

Original research paper

# Characteristics of stable carbon isotopic composition of shale gas<sup>☆</sup>

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## 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.

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**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

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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 ( $I_{\text{H}}$ ) of 640 mg/g and  $T_{\text{max}}$  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

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