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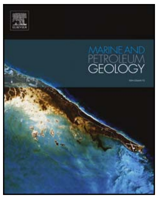

Research paper

# Distinguishing kerogen and oil cracked shale gas using H, C-isotopic fractionation of alkane gases

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## ABSTRACT

The formation mechanism of 23 shale gas samples from the Fuling shale gas field in the Upper Ordovician Wufeng ($O_3w$) Formation-Lower Silurian Longmaxi ($S_1l$) Formation marine shales was investigated based on the carbon and hydrogen isotopes of methane, ethane, and propane. Fuling shale gas is mainly composed of alkane gases, and has a dryness coefficient, $C_1/C_{1\text{-}3}$, of 0.992–0.993. The reversed carbon isotopic trend where $\delta^{13}C_1 > \delta^{13}C_2$ is a typical characteristic indicating mixing of kerogen cracked gas and crude oil cracked gas. The empirical correlations between ln ($C_1/C_2$) vs. ln ($C_2/C_3$) and ln ($C_1/C_2$) vs. $\delta^{13}C$ of alkane gases at different thermal maturity levels were used to distinguish kerogen cracked gas from crude oil cracked gas. Five stages of kerogen cracking and crude oil cracking were identified with a wide range of thermal maturities (vitrinite reflectance $\%R_o$): 1) $\%R_o < 0.8$: shale gas showed a normal isotopic trend ($\delta^{13}C_1 < \delta^{13}C_2$) and was dominated by primary kerogen cracking; 2) $\%R_o$ of 0.8–1.5: primary kerogen cracking ended, and crude oil cracking was initiated, which is associated with a normal isotopic trend of methane and ethane ($\delta^{13}C_1 < \delta^{13}C_2$); 3) $\%R_o$ of 1.5–1.8: the gas is the mixture of gases from both late kerogen cracking and oil cracking, with an initially reversed carbon isotopic trend of $\delta^{13}C_1 > \delta^{13}C_2$; 4) $\%R_o$ of 1.8–2.5: residual kerogen cracking proceeded to generate $CH_4$, and light oil cracking generated heavier gaseous hydrocarbons, with a completely reversed carbon isotopic trend of alkane gases ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$); 5) $\%R_o > 2.5$: further cracking of heavier gaseous hydrocarbons generated $CH_4$.

## 1. Introduction

Shale gas refers to the adsorbed and free gas that exists in pores and fractures in organic-rich shales, interbedded siltstones, and thin carbonate layers. Gaseous hydrocarbons generated within shales rich in organic matter (OM) cannot be easily expelled due to the low porosity, poor permeability, and gas adsorption of the rock. Instead, hydrocarbons are stored within the source rocks (Schettler and Parmely, 1990; Martini et al., 1998). Trapped gaseous hydrocarbons can originate from oil cracking at high temperature or from aromatization of kerogen relics to gas at a high level of thermal maturity, as well as from a mixture of both sources (Behar et al., 1995, 1997; Berner et al., 1995; Boudou et al., 1994; Chung et al., 1988; Jurisch et al., 2012; Kroos et al., 1995, 2005; Tang et al., 2000). For example, natural gas in the Puguang gas field was derived from the cracking of crude oil associated with thermochemical sulfate reduction (TSR) alteration (Hao et al., 2008), while gas in the Hotan River gas field was derived as kerogen cracked gas from sapropelic marine source rocks (Liu et al., 2010). Here, kerogen cracked gas is defined as the gas from both primary kerogen cracking at a low level of thermal maturity and the aromatization of kerogen relics to gas at a high level of thermal maturity.

In conventional gas reservoirs, crude oil cracking is considered as the main gas source in deep buried reservoirs (Liu et al., 2008, 2013). However, kerogen cracked gas derived from OM-rich source rocks at a high level of thermal maturity is often negligible because liquid hydrocarbons expelled from the source rocks become trapped and accumulate in traps along the migration paths. As a result, the pore spaces of the reservoirs become filled with oil, which undergoes thermal cracking to gas at a high level of thermal maturity. Thus, the amount of crude oil cracked gas is much greater than that of kerogen cracked gas (Zhang et al., 2014), and the residual reservoir bitumen in shale confirmed that the crude oil has been cracked (Bernard et al., 2012; Cardott et al.,

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2015). Nevertheless, kerogen cracked gas is a particularly important part of shale gas because the presence of kerogen relics in OM-rich shale not only contributes to gas generation, but also provides OM-hosted pores for gas storage in the kerogen (Zou et al., 2010; Bernard et al., 2012; Xia et al., 2013; Cardott et al., 2015). The proportions of gas from kerogen cracked gas and oil cracking at different levels of thermal maturity lead to variations in shale gas geochemical characteristics.

In recent years, scientists have observed a complete reversal of the normal carbon and hydrogen isotopic trends of alkane gases in shale gas both in the United States and China ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$, $\delta^2H_1 > \delta^2H_2$) (Dai et al., 2014; Hao and Zou, 2013; Tilley et al., 2011). Through a comprehensive analysis of the geochemical characteristics of Barnett and Fayetteville Shale gas, Zumberge et al. (2012) proposed that carbon isotopic reversal occurs in shale gas when the $\%R_o$ value is greater than 1.5 and the wetness coefficient is less than approximately 5%. As a result, the $i$-$C_4$/$n$-$C_4$ ratio rapidly decreases, indicating the onset of thermal cracking of wet gas. Xia et al. (2013) proposed that mixing of kerogen cracked gas from the shale and gas cracked from earlier formed crude oil and condensate in the shale at high thermal maturity is the primary cause of alkane isotopic reversal. By analysing the isotope characteristics of shale gas from the Barnett and Fayetteville Shales, fractured gas reservoirs in the Appalachian Basin, and shale gas and tight gas from the Western Canada Basin, Tilley and Muehlenbachs (2013) classified the thermal evolution of natural gas in an independent and closed petroleum system into three successive stages. These stages included a pre-rollover stage with a typical normal sequence ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$) ($\%R_o \le 1.5$), a rollover stage with $\delta^{13}C_1 > \delta^{13}C_2$ ($1.5 < \%R_o \le 2.0$), and a post-rollover stage with a complete reversal sequence ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$) ($\%R_o > 2.0$) (Xia et al., 2013; Tilley and Muehlenbachs, 2013).

In the post-rollover stage, $CH_4$ becomes enriched in $^2H$ with increasing maturity, and reaches isotope exchange equilibrium with water. Gao et al. (2014) conducted pyrolysis simulation experiments under both wet and anhydrous conditions using type II kerogen, and found that the carbon isotopic reversal occurred at a $\%R_o$ value between 1.49 and 1.65. In addition, it was found that water might be required for both pyrolysis of higher hydrocarbons to methane and for the Fischer-Tropsch synthesis reaction to generate hydrocarbon gases. Suda et al. (2014) studied the $CH_4$-$H_2$-$H_2O$ system of Hakuba Happo hot spring gas and concluded that the water-rock reaction below 150 °C can generate methane with $\delta^{13}C_1$ values between −38.1‰ and −33.2‰. This overlaps with the carbon isotopic composition of organic methane. However, this carbon isotopic composition is slightly more enriched in $^{13}C$ than that of early-formed oil-type methane generated at a low level of thermal maturity. Thus, the current view of carbon and hydrogen isotopic reversals in shale gas remains controversial. The source of the controversy is the identification of shale gas with different origins (i.e., distinguishing the carbon and hydrogen isotopic evidence of crude oil cracked gas from that of residual kerogen cracked gas at a high level of thermal maturity).

To elucidate the variation of carbon and hydrogen isotopic compositions of shale gas, we conducted an analysis of the chemical composition and carbon and hydrogen isotopic characteristics of shale gas in the Fuling shale gas field of the Sichuan Basin in China. A comparison between gas geochemistry in the Fuling shale gas field and the geochemical characteristics of shale gas from major North American shale gas production fields, including 129 gas samples from Barnett and 101 gas samples from Fayetteville, was also performed (Tilley et al., 2011; Tilley and Muehlenbachs, 2013; Zumberge et al., 2012). Moreover, in order to compare the carbon and hydrogen isotopic compositions between $O_3w$-$S_1l$ shale gas in the Fuling shale gas field and conventional natural gas which are both derived from the $O_3w$-$S_1l$ source rocks, we have selected the conventional natural gas in the Carboniferous layers of the Sichuan Basin (16 gas samples) (Liu et al., 2013, 2014a, b). Lastly, we classified genetic types and developed a carbon isotopic fractionation model for Fuling shale gas formation at a high level of thermal evolution, and the results could be extended to other marine shale gas with different thermal maturity. The model will contribute to understand the carbon isotopic fractionation of marine shale gas at different thermal evolution stages.

## 2. Geological background

In the Late Ordovician-Early Silurian, the Sichuan Basin entered a transitional period from a passive continental margin to a foreland basin, which was represented as a "three-uplift and one-depression" shelf with a northern opening (Liang et al., 2008). The Qianzhong palaeohigh, Chuanzhong palaeohigh, and Xuefeng palaeohigh were located on the southern, western, and eastern sides of the Sichuan Basin, respectively. In the Early and Middle Ordovician, the ocean located in the Sichuan narrowed and became surrounded by uplifts, forming a low energy and anoxic depositional environment (Liang et al., 2009). Two global transgressions during the Late Ordovician and Early Silurian resulted in the formation of organic-rich black shales in the Wufeng and Longmaxi formations in the Upper Yantze platform, particularly in the Sichuan Basin (Zou et al., 2010).

The Jiaoshiba structure of the Fuling shale gas field formed as a box-shaped anticline with reverse fault development in the southwest, northwest, southeast, and east. Faults within the main Jiaoshiba structure are relatively undeveloped (Fig. 1). Controlled by the sedimentary environment of deep water shelf, the thickness of shale gas reservoirs in the Wufeng and Longmaxi formations in Fuling ranges from 84 m to 163 m. However, the main production layer of shale gas is distributed at the top of Wufeng Formation and the bottom of Longmaxi Formation with TOC > 2.0%, and the thickness of the black shale in the layer varies from 34 m to 46.7 m, with an average thickness of 38 m (Fig. 2) (Jin et al., 2016). The black shale contains abundant pyrite, siliceous radiolaria, bone needles, and other fossils. The average silica content is 44.82%, indicating that black shale formation was related to reducing deep shelf environment (Dai et al., 2014). According to the calculation from the bitumen reflectance (Rb) after Jacob (1989), the equivalent $\%R_o$ values of shale from the Jiaoye 1 well in the Wufeng-Longmaxi formations vary from 2.2% to 3.1%, with a mean equivalent $\%R_o$ value of 2.79%, suggesting over-mature organic matter (Dai et al., 2014). Nitrogen adsorption experiments have shown that the average pore diameter of reservoirs in the Wufeng Formation-1st Member of Longmaxi Formation is 2.9–3.8 nm (Liu, 2015). Moreover, a petrophysical property analysis using helium showed that the porosity of the gas-bearing horizon in the reservoirs ranges from 2.78% to 7.08%, with an average of 4.8%, and the permeability ranges from $0.0016 \times 10^{-3}\,\mu m^2$ to $216.601 \times 10^{-3}\,\mu m^2$, with a mean of $0.16 \times 10^{-3}\,\mu m^2$ (Liu, 2015).

With the rapid development of US shale gas, driven by the large-scale application of horizontal drilling and multiple-stage fracturing technologies, SINOPEC has evaluated shale gas field exploration since 2006. On November 28, 2012, a high yield shale gas stream of $20.3 \times 10^4\,m^3/d$ was achieved from the Jiaoye 1HF well. The proven geological shale gas reserves in the Fuling shale gas bearing area are $380.6 \times 10^9\,m^3$ (of a total area of $383.54\,km^2$) at the end of 2015, marking the birth of the first large-scale shale gas field in China. As of June 29, 2015, the Jiaoye 1HF well had been in continuous production for 914 days with a hydraulic pressure of 11.2 MPa, a casing pressure of 12.86 MPa, and an average daily gas production of $6.2 \times 10^4\,m^3/d$. The cumulative gas and water productions were $6014.55 \times 10^4\,m^3$ and $283.06\,m^3$, respectively. Moreover, the production rate remained stable, and the pressure decline was very slow (Liu, 2015). By the end of 2014, 178 wells were drilled in the Fuling shale gas field, and 136 wells were completed, with an average well depth of 2885 m. Among them, 89 wells were in gas production; the average single well production rate was 327, 200 $m^3/d$ and the highest yield was up to 591,000 $m^3/d$. The cumulative gas production reached $12.24 \times 10^8\,m^3$ (Liu, 2015).