



Original research paper

Characteristics of stable carbon isotopic composition of shale gas[☆]Zhenya Qu^{a,b}, Jianan Sun^{a,b}, Jianting Shi^{a,b}, Zhaowen Zhan^{a,b}, Yanrong Zou^{a,*}, Ping'an Peng^a^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou 510640, China^b University of Chinese Academy of Science, Beijing 100049, China

Received 7 December 2015; revised 12 January 2016

Available online 17 May 2016

Abstract

A type II kerogen with low thermal maturity was adopted to perform hydrocarbon generation pyrolysis experiments in a vacuum (Micro-Scale Sealed Vessel) system at the heating rates of 2 °C/h and 20 °C/h. The stable carbon isotopic compositions of gas hydrocarbons were measured to investigate their evolving characteristics and the possible reasons for isotope reversal. The $\delta^{13}\text{C}$ values of methane became more negative with the increasing pyrolysis temperatures until it reached the lightest point, after which they became more positive. Meanwhile, the $\delta^{13}\text{C}$ values of ethane and propane showed a positive trend with elevating pyrolysis temperatures. The carbon isotopic compositions of shale gasses were mainly determined by the type of parent organic matter, thermal evolutionary extent, and gas migration in shale systems. Our experiments and study proved that the isotope reversal shouldn't occur in a pure thermogenic gas reservoir, it must be involved with some other geochemical process/es; although mechanisms responsible for the reversal are still vague. Carbon isotopic composition of the Fayetteville and Barnett shale gas demonstrated that the isotope reversal was likely involved with water–gas reaction and Fischer-Tropsch synthesis during its generation.

Copyright © 2016, Lanzhou Literature and Information Center, Chinese Academy of Sciences AND Langfang Branch of Research Institute of Petroleum Exploration and Development, PetroChina. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Keywords: Shale gas; Carbon isotope; Pyrolysis; Kerogen; Isotope reversal

1. Introduction

Model shale gas is of thermogenic or biogenic origin and it may be stored as sorbed hydrocarbons, as free gas in natural fracture and intergranular porosity, as gas sorbed into kerogen and clay particle surface, or as gas dissolved in kerogen and bitumen [1]. Shale gas is a type of accumulation reservoir mainly trapped within dark mudstone or carbonaceous mudstone as sorbed hydrocarbons or free gasses. It can also be found in siltstones, silt-mudstones, mud-siltstones, or even

sandstones of the interlayer [2]. As a new field of oil and gas exploration and development, shale gas has drawn great attention from all over the world. The accelerated exploration of shale gas provides an unprecedented opportunity for us to understand the geochemical processes in oil and gas source rocks [3]. Stable carbon isotopic compositions of natural gasses have significant applications in identifying the genesis of hydrocarbon gas, their parent organic type, the maturity of their source rocks, their post generation alteration, and gas-source relationships [4]. Studying the geochemical characteristics of shale gas, such as chemical compositions, maturities, stable carbon and hydrogen isotopic compositions, et cetera are helpful in reinforcing our understanding of their generation and origin. Not to mention, it lays the foundation for recognizing the potential resource areas. Exploration and development of shale gas are still in its early exploring stage all around the world excluding the North America. Published literature about geochemical characters of shale gas, such as

[☆] This is English translational work of an article originally published in Natural Gas Geoscience (in Chinese). The original article can be found at: 10.11764/j.issn.1672-1926.2015.07.1376.

* Corresponding author.

E-mail address: zouyr@gig.ac.cn (Y. Zou).

Peer review under responsibility of Editorial Office of Journal of Natural Gas Geoscience.

chemical compositions, isotope compositions and so on are still rare. Our understanding on its geochemical characters, including carbon isotopic compositions and hydrogen isotopic compositions, was mostly derived from materials of North America. The $\delta^{13}\text{C}$ values of each gaseous hydrocarbon component in shale gas became more positive with the increasing maturity or with the increasing carbon number from methane to propane at an identical maturity as the conventional reservoirs [3,5]. In addition, gas of different genesis could be seen in shale systems [5–7].

Geochemical characteristics of shale gas in North American are as follows: (1) Shale gas is mainly composed of methane accompanied by a small amount of ethane and propane, it also includes minimal non-hydrocarbon gas [6–10]; (2) Carbon isotope reversal or rollover ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ or $\delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$) is a common occurrence at high level thermal maturity areas [5,10,11]. Isotopic reversal or rollover accentuated for it was often followed by high yields in the productive wells [3,5,8–11]. Some scholars gave their explanations about the reversals or rollovers observed in shale gas wells [3,8,11]. Stable carbon and hydrogen isotope values of natural gasses in conventional reservoirs were mainly controlled by their parent organic matter, their thermal maturities, migration, bacterial oxidization, et cetera. Shale gas is a continuously aggregated gas reservoir and it is stored in situ. There is no short distance migration in the shale system [12]. Thus, isotopic composition evolution model of shale gasses may differ from conventional reservoirs. It's necessary to learn about carbon isotopic composition characteristics of gas hydrocarbons generated at different stages because stable carbon isotope carries the signature of gas origin and thermal evolution stage in the processes of shale gas exploration and development. This paper aims to discuss the carbon isotope evolution model of shale gas according to thermal simulation experiments, to acquire a better understanding of carbon isotope evolution patterns of gas in different stages as well as to provide references for shale gas exploration and development.

2. Material and methods

2.1. Samples

Exploited shale gas was mainly produced in the marine strata. A dark marine oil-shale was taken from the Jurassic Kimmeridgian formation in the North Sea basin of UK. The sample was grounded to 80–100 mesh, and the kerogen was isolated from the shale by HCl and HF treatment. Then it was placed in a Soxhlet extractor with a dichloromethane and methanol (93:7) solvent mixture for 72 h after which, the extracts were collected.

2.2. Geochemical characteristics

Based on the analysis performed by a Rock-Eval (VI), the kerogen contains a total organic carbon (TOC) content of 68.89% with a hydrogen index (I_{H}) of 640 mg/g and T_{max} 418 °C. The parameters illustrate that the kerogen from the

sources is type II within the immaturity stage (Table 1, Fig. 1). The sample is suitable for hydrocarbon-generation thermal simulation experiments.

2.3. Pyrolysis experiment

Pyrolysis experiment is a powerful tool for studying the mechanism of natural gas generation and accumulation [13]. The pyrolysis experiment systems can be categorized into three depending on their degree of openness. The three systems are the open system pyrolysis, close system pyrolysis, and semi-open system pyrolysis. As a self-source and self-storing reservoir, shale gasses were generated and gathered in a relatively close system. Hence, simulating shale gas generation and evolution in a close system pyrolysis were more suitable. High-temperature and high-pressure heat-water simulation equipment, MSSV (micro scale sealed vessel) system, and gold tube system are the most common close systems we are familiar with. The MSSV and gold tube systems have been widely used in studying hydrocarbon generation kinetics, isotopic kinetics, and crude oil pyrolysis kinetics. They sprung up in the 1990s and are still common in simulation experiments nowadays [13].

In this paper, a vacuum MSSV system was used for the pyrolysis of kerogen and extractions. The vacuum MSSV could load more kerogen or extractions than the conventional MSSV system, and it brings much more convenience to carbon isotope analysis which requires a relatively large amount of gas.

The procedural details of the experiments are as follows: The finely dried and ground kerogen was accurately weighted (2–25 mg) and then loaded into a clean glass capillary tube. Pre-cleaned quartz wool was filled in the void volume of the sample tube which was later sealed by a high temperature flame while maintaining the vacuum degree of 0.085–0.09 MPa by means of a vacuum pump. The glass tubes have a length of 8 cm and an inner diameter of 4 mm. Samples in the sealed tubes were pyrolyzed in an oven at the rate of 2 °C/h and 20 °C/h, respectively.

As for temperature programs, the samples were heated from room temperature to 300 °C and then it was held for 1 h. Finally, it was heated from 300 °C to 550 °C at the rate of 2 °C/h and 20 °C/h, respectively. The tubes, in the order of sample number, were removed from the oven every 10 °C. The pyrolysis of the extracts was completely identical.

2.4. Carbon isotopic analysis of gas

The clean sample tube and glass balls were placed into a 20 ml culture tube altogether. The culture tube was flushed with argon for about 2 min to remove air, then a lid was placed on it to ensure the seal. Kerogen derived gasses or extractions derived gasses were released from the sample tube by means of breaking it by shocking the glass balls. Gastight syringes were used to remove gasses in the culture tube then transferred to the Delta plus XLGC-IRMS. The GC oven was programmed from 40 °C (held for 6 min) to

Table 1
Basic geochemical parameters of the sample.

Sample	TOC/%	$T_{max}/^{\circ}\text{C}$	$S_1/(\text{mg}/\text{g})$	$S_2/(\text{mg}/\text{g})$	$S_3/(\text{mg}/\text{g})$	$I_H/(\text{mg HC}/\text{g TOC})$	$I_O/(\text{mg CO}_2/\text{g TOC})$
Kerogen	68.89	418	12.23	440.73	8.45	640	12

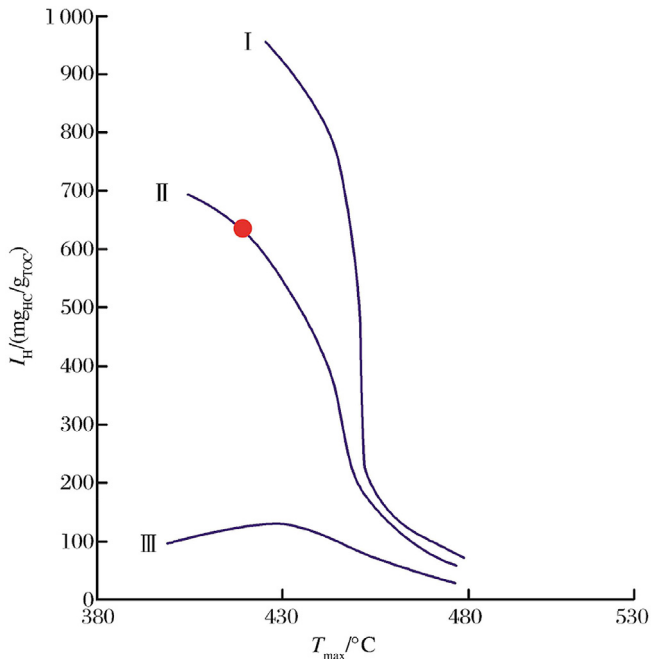


Fig. 1. Kerogen type diagram of the North Sea oil shale.

190 °C (held for 4 min) at 15 °C/min. The stable carbon isotope value of each sample was measured two or three times within a calculated precision of $\pm 0.3\text{‰}$ (PHD standard).

3. Results and discussion

3.1. Results

The $\delta^{13}\text{C}$ values of methane produced from kerogen (NY) and extractions (NC) exhibited a decrease then it changed to an increase as the pyrolysis temperatures elevate (Fig. 2a, b). The results are consistent with several studies of pyrolysis experiments conducted previously [10–21]. The $\delta^{13}\text{C}$ values of ethane (Fig. 2c, d) and propane (Fig. 2e, f) became heavier with the increasing pyrolysis temperatures. The values of the vitrinite reflectance (R_o) were calculated based on the relationship between Easy% R_o and pyrolysis temperatures [22].

Whenever the values of R_o are lower than 1.15%, the $\delta^{13}\text{C}$ values of methane generated from kerogen (NY) and extractions (NC) decreases with as the pyrolysis temperatures elevate. Meanwhile, the $\delta^{13}\text{C}$ values of ethane and propane showed an opposite trend. Kerogen was in the main oil generation stage [23], which co-produced small amounts of primary gasses. Carbon isotopes of methane generated from both the close and open system showed this evolutionary trend (Fig. 2a, b). Shuai et al. [18] attributed it to the heterogeneity of gas precursors. The $\delta^{13}\text{C}$ values of methane, ethane, and

propane cracked by extractions were significantly lighter than those generated from kerogen at this stage.

Whenever the values of R_o are between 1.15% and 1.8%, the $\delta^{13}\text{C}$ values of methane, ethane, and propane produced from kerogen (NY) and extractions (NC) became more positive as the pyrolysis temperatures increase. The $\delta^{13}\text{C}$ values of extraction derived gasses increased more rapidly than those derived from kerogen. In the oil cracking stage [23] little primary gas is still included. The difference between $\delta^{13}\text{C}$ values of hydrocarbon gasses with the same number of carbon atoms from kerogen and extractions diminished as the pyrolysis temperatures increase.

Whenever the values of R_o are higher than 1.8%, the $\delta^{13}\text{C}$ values of methane, ethane, and propane produced from both NY and NC became heavier with the elevating extent of thermal evolution. The $\delta^{13}\text{C}$ values of hydrocarbon gasses cracked by NC increased much more rapidly than those generated from NY and they finally became close. Propane could not be examined at $R_o > 2.3\%$ for its rapid cracking in the close system, because it entered the wet gas cracking stage [23]. The $\delta^{13}\text{C}$ values of propane derived from NY and NC tended to be close to wet gas cracking stage (Fig. 2e, f).

3.2. Carbon isotope characteristics of pyrolysis gas

Shale gas can be of biogenic [6,7], thermogenic [3,5,6,10] or even a mixture of both. The exploration practices in foreign countries demonstrated that thermogenic shale gas is the main exploration target. Shale gas wells with high yields in North America are all thermogenic.

Thermogenic shale gasses are mainly composed of primary gasses generated from the kerogen and secondary gasses cracked by oil. The carbon isotopic compositions of gaseous hydrocarbons cracked by oil and derived from bitumen share similar variation rule with thermal evolution [24]. In order to avoid disputes in gas origin, the extractions, rather than crude oil, were used in the pyrolysis experiments. Tian [25] proposed a plot of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ vs $\delta^{13}\text{C}_1$ to discriminate the oil derived gas from the kerogen derived gas. The $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ difference in the oil derived gas was greater than that in the kerogen derived gas with increasing thermal stress [25,26]. The plot of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ vs $\delta^{13}\text{C}_1$ based on the NY and NC gas data showed a similar trend (Fig. 3). When R_o is below 1.38%, the $\delta^{13}\text{C}$ values of methane derived from NC (extracts) were lighter than those derived from NY (kerogen) under the same values of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$. The $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ values of the NY derived gasses ranged from -2.47‰ to -0.76‰ and had slight variations which did not give off much dissimilarity with data (-2.8‰ to -0.24‰) that was reported by Guo et al. [26]. At this stage, hydrocarbons gasses were mainly derived from the kerogen and the liquid hydrocarbons were rarely cracked

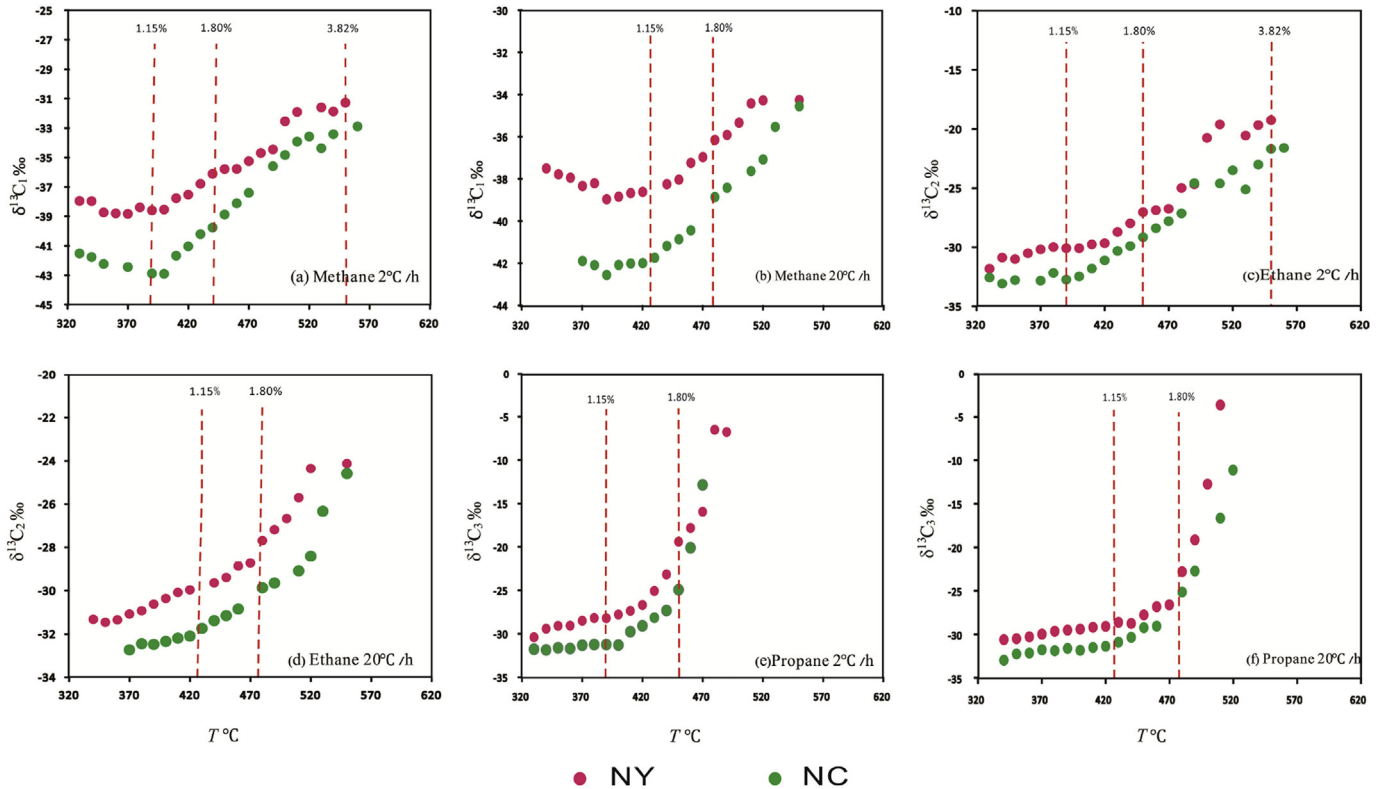


Fig. 2. Stable carbon isotopic composition of methane, ethane, and propane with the increasing temperature at the heating rates of 2 °C/h and 20 °C/h.

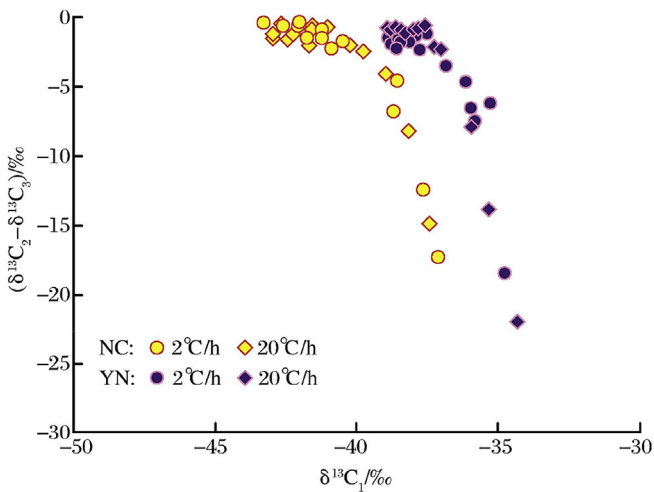


Fig. 3. Cross plot of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ vs $\delta^{13}\text{C}_1$ of the gasses from kerogen and cracked oil.

to gasses. As the thermal stress increases the $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_3$ values of the NY derived gasses increases rapidly (up to -22.01‰ to -18.54‰) after $R_o > 1.38\%$. This is comparable to the trend of oil derived gasses. A lot of liquid hydrocarbons begin to crack to small-molecule gasses wherein most of them convert to methane. Chemical reaction in the MSSV system includes pyrolysis of kerogen, oil or wet gasses' cracking and polymerization reactions, et cetera. Gasses in the system were chiefly from oil cracking, only a small amount of kerogen derived gasses were included at this stage.

Chung et al. [27] proposed that an unaltered isotope type curve is nearly linear on the δC_n versus $1/n$ diagram called Nature Gas Plot (NGP). The slope of the line was determined by gas source rock and its thermal maturity. Zou et al. [4] proposed that isotope type curve pattern of oil-associated gas is a concave while isotope type curve pattern of coal-derived gasses is convex based on the statistical and experimental data as well as the drawn carbon isotope range boundaries of oil-associated gas and coal gas. On the plot of NGP, carbon isotopes of NC-derived gasses and NY derived gasses were nearly linear and they fall in the isotope range of the oil-associated gas at the low-temperature stage. The $\delta^{13}\text{C}$ values of methane were still in the isotope range of oil-associated gas, whereas the $\delta^{13}\text{C}$ values of ethane and propane were beyond the isotope range of oil-associated gas at high-temperature stage. The isotope type curve was downward which demonstrated that the wet gasses started cracking. However, there were no carbon isotope reversals observed (Fig. 4). Those proved that reactions in the MSSV system were not the main reason that caused the isotopic reversal. Reactions in the system include thermal degradation of kerogen and secondary cracking of oil or wet gasses.

3.3. Carbon isotope reversal or rollover

Gasses stored in the shale gas reservoir are in situ. Only a limited migration or expulsion occurred in shale system due to low porosity and permeability of the shale [28]. Thus, carbon isotopic compositions of shale gasses were mainly controlled by

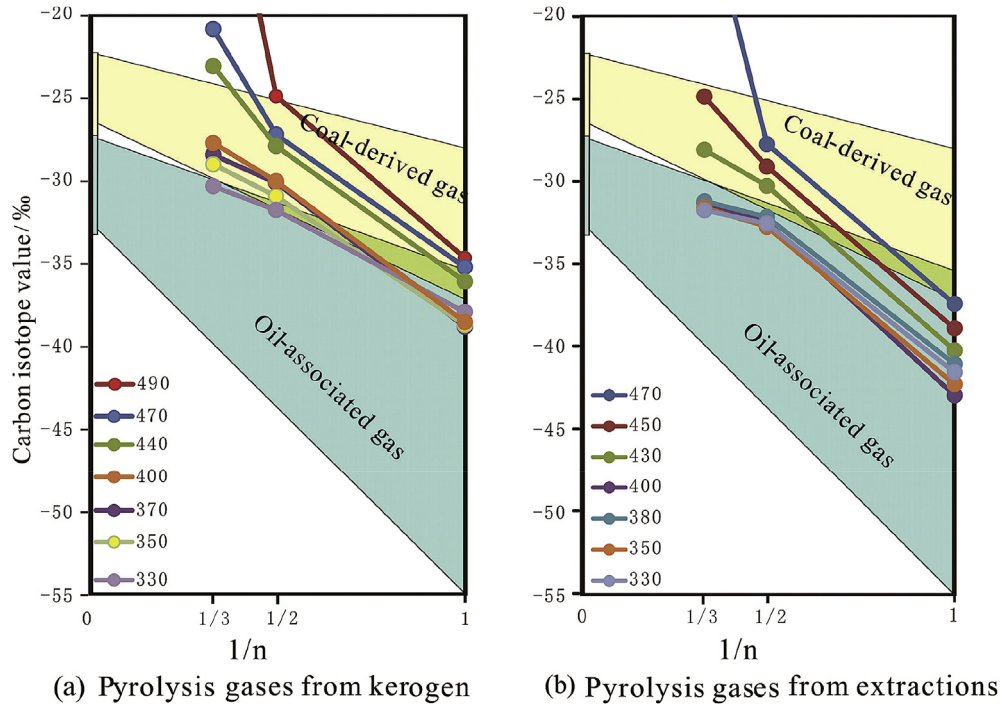


Fig. 4. Isotope type curves' plot.

their parent organic matter, processes of their thermal evolution, and micro-migration fractionations. Carbon isotopic compositions of kerogen derived gasses in the simulation only depended on their parent organic matter and the pyrolysis temperature. Like the conventional reservoirs, the $\delta^{13}\text{C}$ values of gasses became more positive with the increasing carbon number at an identical maturity or the $\delta^{13}\text{C}$ values of each gaseous hydrocarbon component became more positive with the increasing maturity can also be observed in shale gas reservoirs. However, the isotopic reversal or rollover of gasses produced from Barnett, Fayetteville, Appalachian, and Woodford shale in America as well as Horn River shale in Canada are commonly in the productive wells with high yields, especially in the Fayetteville

shale gas. The mechanism responsible for isotopic reversal or rollover is still controversial, though there are no objections that shale gas is mainly organic in origin.

Fig. 5 shows that isotopic reversal was attested in dry gas stage and primarily takes place when gas wetness decreases below 2%. The values of $\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1$ ranged from -8‰ to 0‰ at this stage. The values of $\delta^{13}\text{C}_2$ ranged from -45‰ to -40‰ and exhibited the isotope rollover with decreasing wetness (Fig. 5b). The values of $\delta^{13}\text{C}_1$ ranged from -41‰ to -35‰ and the isotope range of oil-associated gas decreased. The key question is: How can a geochemical process produce ethane with the carbon isotope ranging -45‰ to -40‰ ? Pyrolysis experiments proved that ethane with light carbon

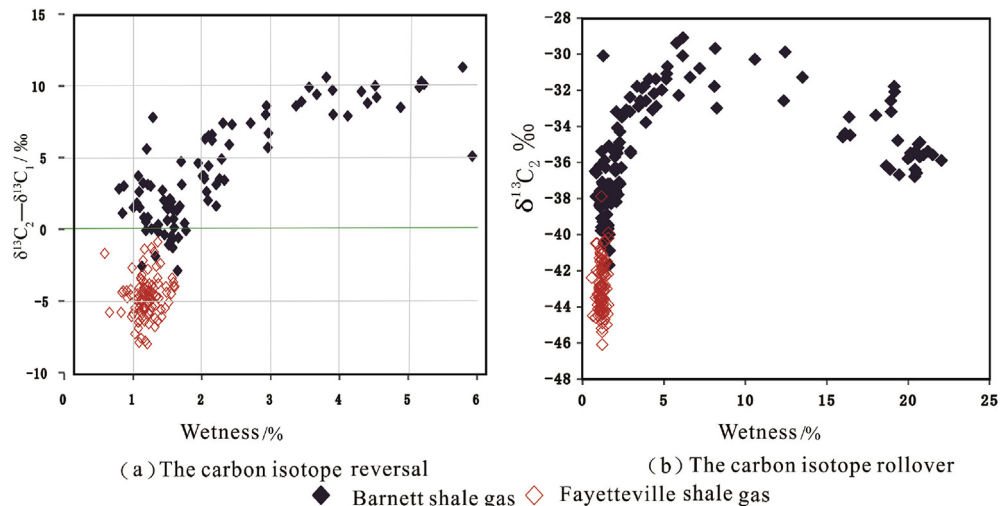


Fig. 5. The relationship between stable carbon isotope and gas wetness.

isotopes should not take place in the process of hydrocarbons generation from organic matters. This includes the reactions such as pyrolysis of kerogen, oil or wet gasses cracking, or the mixture of both. Pyrolysis experiments [29] in gold cells in the presence and absence of added water conducted by Gao demonstrated that the overall quantities of hydrocarbon gasses that were generated from experiments with added water were lower compared to the experiments without water under the same pyrolysis temperature, although the relative abundance of methane among other gas species was higher in the experiment where water was introduced. The isotopic rollovers were only observed in hydrocarbons generated from pyrolysis experiments with added water. The possible reason is that the water involved in the reaction of kerogen degradation has promoted an effect on C_{2+} hydrocarbons cracking [29]. Tang et al. [11] proposed that iron (II) oxide might be the catalyst promoting reactions between water and organic matter in a reduction subsurface environment that eventually produced H_2 and light carbon isotope CO_2 , then the ethane with more negative carbon isotopes was generated from reactions between H_2 and CO_2 . The aforementioned reactions might be the reason for the carbon isotopic rollover. Xia et al. [3] held that the reversal might be the result of the indigenous primary gas and secondary gas mixing with different proportions as the maturity increases. The secondary gas is wetter and it has more negative $\delta^{13}C$ value than the primary gas at high maturity. As a result of the mixture of primary and secondary gas at high maturity, methane is dominantly contributed by the former and ethane is dominantly from the latter. Thus, resulting in a carbon isotopic reversal. Meanwhile, the isotope of ethane from secondary cracking became negative with the increasing maturities. As a consequence, a $\delta^{13}C_2$ rollover takes place with respect to the maturity trend. In any case, they proposed a calculated mixing model of primary gas and secondary gas. Gai et al. [28] concluded that isotopic fractionation of paraffin hydrocarbons in gas diffusion reduces as the carbon number increased in a confined system, which makes isotopic compositions of methane heavier, but has minimal impact on isotopic compositions of ethane and propane. The isotopic fractionation of hydrocarbons became larger with the increasing carbon number in the process of absorption and desorption, which makes isotopic compositions of ethane and propane more negative with less impact on isotopic compositions of methane. The preceding mechanisms might account for the isotopic reversal.

Reports of isotopically reserved shale gas in our country are rare. Studying shale gas from Barnett, Fayetteville, and Marcellus shale provided us a better understanding of the isotopic reversal or rollover. Figs. 5–8 showed the changing laws of hydrocarbon yields with the variety of isotopic compositions in the productive wells according to published statistical of the Barnett and Fayetteville shale gas [5,30].

Fig. 6 indicated that the carbon isotopic reversal was very common in Fayetteville and Marcellus shale gas. Carbon isotopic reversal was only observed in a portion of the Barnett shale gas (Fig. 5b). The isotope values of methane in these

shale gasses were in the range of oil-associated gas and they were roughly consistent with the data from our experiments. However, the isotope reversed ethane and propane was much negative and they showed some qualities of non-pyrolysis in origin. In Fig. 7a, the CH_4 and CO_2 content in the Fayetteville shale gas presented a negative linear trend. Fig. 8a showed that a positive correlation exists between CH_4 and CO_2 content in the Barnett shale gas under the condition that the content of methane is low and the isotope reversal did not materialize. The correlation reversed to the opposite direction gradually when the amount of methane increased to 95%, which indicated that the increase of methane and the decrease of CO_2 might have an intimate relationship with the isotopic reversal. The interesting part is that more CO_2 followed the heavier carbon isotopes of CO_2 in the Fayetteville shale gas (Fig. 8b), whereas, the CO_2 showed an initial trend towards less negative $\delta^{13}C$ values that followed an opposite trend towards more negative $\delta^{13}C$ values in the Barnett shale gas. The heavier carbon isotope of CO_2 in the Barnett and Fayetteville shale gas followed the heavier carbon isotope of methane and ethane (Figs. 7c, d and 8c, d), which means that CO_2 and hydrocarbon gasses in the shale system might have close relationships in origin.

Zumberge et al. [5] noticed that the $\delta^{13}C$ values of ethane in both the Barnett and Fayetteville shale gas were more negative than it is in inorganic gas. The attributed isotope reversal to the following two-stage reactions is as follows: First, the light CO_2 was generated by the hydrocarbon oxidation with deep formation water. Secondly, CO_2 and H_2 further reacted to form isotopically light ethane. As we all know, methane is the most stable molecule among alkane hydrocarbons. It might not have any other hydrocarbons including the solid organic matters if all methane were oxidized to CO_2 in the system. Even if such reactions had happened, the carbon isotope of methane in shale gas reservoir should be more negative than that of the observed due to the $\delta^{13}C$ values of CO_2 from oxidation being much lighter than the ones from organic matters. Though, the methane in gas reservoir is a mixture of unoxidized methane and the normal one.

The $\delta^{13}C$ values of the remaining CO_2 in the Fayetteville shale gas ranged from -20‰ to -4‰ with a dominant frequency of -9‰ to -8‰ . The $\delta^{13}C$ values of CO_2 remained in the Barnett shale gas ranged from -12‰ to -4‰ with a dominant frequency of -8‰ to -6‰ . They were mainly organic in origin. On an average, isotope fractionation of CO_2 and CH_4 is among 15‰ – 25‰ in a natural environment [31]. The $\delta^{13}C$ values of CO_2 generated from pyrolysis of organic contents with added water ranged from -28.8‰ to -25.5‰ [29]. Carbon isotope of synthesized methane ranged from -54‰ to -40‰ from the perspective of isotope fractionation. The $\delta^{13}C$ values of methane ranged from -43‰ to -34‰ according to our simulation while the $\delta^{13}C$ values of methane generated from the experiments performed by Gao ranged from -46‰ to -37‰ [29]. Considering the mixture of methane of thermal genetics, the isotope composition of

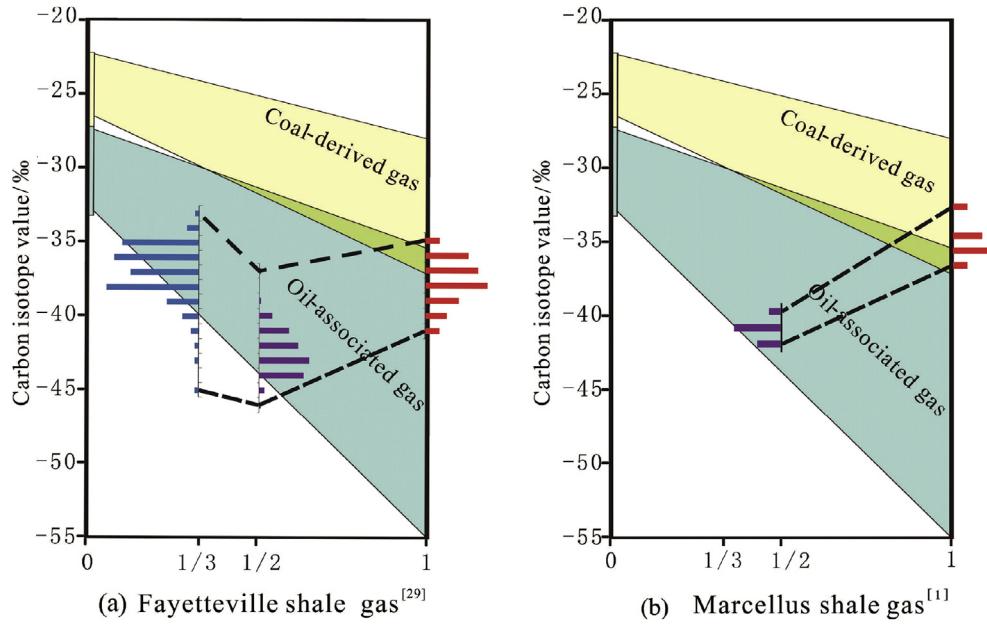


Fig. 6. Statistical distribution of carbon isotope values.

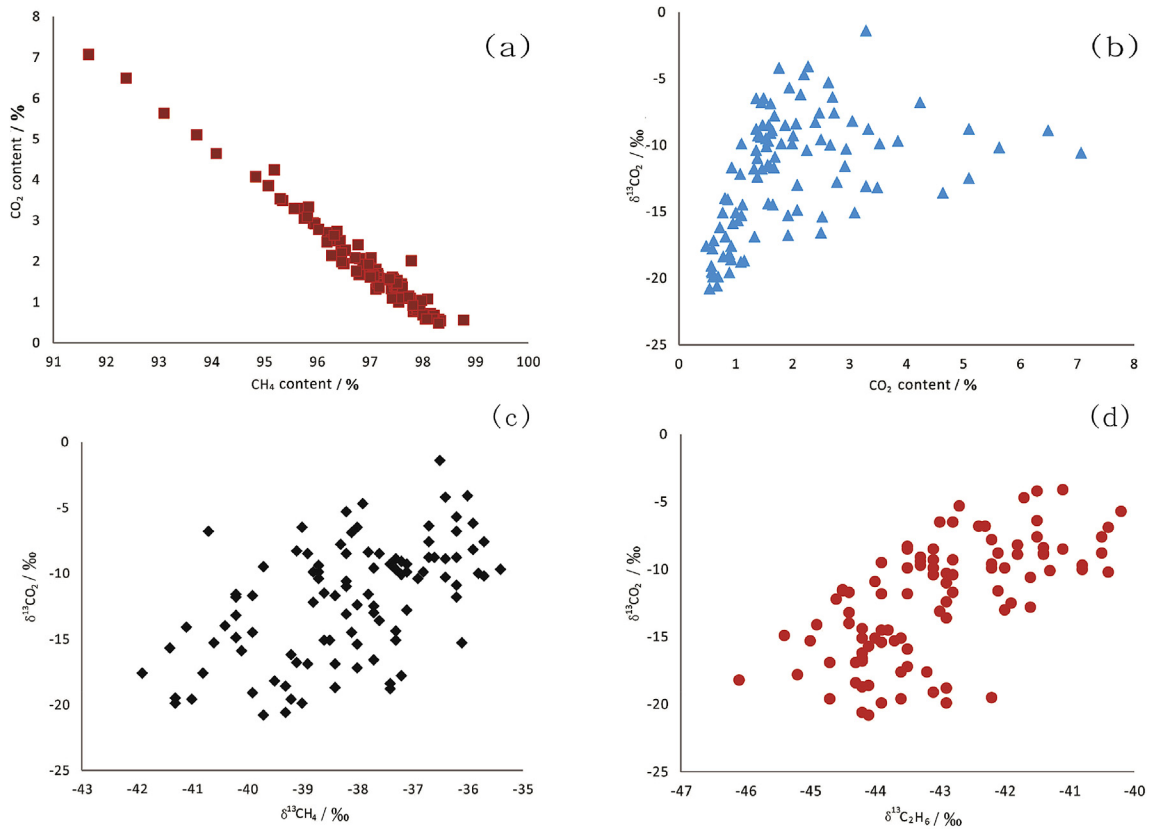


Fig. 7. Variation in the contents and carbon isotope compositions of methane and CO₂ in the Fayetteville gases.

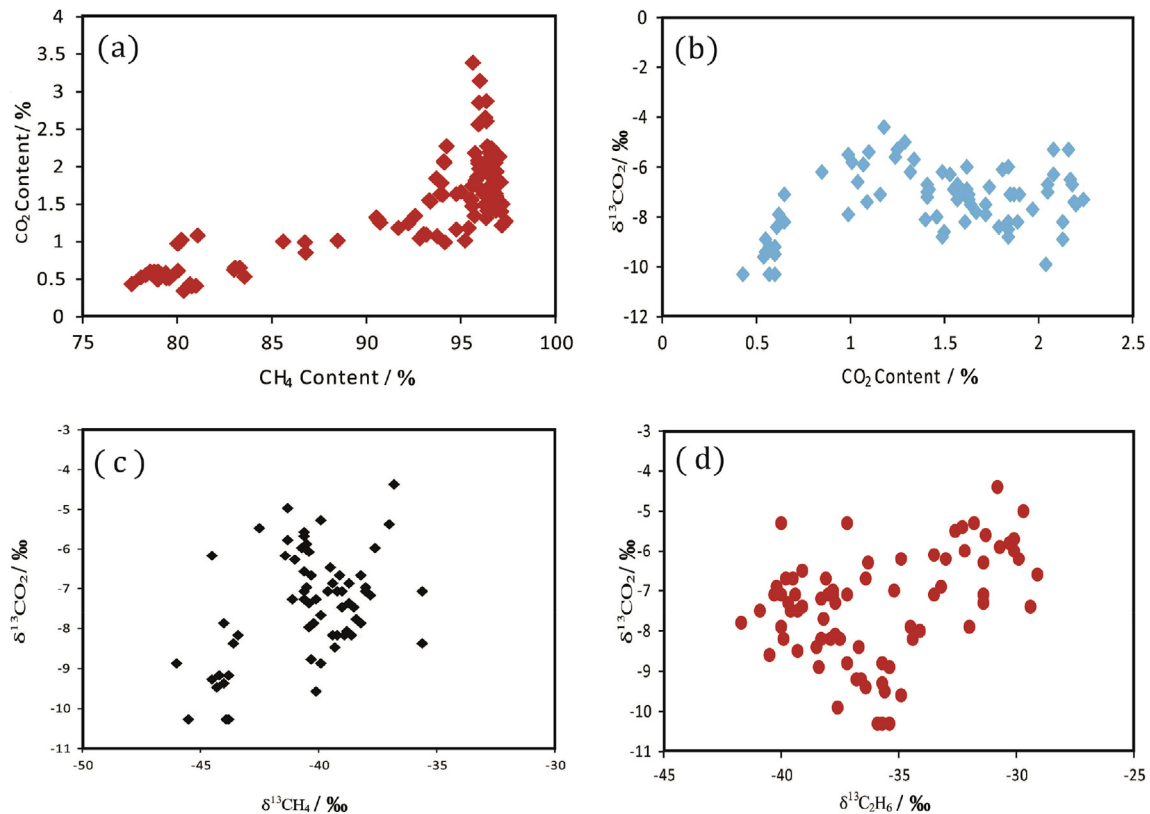


Fig. 8. Variation in the contents and carbon isotope compositions of methane and CO₂ in the Barnett gases.

methane observed in the reservoir is quite possible. The heavier carbon isotope of the remaining CO₂ indicated the high degree of the synthesis reaction. Carbon isotope of ethane and propane observed in the shale gas reservoir is much lighter than the carbon isotope of pyrolysis gas, and as shown by some characters of synthesis gasses. This may be involved with the low contents of the heavy hydrocarbon components at high maturity stage.

4. Conclusions

Pyrolysis of type II kerogen and extractions in the MSSV system as well as the study of the chemical and isotopic compositions of shale gas in productive wells, we arrived at the conclusions that:

- (1) Carbon isotope values of the pyrolysis gasses became heavier with the increasing temperatures, the isotope of alkane hydrocarbons showed a positive trend, that is $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$. The isotope reversal or rollover was not seen in pyrolysis gas, which proved that the isotope reversal may not always be present in shale gas and it should not happen in a pure thermogenic gas reservoir.
- (2) Isotope reversal in shale gas is involved with other geochemical process/es. Isotope reversal for both the Fayetteville and Barnett shale gas is likely to result from reactions between organic matter and H₂O. Ethane with light isotope composition was generated by means of the Fischer-Tropsch synthesis.

- (3) The isotope reversals were mainly witnessed in high/over mature stage. The small amount of C₂₊ components represented isotope characters of synthesized ethane.

Foundation item

This work was financially supported by National Natural Science Foundation of China (Grant No. 41273059) and Chinese Academy of Sciences Strategic Leading Science and Technology Project (Class B, Grant No. XDB10010202).

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

The authors are very grateful to Andrew Carr of Global Exploration Services Ltd. and Advanced Geochemical Systems Ltd. for providing the samples used in the experiment for this paper.

References

- [1] J.B. Curtis, Fractured shale-gas systems, *AAPG Bull.* 86 (11) (2002) 1921–1938.
- [2] J.C. Zhang, Z.J. Jin, M.S. Yuan, Reservoiring mechanism of shale gas and its distribution, *Nat. Gas Ind.* 24 (7) (2004) 15–18.

- [3] X. Xia, J. Chen, R. Braun, Y. Tang, Isotopic reversals with respect to maturity trends due to mixing of primary and secondary products in source rocks, *Chem. Geol.* 339 (2013) 205–212.
- [4] Y.R. Zou, Y.L. Cai, C.C. Zhang, X. Zhang, P.A. Peng, Variations of natural gas carbon isotope-type curves and their interpretation: a case study, *Org. Geochem.* 38 (8) (2007) 1398–1415.
- [5] J.E. Zumberge, K.A. Ferworm, S. Brown, Isotopic reversal ('rollover') in shale gases produced from the Barnett and Fayetteville formations, *Mar. Pet. Geol.* 31 (1) (2012) 43–52.
- [6] A.M. Martini, L.M. Walter, J.C. McIntosh, Identification of microbial and thermogenic gas components from Upper Devonian black shale cores, Illinois and Michigan Basins, *AAPG Bull.* 92 (3) (2008) 327–339.
- [7] A.M. Martini, L.M. Walter, T.C.W. Ku, J.M. Budai, J.C. McIntosh, Schoell, Microbial production and modification of gases in sedimentary basins: a geochemical case study from a Devonian shale gas play, Michigan Basin, *AAPG Bull.* 87 (8) (2003) 1355–1375.
- [8] R.C. Burruss, C.D. Laughrey, Carbon and hydrogen isotopic reversals in deep basin gas: evidence for limits to the stability of hydrocarbons, *Org. Geochem.* 41 (12) (2010) 1285–1296.
- [9] B. Tilley, K. Muehlenbachs, Isotope reversals and universal stages and trends of gas maturation in sealed, self-contained petroleum system, *Chem. Geol.* 339 (2013) 194–204.
- [10] Y.C. Tang, X.Y. Xia, K. Ferworm, Interpretation of gas isotope reversal in natural gas from high mature source rocks, in: *Isotopic Reversal ('Rollover') in Shale Gases Produced from the Barnett and Fayetteville Formations*, 2012, pp. 43–52.
- [11] Y.C. Tang, X.Y. Xia, Kinetics and mechanism of shale-gas formation: a quantitative interpretation of gas isotope 'rollover' for shale gas formation, in: *AAPG Hedberg Conference*, 2010, pp. 5–10.
- [12] J.W. Zheng, D.Q. Sun, X.Y. Li, J.L. Zhang, Advances in exploration and exploitation technologies of shale gas, *Nat. Gas Geosci.* 22 (3) (2011) 511–517.
- [13] Z.H. Chen, Research progress of oil cracking into gas, *J. Shandong Univ. Sci. Technol. Nat. Sci.* 31 (3) (2012) 22–31.
- [14] A.D. Chen, W.Z. Zhang, Y.C. Xu, Isotope characteristics and its application of products from hydrocarbon generating thermal simulation experiments on sedimentary rock, *Sci. China Ser. B* 23 (2) (1993) 209–217.
- [15] J.G. Du, Z.J. Jin, H.S. Xie, L.P. Bai, W. Liu, Stable carbon isotope compositions of gaseous hydrocarbons produced from high pressure and high temperature pyrolysis of lignite, *Org. Geochem.* 34 (1) (2003) 97–104.
- [16] E. Tocque, F. Behar, H. Budzinski, Carbon isotope balance of kerogen pyrolysis effluents in a closed system, *Org. Geochem.* 36 (6) (2005) 893–905.
- [17] R.J. Hill, Y. Tang, I. Kaplan, Insight into cracking based on laboratory experiments, *Org. Geochem.* 34 (12) (2003) 1651–1672.
- [18] Y.H. Shuai, Y.R. Zou, P.A. Peng, Kinetic model for the stable isotope of methane: the stable of the art, *Adv. Earth Sci.* 18 (3) (2003) 405–411.
- [19] E.M. Galimov, *Isotope Organic Geochemistry* (translated by S. Gong, J. Li and G. Hu), Petroleum Industry Press, Beijing, 2007, pp. 1–178.
- [20] S.F. Lu, J.J. Li, H.T. Xue, Y.G. Huang, L.H. Xu, Comparison of fractionation models of carbon isotope, *Nat. Gas Ind.* 26 (7) (2006) 1–4.
- [21] X.Q. Tang, G.H. Huang, M. Zhang, C.o Chen, J.P. Han, D. Wu, X.S. Zhou, Stable carbon isotope compositions of gaseous hydrocarbons in pyrolysis experiment and geochemical significance, *Nat. Gas Geosci.* 21 (6) (2010) 1029–1035.
- [22] J.J. Sweeney, A.K. Burnham, Evaluation of a simple model of vitrinite reflectance based on chemical kinetics, *AAPG Bull.* 74 (10) (1990) 1559–1570.
- [23] W.L. Jia, Q.L. Wang, J.Z. Liu, P.A. Peng, B.H. Li, J.L. Lu, The effect of oil expulsion or retention on further thermal degradation of kerogen at the high maturity stage: a pyrolysis study of type II kerogen from Pingliang shale, China, *Org. Geochem.* 71 (2014) 17–29.
- [24] M. Zhang, G.H. Huang, G.Y. Hu, H.J. Zhao, J. Li, C.S. Zhu, Z.Y. Xiao, Geochemical study on oil cracked gases and kerogen-cracked gases (I): experimental simulation and products analysis, *Sci. China Ser. D* 52 (Suppl. 2) (2009) 1–9.
- [25] H. Tian, A Study on the Kinetic Modeling of Natural Gas Generation and Gas Accumulation in the Platform Area of Tarim Basin, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou, 2006, pp. 35–43.
- [26] L.G. Guo, X.M. Xiao, H. Tian, Z.G. Song, Distinguishing gases derived from oil cracking and kerogen maturation: insights from laboratory pyrolysis experiments, *Org. Geochem.* 40 (10) (2009) 1074–1084.
- [27] H.M. Chung, J.R. Gormly, R.M. Squires, Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution, *Chem. Geol.* 71 (1) (1988) 97–104.
- [28] H.F. Gai, X.M. Xiao, Mechanism and application of carbon isotope reversal of shale gas, *J. China Coal Soc.* 38 (5) (2013) 827–833.
- [29] L. Gao, A. Schimmelmann, Y. Tang, M. Mastalerz, Isotope rollover in the shale gas observed in laboratory pyrolysis experiments: insight to the role of water in thermogenesis of mature gas, *Org. Geochem.* 68 (2014) 95–106.
- [30] F. Baldassare, The origin of some natural gases in Permian through Devonian age systems in the Appalachian Basin and the relationship to incidents of stray gas migration, in: *Presentation Prepared for Proceeding of Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods*, [S.L.], 2011.
- [31] Y.R. Zou, Z.F. Wei, Y.L. Cai, W. Tao, J.Z. Liu, Abiogenic gas and the deep gas in the Songliao Basin: an overview and consideration, *Nat. Gas Geosci.* 20 (5) (2009) 657–663.