Gas geochemistry characteristic of shale gas in Longmaxi Formation, SE Sichuan Basin, China

Chunhui Cao[1, 2, 3], Li Du[1], Liwu Li[1], Jian He[1] and Zhongping Li[1]

[1] Key Laboratory of Petroleum Resources, Gansu Province/ Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[2] Key Lab of Mineral Resources in Western China (Gansu), School of Earth Sciences, Lanzhou University, Lanzhou 730000, China

E-mail: caochunhui@lzb.ac.cn

Abstract. Shale gas samples collected from Lower Silurian Longmaxi Formation of Southern Sichuan Basin in Weiyuan were analysed for stable isotope composition of noble gases and molecular composition, stable carbon isotope composition of hydrocarbons. Results show these shale gases are of organic origin gas, and produced at high-over maturity stage. All the analysed hydrocarbon gases reveal complete inversed isotopic trends from methane to propane, and $\delta^{13}C_1$, $\delta^{13}C_2$ have obviously different between Weiyuan and Changning areas. CO_2 was mainly generated during thermogenic processes of transformation of organic matter, although some gases can contain components from endogenic processes and from thermal destruction of carbonates. He and Ar are mainly product of α-decay of U and Th enriched in crustal materials. A small contribution of mantle origin He was found in the gas reservoirs. Continuous monitoring data indicate $^3He/^4He$ ratio didn't change with the mining time.

1. Introduction

An enormous amount of potential shale gas resources exist in the Chinese Sichuan Basin and the amount of recoverable resources in the area of Weiyuan-Neijiang-Luzhou-Yibing reaches roughly 3 trillion m^3. Of this amount, there are (4.1-10.3) × 10^{12} m^3 of shale gas resource reserves in the Longmaxi Formation stratum, lying at a burial depth of less than 4000 m [1]. Exploratory development of shale gas in the areas of Changning-Weiyuan, Zhaotong, Fushun-Yongchuan and Fuling in the Sichuan Basin has achieved quite a high rate of commercial gas production, where the average gas yield of each trial-produce well now reaches as high as 1.5 × 10^5 m^3/ day.

Methane is the main component of shale gas produced by horizontal well fracturing in Longmaxi Formation of the Sichuan basin, and this type of shale gas has the lowest humidity of all gases on Earth (0.24–0.70%). Results of carbon isotope analysis for shale gas emanating from a well in the Longmaxi Formation in the Changning-Weiyuan area indicate that the carbon isotopic reversal has the following order: $\delta^{13}C_1>\delta^{13}C_2>\delta^{13}C_3$. However, there is an evident difference in the carbon isotope composition between the areas of Changning and Weiyuan; the $\delta^{13}C_1$ and the $\delta^{13}C_2$ values in the Weiyuan area are roughly 8‰ and 6‰ lighter, respectively, than in the Changning area [2, 3]. Differences in the carbon isotope composition of methane between Changning and Weiyuan could possibly be attributed to the following two causes: firstly, it is possible that the shale gas went through different geochemical processes during its generation and evolution in these two areas [4], and secondly, shale gas possibly currently undergoes different physical processes (adsorption/desorption) during the storage and exploitation processes conducted in these two areas.

In recent years, stable isotopes and noble gases have been used to discuss natural gas geochemistry, and have particularly been used to distinguish bacterial and thermogenic gas origins where characterization of parameters relate to the genesis of thermogenic gas (such as primary versus secondary cracking, system openness, relations between gas isotope signatures, and biodegradation) [5-7]. This paper uses noble gas isotopes, gas composition, and stable carbon isotopes to analyze free gas in the Longmaxi shale of SE Sichuan Basin. The original/carbon isotopic difference between the shale gases in SE Sichuan Basin is then discussed. The aim of this paper is to provide theoretical guidance for the exploration and development of shale gas in the Changning and Weiyuan areas, as well as in other areas with marine organic-rich shale.

2. Geological setting

The Sichuan Basin in southeast China is located to the west of the Yangtze Craton and covers an area of more than 18×10^4 km^2. It is a multiple-cycle sedimentary basin, confined in the north by the Micang Mountains (uplift) and the Daba Mountains (fold belt), in the south by the Daxiangling and Lou Mountains (fold belt), in the west by the Longmen Mountains (fold belt), and in the east by the Dalou Mountains (Figure 1). The Caledonian, Hercynian, Indosinian, and Yanshanian orogenies and the Himalayan movement are all recorded in this basin; these tectonic movements resulted in complex deformation and denudation [8, 9]. The Sichuan Basin experienced a transition from marine facies to continental facies sedimentation at the end of the Middle Triassic, and there are six sets of source rocks within the basin: the Lower Cambrian, Lower Silurian, Lower Permian, Upper Permian, Lower Jurassic and Upper Triassic. Of these, the first four sets represent the dominant source rocks [10, 11], and the area is an important oil- and gas-bearing superimposed basin. The Longmaxi Formation of the Lower Silurian is widely distributed throughout the Sichuan Basin and consists of black graptolitic shale in the lower section and nodular limestone in the upper section [12].

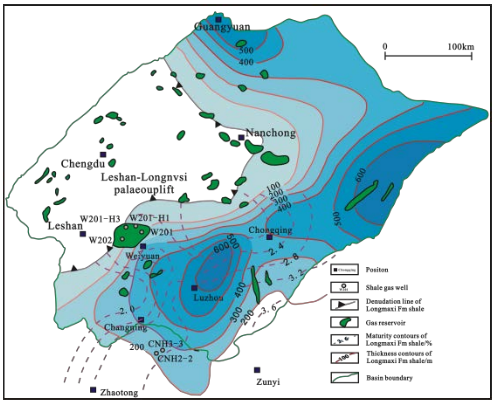

Figure 1. Geological sketch map of Sichuan Basin showing locations of main gas sampling sites, isolines of Ro values, and shale thickness of Longmaxi Formation

3. Samples and experiments

Natural gas samples were collected from the Longmaxi Formation in the Lower Silurian strata, the southwest of the Sichuan Basin. Free gases were collected directly at the well head using a high pressure cylinder (~1000 cm^3, 15 Mpa) with metal valves on both ends, and atmospheric contamination during sampling was minimized by allowing the gas to flush through the system for approximately 5 min [13]. After collecting samples, the pressure of the metal container was retained at higher than 1 atm to prevent possible atmospheric leakage into the container. General information of sampling site locations is given in Figure 1.

Chemical composition, C isotopic compositions and noble gas isotope compositions were analyzed in the Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences at Lanzhou. Chemical composition and isotopic compositions analysis methods were described in Cao et al. (2016). The purification and analysis steps of noble gas and data correction procedures were described in details in previous works [14, 15].

4. Results and discussion

Carbon isotope analysis results of Longmaxi Formation in SE Sichuan basin are shown in Figure 2. $\delta^{13}C_1$=-27.2‰~-36.8‰, $\delta^{13}C_2$= -33.7‰~ -41.9‰; There are obvious differences of carbon isotope composition in Changning and Weiyuan Longmaxi Formation shale gas. Carbon isotopic composition is lighter in Weiyuan than Changning area. $\delta^{13}C_1$= -34.5‰ ~ -36.8‰，$\delta^{13}C_2$= -37.6‰ ~ -41.9‰, in Weiyuan; $\delta^{13}C_1$= -27.2‰ ~ -27.3‰，$\delta^{13}C_2$= -33.7‰ ~ -34.1‰, in Changning. In Weiyuan $\delta^{13}C_1$ is almost 8‰ lighter and $\delta^{13}C_2$ is almost 6‰ lighter than Changning. However, Changning and Weiyuan shale gas carbon isotope distribution patterns are all reversals: $\delta^{13}C_1$>$\delta^{13}C_2$.

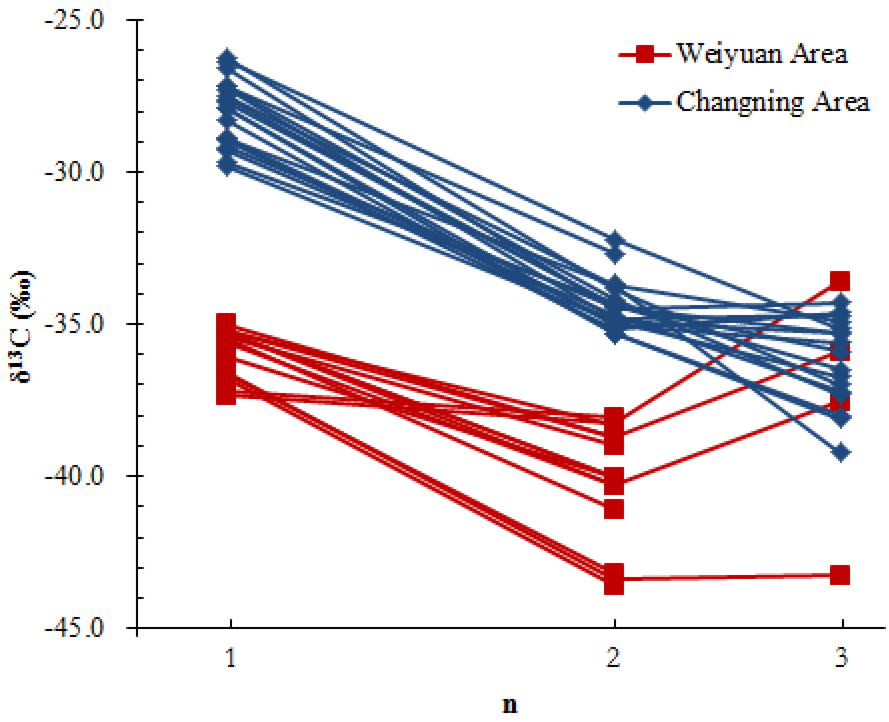

Figure 2. Carbon isotope composition of hydrocarbon from Longmaxi Formation in **SE** Sichuan basin

Molecular and stable isotopic compositions (Figure 3) show that both Weiyuan and Changning shale gases are genetically related to thermogenic activity (thermocatalytic). The genetic correlation determined between the hydrocarbon index and $\delta^{13}C_1$ (Figure 3), and the geochemical analysis of dispersed organic matter revealed the occurrence of mainly mixed type II and III kerogens. A significant proportion of the shale gases in the Weiyuan area are generated from type II kerogen, whereas Changning shale gases are mainly generated from type III kerogen. Weiyuan and Changning shale gases are the driest natural gases in the world [4], and the absence of butanes, pentanes, hexanes, and heptanes in the analyzed gases also indicates that they are genetically connected to the high-over maturity stage.

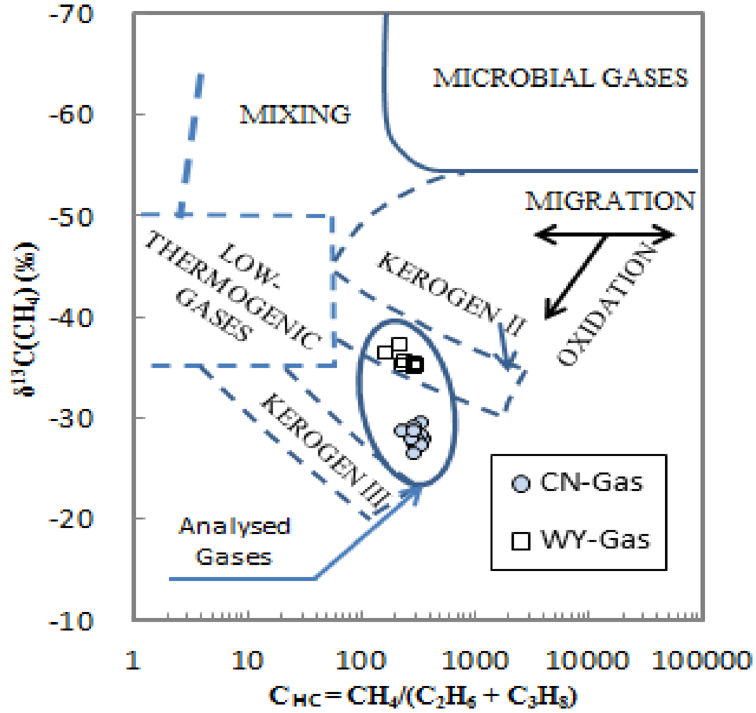

Figure 3. $\delta^{13}C$ of methane versus hydrocarbon index C_{HC} (i.e., CH_4/ [C_2H_6 + C_3H_8]) of methane for analyzed natural gases

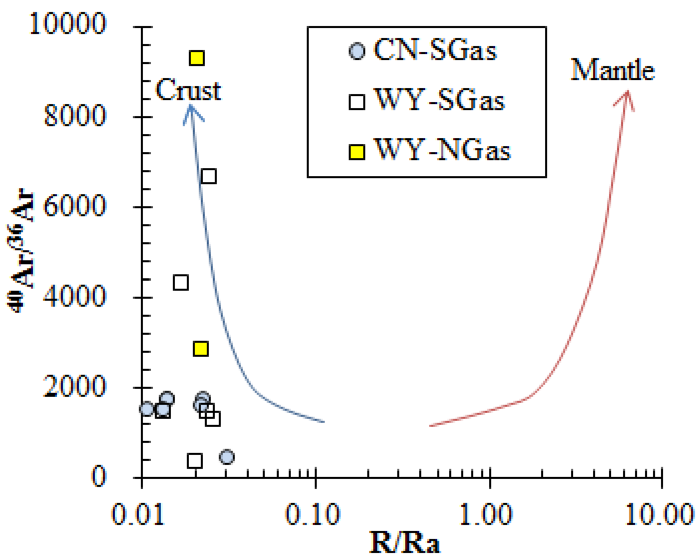

Figure 4. Plot of $^{3}He/^{4}He$ vs. $^{40}Ar/^{36}Ar$

Two main trends can be identified in the plot of helium and argon isotopic ratios (Figure 4). One trend has a negative slope and corresponds to the addition of radiogenic ^{4}He and ^{40}Ar, which is related to the natural radioactivity of sediments and possibly the underlying continental basement. The other trend is a positive slope, which corresponds to mixture with a mantle end-member. However, almost all the samples obtained are under the negative slope line, which suggests that only a small amount of mantle end-member helium and argon are present. Furthermore, there is more ^{40}Ar in Weiyuan shale gas than in Changning shale gas.

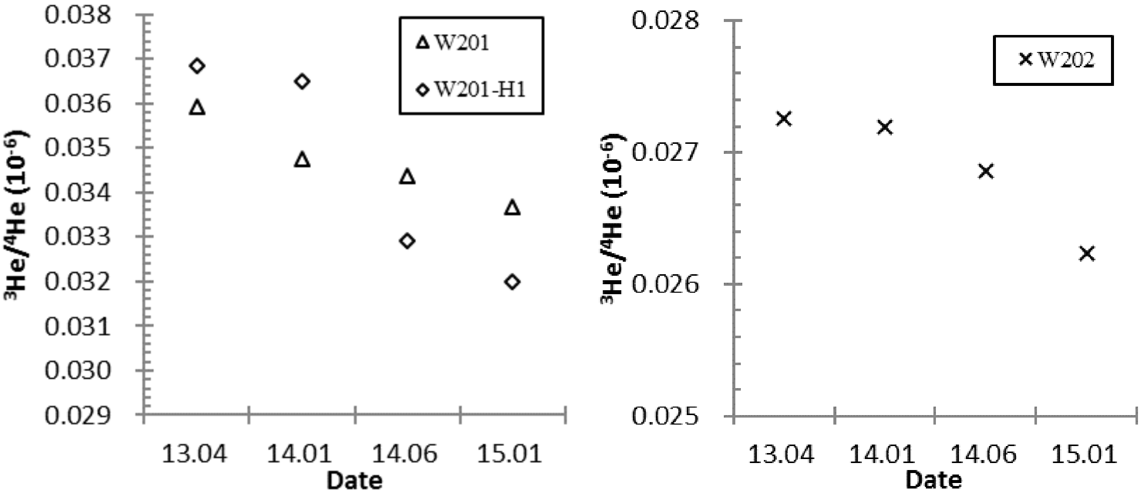

Figure 5. Variations in $^3He/^4He$ with time

W201 and W201-H1 wells were sampled four times between 2014 and 2015, and well W202 was sampled three times (Figure 5, data of 13.04 is from [4]). There were no evident changes in values of $^3He/^4He$ throughout the mining time, but the value of $^3He/^4He$ in W201-H1 tended to be higher than in W201 and W202. This could be because a small amount of He is introduced into the shale when using the horizontal fracturing technique, as fracturing fluids are not added. Despite the yield of shale gas being improved when using the horizontal fracturing technique, to some degree a certain amount of atmospheric constituents are also brought into the shale, which consequently destroys the original characteristics of shale gas.

5. Conclusion

The distribution patterns of carbon isotope compositions are reversals ($\delta^{13}C_1>\delta^{13}C_2$) both in Changning and Weiyuan shale gas. The carbon isotope composition is different in Changning and Weiyuan Longmaxi Formation shale gas. In Weiyuan area, $\delta^{13}C_1$ is almost 8‰ lighter and $\delta^{13}C_2$ is almost 6‰ lighter than Changning area.

Longmaxi shale gases are one of the driest natural gases in the world. They are genetically related to thermogenic gas, and generated from type II and III kerogen. Longmaxi shale gases are genetically high-over maturity gases.

Longmaxi shale gases are mainly Crust origin. Horizontal fracturing technique may change the original chemical characteristic of shale gases.

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