Halashazi of Altay in Xinjiang Uygur Autonomous Region (48°06′59″N; 88°21′52″E). The peat has the depth of 1.5 m−3.0 m and organic carbon content of 32.3%. Rock-Eval analysis of the peat sample showed that the S_2/S_3 ratio value was 1.7 and the Tmax value was 330 °C, indicating type III and extremely immature organic matter characteristic. The swamp region is from 350 mm to 600 mm in average annual rainfall and 1816 mm in average annual evaporation and from −3.8 °C to 1.8 °C in average annual temperature, being a cold and arid climatic environment. The sample was dried at room temperature and crushed to 60-mesh, and then placed in thermal reactor for anhydrous and hydrous simulation experiment. The water used for the hydrous simulation experiment (sample No.W2) came from Gahai freshwater. The water has a δD value of −53‰, a pH value of 6.3 and a salinity of 6‰.

In order to fully immerse the sample in water so that there is enough water to participate in the chemical reaction [7], a sample volume to water ratio of 1 g: 1.5 mLwas usded. The sample amount is 2 g in the simulation temperature range of 250−350 °C and 1 g in the simulation temperature range of 400−650 °C. The reactor (with an internal volume of 0.27 L) loaded with sample is vacuumized and replaced with He gas for 3 times. After sealing reactor, it is placed in a muffle furnace and a closed system simulation experiment was performed for 72 h at the temperatures ranging from 250 to 650 °C with an interval of 50 °C and heating rate of 1 °C/min. Hydrogen isotope of pyrolysis gas was determined on gas chromatography-high temperature thermal transformation-isotope ratio mass spectrograph (GC-TC-IRMS), with a standard deviation of less than 3‰, Determination of vitrinite reflectance R_o for pyrolysis residual products and analytical standard deviations are similar to those reported previously [5,10].

3. Results and discussion

3.1. Characteristic and evolution of hydrogen isotopic composition of pyrolysis hydrocarbon gas

It was observed from Fig. 1 that the δD value of methane generated in hydrous simulation experiment of peat was from −383‰ to −29‰, averaging at −183‰ and the δD value of methane generated in anhydrous simulation experiment was from −363‰ to −122‰, averaging at −257‰. The hydrogen isotopic composition of methane generated in hydrous experiment was slightly lighter than that in anhydrous experiment at the simulated temperature of 250 °C. However, the hydrogen isotopic composition of methane formed in hydrous experiment at 350 °C and beyond was obviously heavier than that formed in anhydrous pyrolysis experiment. It was observed from comparison of the two experiments showed that average hydrogen isotopic composition of methane generated in hydrous experiment was 74‰ higher than that in anhydrous experiment. As the simulated temperature rises, the δD value of the generated methane increases.

δD value of ethane generated in hydrous experiment was from −264‰ to −98‰, averaging at −166‰, and δD value of ethane generated in anhydrous experiment was from −291‰ to −104‰, averaging at −208‰. During thermal simulation, hydrogen isotopic value of ethane generated in hydrous experiment was higher than that in anhydrous experiment, being −42‰ heavier on average. Hydrogen isotopic value of ethane generated in thermal simulation increased with increasing simulation temperature.

δD value of propane generated in hydrous experiment was from −244‰ to −130‰, averaging at −163‰, and δD value of ethane generated in anhydrous experiment was from −284‰ to −153‰, averaging at −229‰. It was observed from comparison with anhydrous experiment that hydrogen

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