Fuel 231 (2018) 387–395

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Gas generation and its isotope composition during coal pyrolysis: Potential mechanism of isotope rollover

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ARTICLE INFO

Keywords:
Isotope rollover
Carbon isotope
Hydrogen isotope
Coal-derived gas
Shale gas

ABSTRACT

Recent studies on both conventional (thermogenic gas) and unconventional (shale gas) gases show comparable carbon/hydrogen isotope rollover, i.e., before the rollover point, carbon/hydrogen isotope increases with increasing thermal maturity (or decreasing gas wetness), while after the rollover point, the gas component (i.e., ethane, propane, etc.) becomes more depleted in ^{13}C or ^{2}H with increasing thermal maturity. In order to further investigate potential mechanism of the isotope rollover, combined with previous researches on isotope rollover, this study carried out two batches of pyrolysis experiments on a low mature coal sample from the Songliao Basin, China at constant temperatures for about 72 h under the condition with added water and without added water. The results demonstrate that carbon and hydrogen isotope rollover of ethane and propane started at 500 °C, no matter with added water or without added water. Combined with previous studies on gases of various origins, it is found that such isotopic anomalies were a common phenomenon at high thermal mature stage, despite of what kind of the source rocks and whether adding water or not under the laboratory condition. This is likely caused by the mixing of gases directly from the decomposition of macromolecule of kerogen and those from the tightly entrapped straight-chain species in kerogen at relatively high thermal mature stage. These straight-chain species are normally entrapped in the kerogen, and will probably be released at high thermal maturation stage. Marine facies source rocks from southern China also demonstrate the existence of such tightly entrapped hydrocarbons at very high thermal maturity. The results may have important significance on the gas exploration at relatively high mature stage and have a guidance on the gas production changes during the exploration.

1. Introduction

Since natural gases mainly consist of small simple molecules, isotope geochemistry has long been an important tool for gas origin and accumulation research [1–6]. Due to the kinetic isotopic fractionation during kerogen cracking process, both $\delta^{13}C$ and $\delta^{2}H$ isotopic compositions of methane were found to be dependent on the maturity of their source rocks and increase with increasing thermal maturity [2,4,5,7]. For thermogenic gas which has not undergone secondary alteration, carbon isotopes of methane and its homologues will increase with increasing carbon numbers ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$) [1].

Recently two studies have shown that gases from conventional reservoirs demonstrate isotope rollover (i.e., carbon/hydrogen isotope of ethane or propane decreases with increasing thermal maturity) at high thermal maturity [8,9]. For example, Dai et al. [9] found that the carbon isotopes of coal-derived gases from the Ordos Basin, China become reversed at high thermal maturity and attributed it to the high temperature. Zhang et al. [8] proposed that gases from the marine carbonate formations in the Sichuan Basin also show such carbon and hydrogen isotope rollover. They believed that the carbon isotopic reversal was mainly caused by the mixing of oil-cracking gas with various maturities and mature or overmature kerogen-cracking gas, while the hydrogen isotopic reversal was due to the water-organic matter reactions. Actually, carbon isotopic reversal is a common phenomenon and has been found in gas samples of various origins. Complete carbon isotopic reversal ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$) has been found in many abiogenic gases [10–13]. Partial carbon isotope reversal (e.g., $\delta^{13}C_1 < \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$, $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 > \delta^{13}C_4$) in the conventional gas reservoirs has been attributed to various causes such as the mixing of gases derived from different source rocks or gases with the same source rocks but different thermal maturities, or biodegradation and migration [1,14].

Recently, a series of studies have demonstrated the carbon and/or hydrogen isotope rollover of gases of various origins and tried to explain the causes of the isotopic anomalies [9,15–23]. These studies can be summed up in several viewpoints: (1) Cracking of C_{2+} hydrocarbons

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https://doi.org/10.1016/j.fuel.2018.05.029
Received 25 January 2018; Received in revised form 24 April 2018; Accepted 7 May 2018
Available online 29 May 2018
0016-2361/

[20,22,23]; (2) Rayleigh fractionation during redox reactions at high thermal maturity causing the carbon isotopic reversal and isotopic exchange with formation water causing the hydrogen isotopic reversal [15]; (3) Simultaneous cracking of kerogen, retained oil and wet gas and associated isotopic fractionation at higher thermal maturity [17,21]; (4) water reacting with methane to generate isotopically light carbon dioxide and hydrogen with subsequent formation of light ethane and propane [16]; (5) mixing of indigenous primary gas (generated directly from kerogen) and secondary gas (generated from oil and condensate) within source rocks[19,24]; (6) secondary alteration under high temperature [9]. In addition, pyrolysis experiments on type II kerogen also demonstrated that carbon isotope rollover in productive shale gas plays is not an oddity but can be reproduced in the laboratory [20].

Can the isotope rollover be reproduced on coal sample in laboratory? We conducted a series of pyrolysis experiments on coal samples from the Shahezi Formation in the Songliao Basin in China with added water and without added water under constant temperatures for 72 h. Gao et al. [25] has discussed the catalytic effects of nickel and magnetite on gas generation and isotope composition during the course of coal pyrolysis, in this study we will investigate the potential mechanism of isotope rollover during high thermal mature stage.

2. Geological settings and gas geochemical information

The coal sample was collected from the Cretaceous Shahezi Formation in the Songliao Basin (Fig. 1). Songliao Basin is a large Cenozoic continental sedimentary basin in the Northeast China, with an area of 255.5×10^3 km^2. Natural gases from the deep Songliao Basin demonstrate a carbon isotopic anomaly among the C_1-C_4 alkanes (complete or partial carbon isotopic reversal) and their origin has long been a hot debate [10,26–29]. The detailed evolution and sedimentary sequence stratigraphy of the Songliao Basin have been described by previous studies [29,30]. Briefly, in the deep strata of the Songliao Basin, there are totally five sets of source rocks, among them, the Cretaceous Shahezi Formation is a main source rock layer. The period of Shahezi Formation is a strong chasmic stage of the basin, belonging to structural and thermal subsidence, which is also a most developed period for the deposition of lacustrine mudstone and coal measures. This is a set of very good source rocks. In this formation, the dark mudstone is the most developed and coal measure is also developed. Source rocks are characterized by wide distribution and large thickness. Mudstone has thickness generally of > 100 m and even up to 600 m, and coal has accumulated thickness up to 105.5 m. These source rocks are characterized by type III kerogen, with average TOC value of about 2.2% and thermal maturity (Ro%) from 1.4% to 3.6% [26].

Three sets of natural gas geochemical data were compared in this study. Among them, two sets were from the Ordos and Sichuan basins in China (Fig. 1) and one is from the Fort Worth Basin in USA. The molecular and carbon isotopic compositions of the natural gases from these three basins, and the related geological conditions have been described in detail by previous studies [8,16,31–33].

Geochemical characteristics of source rocks from the southern China have also been investigated in this study. The southern China has experienced long and complex tectonic activities, such as the caledonian, Hercynian, Indosinian, Yanshanian and Himalayan movements, and is characterized by a technique feature with multicycle and superposition of structures. The most significant characteristic is that the source rocks in southern China have generally experienced long thermal evolution and have very high thermal maturity. Source rocks from Permian or formations under Permian normally have thermal maturity (Ro%) greater than 2%, H/C ratios less than 0.7 and HI ratios less than 50 mg/g. Vertically, thermal maturity of source rocks increases with increasing burial depth and geological ages.

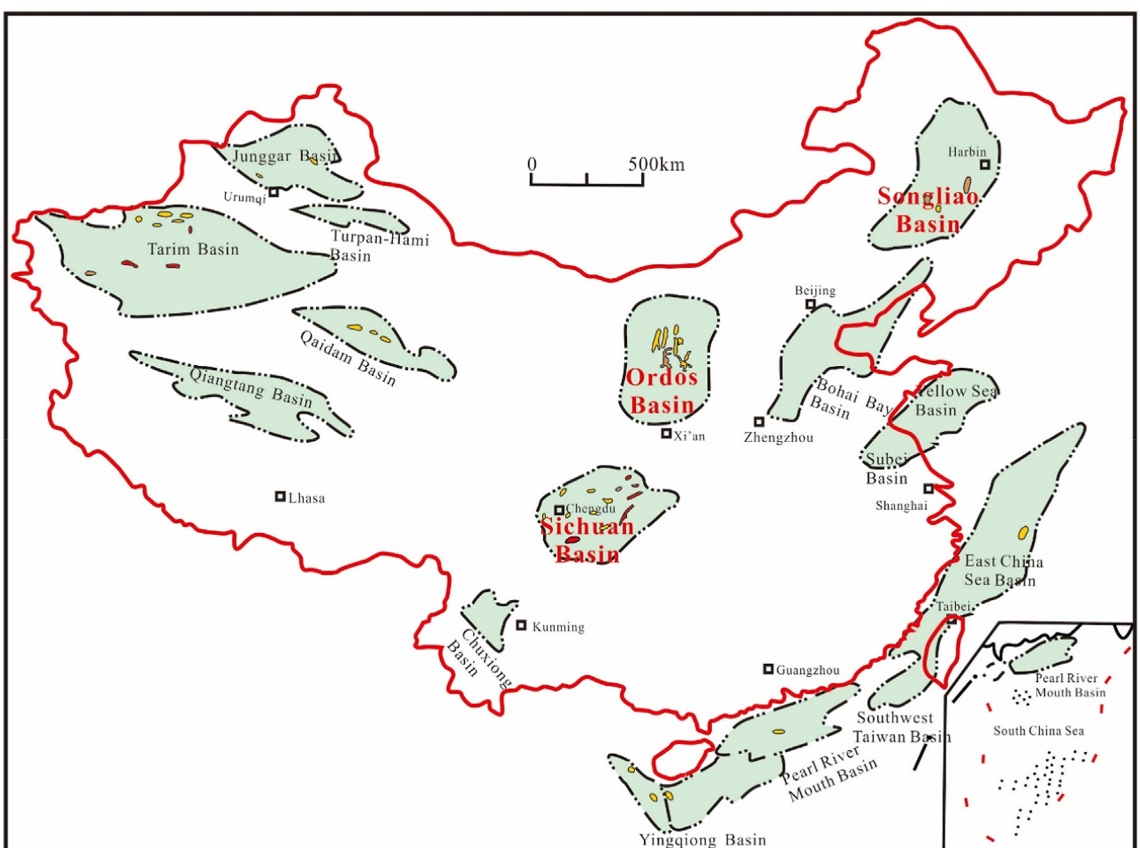

Fig. 1. Location map of the Songliao, Ordos and Sichuan basins in China.