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Original research paper

Geochemical characteristics and implications of shale gas from the Longmaxi Formation, Sichuan Basin, China☆

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Abstract

Gas geochemical analysis was conducted on the shale gas from the Longmaxi Formation in the Weiyuan-Changning areas, Sichuan Basin, China. Chemical composition was measured using an integrated method of gas chromatography combined with mass spectrometry. The results show that the Longmaxi shale gas, after hydraulic fracturing, is primarily dominated by methane (94.0%−98.6%) with low humidity (0.3%−0.6%) and minor non-hydrocarbon gasses which are primarily comprised of CO_2, N_2, as well as trace He. $\delta^{13}C_{CO_2} = -2.5‰-6.0‰$ $^3He/^4He = 0.01-0.03Ra$.The shale gas in the Weiyuan and Changning areas display carbon isotopes reversal pattern with a carbon number ($\delta^{13}C_1 > \delta^{13}C_2$) and distinct carbon isotopic composition. The shale gas from the Weiyuan pilot has heavier carbon isotopic compositions for methane ($\delta^{13}C_1$: from −34.5‰ to −36.8‰), ethane ($\delta^{13}C_2$: −37.6‰ to −41.9‰), and CO_2 ($\delta^{13}C_{CO_2}$: −4.5‰ to −6.0‰) than those in the Changning pilot ($\delta^{13}C_1$: −27.2‰ to −27.3‰, $\delta^{13}C_2$: −33.7‰ to −34.1‰, $\delta^{13}C_{CO_2}$: −2.5‰ to −4.6‰). The Longmaxi shale was thermally high and the organic matter was in over mature stage with good sealing conditions. The shale gas, after hydraulic fracturing, could possibly originate from the thermal decomposition of kerogen and the secondary cracking of liquid hydrocarbons which caused the reversal pattern of carbon isotopes. Some CO_2 could be derived from the decomposition of carbonate. The difference in carbon isotopes between the Weiyuan and Changning areas could be derived from the different mixing proportion of gas from the secondary cracking of liquid hydrocarbons caused by specific geological and geochemical conditions.

Keywords: Stable isotope; Chemical composition; Shale gas; Longmaxi formation; Sichuan basin

1. Introduction

Shale gas is a self-generated, self-stored, and self-enveloped unconventional natural gas gathered in the dark or high carbon mud shale. The shale gas exploration and development in North America has changed the energy structure of the world and has become extremely vital. Shale gas resource is rich in our country [1], especially the Paleozoic Marine black shale generated in the Sichuan Basin, which has a huge potential in terms of shale gas resource, and the dragon stream group of shale in the Lower Silurian series is considered as the most favorable layers for the development of shale gas. There is a humongous gas reserve in Neijiang-Luzhou-Yibin region. Shale gas exploration has gained high-yield commercial production in the Longmaxi Formation in the Changning-

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Weiyuan region of the Sichuan Basin [2] and Jiaoshiba region [3].

Carbon isotope is one of the most important indicators of both natural gas and gas. It is a universal phenomenon. The composition of carbon isotope in shale gas is in inversion with the carbon number distribution patterns all over the world. For example, shale gas that is widespread worldwide possesses carbon isotopic composition of the inversion occurrence with the carbon number distribution patterns. Examples are as follows: The four main shale gas production regions are the Barnett, Woodford, Haynesville, and Fayetteville in America and the Appalachian shale gas production region in Canada. They comprehended phenomenon [4−8] of gaseous hydrocarbon carbon isotopic inversion confirms that most of the carbon isotope inversion are related to the production of shale gas, which can indicate the "core" region of shale gas [5,6,8]. The reason behind carbon isotope inversion of the dragon stream group in Sichuan Basin still lacks systematic research, and it requires further investigation to find out whether it is related to the shale gas production.

The geochemical gas research of shale gas offers an important and direct basis for the forming mechanism of shale gas especially the contribution of the secondary cracking of crude gas content on shale gas, the tectonic activity on the preservation, dispersion of shale gas, and the gas content in shale and the development of air source. This paper analyzes the chemical composition and carbon isotope of the dragon stream group of the Silurian system in the Changning and Weiyuan regions in the south of the Sichuan Basin. Geochemical features of the shale gasses from the two regions were compared with one another as well with the shale gas from Barnett, America. The origin of hydrocarbon and nonhydrocarbon gasses and the factors and significance of the shale gas isotope inversion in the area are to be discussed.

2. Regional geologic setting

Sichuan basin is a complex superimposed basin with both sea and land in the Tethys tectonic domain. Its basement consists of a set of pre-Sinian system, lower Sinian metamorphic rocks, and magmatic rocks. From Paleozoic to Mesozoic up until Cenozoic, Sichuan Basin completely evolved the craton basin to foreland basin. Thick carbonatite (4000−7000 m) was formed from Sinian to the Early Triassic, and it became thinner in the west, yet thicker in the east [9]. It includes six main effective hydrocarbon source rocks, namely, the Lower Cambrian series, Upper Ordovician series, Wufeng Formation-Lower Silurian series, Lower Permian series, Upper Permian series, Upper Triassic series, and the Lower Jurassic series. The Lower Cambrian and the Upper Ordovician-Lower Silurian series are the main exploration targets [2], especially the Upper Ordovician series and the Wufeng Formation-Lower Silurian series of the Longmaxi Formation have high quality black rich organic shale (100−600 m thick), it became the most favorable shale gas development strata (Fig. 1).

Longmaxi Formation is comprised of dark gray to black graptolite shale, carbonaceous shale, siliceous shale, silty shale, and argillaceous siltstone. Kerogen is mainly type I or II_1, there was high carbon content, the TOC ranges from 0.35% to 8.4% (average 2.52%), but it usually 1%−2%. The black shale had an effective thickness of 20−268 m with high thermal evolution degree. The vitrine reflectance ranges from 1.85% to 4.2% (average 2.69%), the porosity is low (1.2%−10.8%), and there was low permeability (0.25μD−1.737 mD). Not to mention, it was rich in brittle minerals (40%−70%, on average, 56.3%) and organic matter nanopore, it had high gas content (0.3−5.1 m^3/t, an average of 1.9 m^3/t), and the depth is moderate (2000−3600 m) [1,10]. These conditions are conducive to the formation and enrichment of shale gas. Medium and upper shale clip in thin-layer limestone, siltstone, single layer are 1−10 m thick; the cumulative thickness is 20−40 m, but the thickest was more than 100 m. The lower shale is rich in organic matter and it had high carbon content, the TOC content was 1.5% [11], thickness is 30−80 m. It is the most advantageous zone for shale gas exploration and development in the south.

The Longmaxi Formation in both the Weiyuan and Changning district has dissimilar geology and geochemical characteristics. The Weiyuan district is a shallow deep shelf facie that's uplifted and denudated by the Caledonian movement. The shale residual thickness ranges 0−300 m, buried within 1500−3700 m [10], the TOC is more than 2%, organic-rich shale about 40 m, on average TOC is 3.0%, $R_O = 2.7\%$, permeability is 0.042μD; However, it is deep shelf facies in Changning, and buried in 0−3000 m. The thickness of organic-rich shale (TOC > 2%) is about 40 m, TOC content is 3.5% on an average, and the $R_O = 3\%$, permeability is 0.30μD [12].

3. Material and methods

3.1. Collected shale gas samples

Shale gas samples were collected from the shale gas production wells of both the Weiyuan and Changning district within the Longmaxi Formation. Using a high-pressure steel cylinder, 6 gas samples were collected from the shale gas production wells. High-pressure steel cylinder was pumped to a vacuum in the laboratory, recurrent washing using shale gas when collecting samples was carried out. Shale gas inlet pressure is 0.6−0.7 MPa in Weiyuan (Samples: LZ-1, LZ-2, LZ-3). The inlet pressure of LZ-4 is 3.1 MPa. LZ-5 and LZ-6 in the Changning district measure 3.04 MPa and 3.4 MPa, respectively.

3.2. Experimental analysis

Chemical composition, carbon and hydrogen isotopes, and rare gas isotopes of shale gas were analyzed in the Key Laboratory of Petroleum Resources of Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics, CAS. Chemical composition was detected by a gas chromatograph and gas mass spectrometer [13]. The absolute content of nonhydrocarbon gasses, methane, and ethane was detected by

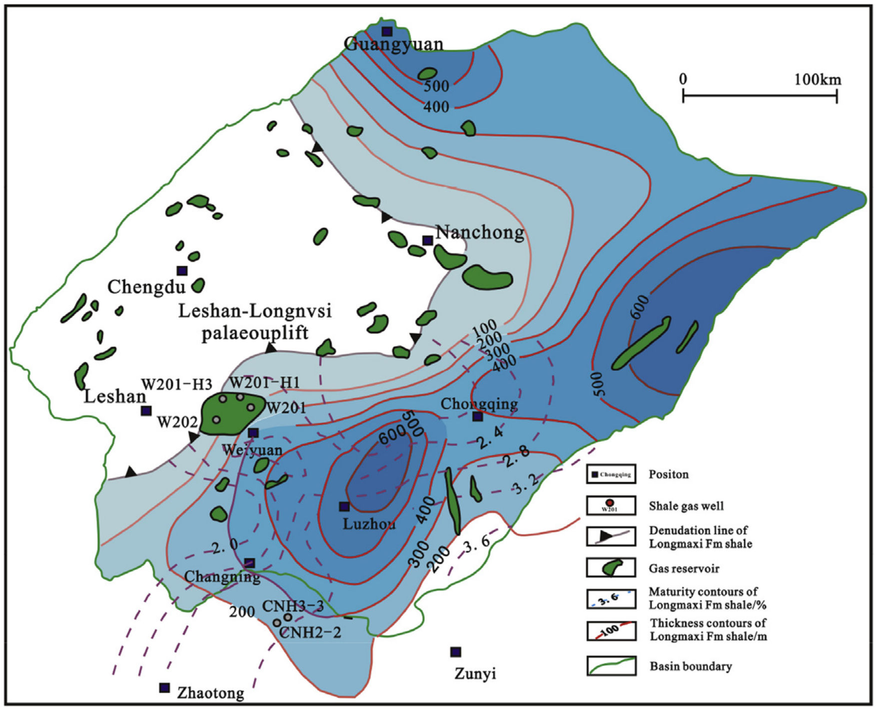

Fig. 1. Gas field distribution, isolines of R_O values as well as shale thickness of the Longmaxi Formation in the Sichuan Basin [2].

MAT271 gas mass spectrometer. High carbon number hydrocarbon gas (C_{3+}) were analyzed and calibrated by GC-9160 gas chromatograph. Then methane data was normalized by means of mass spectrum and gas chromatograph data. The standard deviation of this analysis method in detecting relative components is higher than 0.5% (Table 1). Repetitive experiments were carried out on LZ-4.

Carbon isotope analysis is completed using the GC-C-MS system [14]. Agilent 6890 gas chromatograph separated the different gas composition in the shale gas. Then high-temperature oxidation furnace (C) oxidized the hydrocarbons into CO_2. CO_2 was analyzed by DeltaPlus XP carbon isotope mass spectrometer. Z202 was used to meet laboratory standards; the calibration standard used was VPDB. The analytical error of CH_4 and C_2H_6 is greater than 0.5‰; analytical error for CO_2 is superior (1.10‰). The hydrogen isotope was analyzed by a GC-TC-MS system. Agilent GC6890 separated the different hydrocarbon components in shale gas. Then high-temperature pyrolysis furnace (TC) converted the hydrogen into H_2. Hydrogen isotope was analyzed by MAT253 mass spectrometer. Z202 was used to meet laboratory standards; the calibration standard used was V-SMOW. Analytical error is greater than 5‰ and repetitive experiments were carried out using LZ-4 collected in the Weiyuan region and LZ-5 collected in the Changning region.

Helium isotope was analyzed by a rare gas mass spectrometer: noblesse. The air from the Gaolan mountain top was used to meet laboratory standards ($^3He/^4He = 1.4 \times 10^{-6}$). Two-stage separation and purification system were used for rare gas enrichment [15,16]; $^3He/^4He$ analysis error is less than ±1.5%.

Table 1
Chemical composition (%) of shale gas for parallel experiments.

LZ-4	CH_4	C_2H_6	C_3H_8	CO_2	N_2	He	Ar
1	96.7	0.5	0.02	0.5	1.8	0.1	0.01
2	97.8	0.4	0.02	0.5	1.2	0.1	0.01
3	97.9	0.4	0.02	0.5	1.2	0.1	0.01
4	97.9	0.4	0.02	0.5	1.2	0.1	0.01
5	97.9	0.4	0.02	0.5	1.2	0.1	0.01
6	97.8	0.4	0.02	0.5	1.2	0.1	0.01
Average	97.7	0.4	0.02	0.5	1.3	0.1	0.01
SD	0.5	0.1	0.00	0.0	0.3	0.0	0.00

4. Results

4.1. Repetitive experimental results of shale gas composition

The chemical composition analysis was repeated six times using LZ-4. The results are as shown in Table 1. The chemical composition analysis data is stable. The standard deviation of CH_4 and N_2 is not greater than 0.5% and 0.3%, respectively. The composition of the rest of the chemicals is all less than 0.1%.

The carbon isotope analysis was repeated six times using LZ-4 and LZ-5. The results are shown in Table 2. The standard deviation of $\delta^{13}C_1$ and $\delta^{13}C_2$ are not more than 0.4‰. The standard deviation of $\delta^{13}C_{CO_2}$ is 0.62‰ and 1.10‰, respectively.

The repeated experiment gave results that show this experimental method can detect more gas composition, also,

Table 2
Carbon isotopic compositions ($\delta^{13}C$, ‰VPDB) of shale gas for parallel experiments.

	LZ-5			LZ-4		
	CH_4	C_2H_6	CO_2	CH_4	C_2H_6	CO_2
1	−27.2	−34.1	−4.3	−36.5	−37.5	−3.9
2	−27.1	−34.1	−5.0	−36.9	−37.5	−3.2
3	−27.2	−34.4	−5.3	−36.9	−37.0	−5.5
4	−27.2	−34.0	−3.9	−36.8	−37.6	−6.0
5	−27.4	−34.2	−4.2	−36.7	−38.0	−3.9
6	−27.3	−34.6	−3.7	−36.7	−37.8	−3.7
Average	−27.2	−34.2	−4.34	−36.8	−37.6	−4.4
SD/%	0.1	0.2	0.6	0.2	0.4	1.1

methane and other major components have high repeatability and low system error.

4.2. Chemical composition of shale gas

Chemical composition results of the Weiyuan and Changning areas of the Longmaxi Formation in the Sichuan Basin are shown in Table 3. The content of CH_4 is high (94.03%−98.59%), C_2H_6 content ranges 0.30%−0.30%, C_3H_8 content ranges 0.01%−0.02%. Humidity ($\sum C_{2-3}/\sum C_{1-3}$) of the output shale gas is low (0.33%−0.62%). It is one of the world's driest gas [2]. Non-hydrocarbon gas content, mainly N_2 and CO_2, is low; the average content is 1.7% for N_2 and 0.7% for CO_2. Helium content ranges 0.02%−0.14%, Argon content ranges 0.01%−0.03%. However, H_2S was not detected.

The CH_4 content in the Changning region are of the Longmaxi Formation is higher than it is in the Weiyuan region. In the Weiyuan region, CH_4 content ranges 94.03%−94.03% with an average of 96.40%. The C_2H_6 content ranges 0.30%−0.30% with an average of 0.42%. The C_3H_8 content is 0.01%. In the Changning region, CH_4 content ranges 98.31%−98.31%w with an average of 98.45%. The C_2H_6 content ranges 0.43%−0.43% with an average of 0.50%. The C_3H_8 content ranges 0.01%−0.02% with an average of 0.02%. Non-hydrocarbon content is higher in Changning than in the Weiyuan region. The CO_2, N_2, He, Ar content were 0.5%, 0.5%, 0.02%, 0.01% in Changning, whereas they were 0.8%, 2.2%, 0.09%, 0.02%, in the Weiyuan region.

Table 3
Chemical and Isotopic compositions of shale gas in the Longmaxi Formation in the Sichuan Basin.

Samples	Composition/%								Humidity/%
	CH_4	C_2H_6	C_3H_8	CO_2	N_2	He	Ar	H_2S	
LZ-1	97.8	0.6	0.01	0.9	0.6	0.14	0.02	–	0.6
LZ-2	94.0	0.3	0.01	1.0	4.4	0.03	0.01	–	0.3
LZ-3	95.8	0.3	0.01	1.0	2.7	0.13	0.03	–	0.4
LZ-4	97.9	0.4	0.01	0.4	1.1	0.05	0.01	–	0.5
LZ-5	98.3	0.6	0.02	0.5	0.6	0.02	0.01	–	0.6
LZ-6	98.6	0.4	0.01	0.4	0.5	0.02	0.01	–	0.5

Note: humidity = ($\sum C_{2-3}/\sum C_{1-3}$).

4.3. Shale gas isotopic composition

Carbon isotope, hydrogen isotope, and helium isotope analysis results of the Weiyuan and Changning in the Longmaxi Formation within the Sichuan Basin are shown in Figs. 2−4.

$\delta^{13}C_1$ = −27.2‰ to −36.8‰, $\delta^{13}C_2$ = −33.7‰ to −41.9‰; $\delta^{13}C_{CO_2}$ almost the same, $\delta^{13}C_{CO_2} > -8‰$. $^3He/^4He$ is 0.01−0.03 Ra (Ra = Rs/Ra). There are apparent differences in 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‰ to −36.8‰, $\delta^{13}C_2$ = −37.6‰ to −41.9‰, in Weiyuan; $\delta^{13}C_1$ = −27.2‰ to −27.3‰, $\delta^{13}C_2$ = −33.7‰ to −34.1‰, in Changning. In Weiyuan $\delta^{13}C_1$ is almost 8‰ lower and $\delta^{13}C_2$ is almost 6‰ lower than Changning. However, Changning and Weiyuan shale gas carbon isotope distribution patterns are all reversals: $\delta^{13}C_1 > \delta^{13}C_2$.

5. Discussions

5.1. Non-hydrocarbon gas source

The Longmaxi Formation in the Sichuan Basin contains a certain amount of non-hydrocarbon gas such as N_2, CO_2, and He. It is one of ideal means to identify the source of shale gas. These gasses may be derived from the pyrolysis of organic matters, carbonate mineral decomposition (e.g., CO_2), atmosphere, and mantle degassing. By the value of $\delta^{13}C_{CO_2}$ and $^3He/^4He$ we can effectively judge its source [17−19]. The content of CO_2 ranges from 0.4% to 1.0% in the Weiyuan and Changning shale gas. Meanwhile, $\delta^{13}C_{CO_2}$ is higher of about 2.20‰−5.98‰. The carbon isotope value belongs carbonate mineral decomposition (R/Ra < 1). The shale of marine origin have high organic carbon content (TOC > 2%), carbonate minerals are abundant as well. After a deep burial (1500−4000 m) and evolution, the organic origin of CO_2 and CO_2 comes from carbonate mineral dissolution mixed

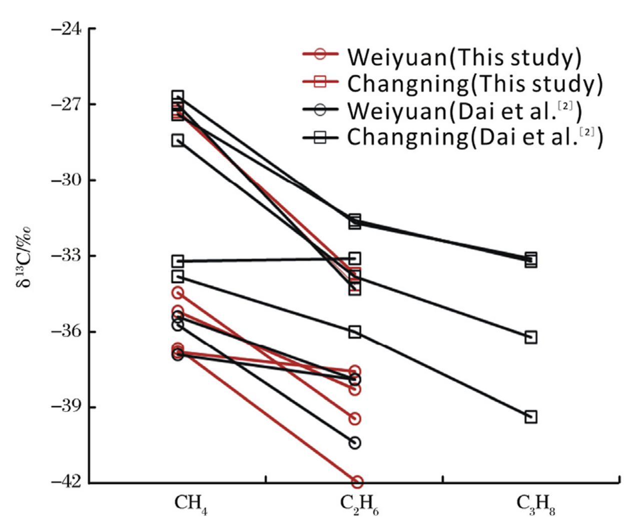

Fig. 2. Carbon isotope characteristic of Longmaxi Formation in Sichuan Basin.

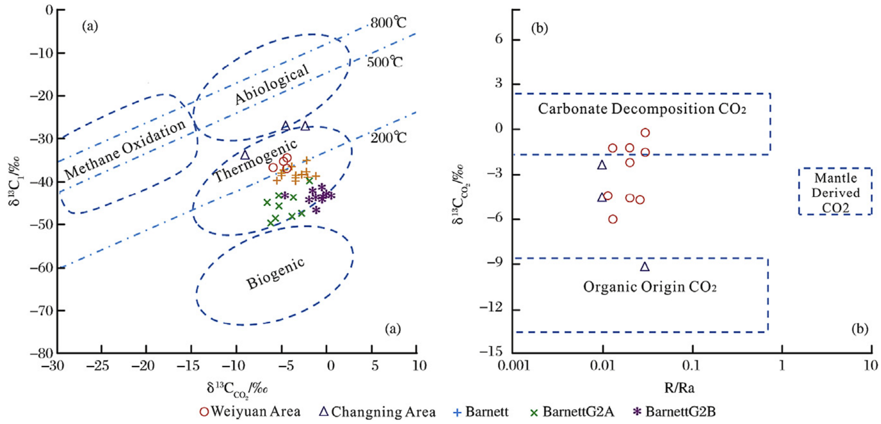

Fig. 3. $\delta^{13}C_{CO_2}$ versus $\delta^{13}C_1$ (a) and R/Ra (b) of shale gas in the Longmaxi Formation in the Sichuan Basin.

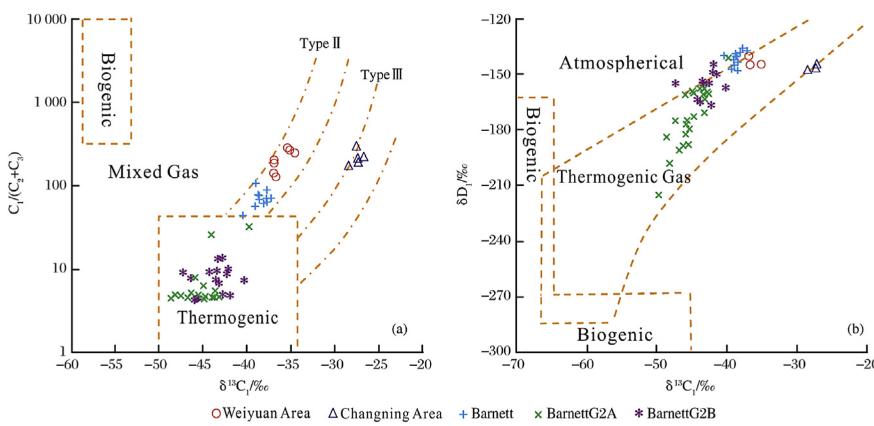

Fig. 4. Relationship of $\delta^{13}C_1$ and $C_1/(C_2 + C_3)$ of shale gas in the Longmaxi Formation in the Sichuan Basin.

together. $\delta^{13}C_{CO_2}$, $\delta^{13}C_1$, and R/Ra support the inference (Fig. 3a, b).

The origin of highly concentrated N_2 in the Sichuan Basin Longmaxi Formation maybe of organic, atmospheric, or mantle source [20,21]. Atmospheric N_2 includes the blended atmospheric composition when the shale gas developed and N_2 in the atmosphere that saturated water into shale; mantle source of N_2 comes from volcanic activity or mantle fluid. The Ar: N_2 ratio (0.002:0.039) is not the same as the atmospheric value (0.012). $^3He/^4He$ (0.01–0.03Ra) is lower than the value of the atmospheric (1 Ra $= 1.4 \times 10^{-6}$) and mantle source (1.1×10^{-5}). The atmosphere and mantle-derived gas mixed can be ruled out. So the high content N_2 should come from organic matter thermal evolution process.

After microbial ammoniation, in the organic matters' immature stage, organic matters yield an increasing number of nitrogen and stored them [22]. Then, with the maturity of organic matter increase, the energy can make the amino group (NH_2) fracture (205 kJ/mol) [21]. Ammoniation can take place under the effect of a thermal catalyst and could produce Ammonia (NH_3). Ammonia could generate N_2 in two ways:

$$8NH_3 + 3CO_2 \rightarrow 3CH_4 + 4N_2 + 6H_2O \quad (1)$$

$$2NH_3 + 3Fe_2O_3 \rightarrow 6FeO + N_2 + 3H_2O \quad (2)$$

When the organic matter goes into the mature stage ($R_O > 2.0\%$), the energy can break nitrogen compounds to release nitrogen (>230 kJ/mol). Cracked organic matters produce N_2. N_2 origin from organic matters crack at the high over mature stage is the main source of oil and gas basin [21]. Shale in Sichuan basin experience high over mature stage, the N_2 (<5%) should come from pyrolysis of organic matter. The high content of N_2 in residual gas in shale supports the inference [23]. It also shows that organic matter evolution comes into a high over mature stage.

5.2. Production cause of shale gas hydrocarbon gas

Compared to North America's Barnett shale gas, the shale gas in the Sichuan basin has more CH_4. The carbon isotope of CH_4 is heavier and the value of $C_1/(C_2 + C_3)$ is higher (Fig. 4). Shale gas in the Longmaxi Formation comes from type II–III kerogen that's in a high mature stage. The Changning kerogen is not I or II_1 type. This shows that shale gas may be kerogen thermal degradation gas and liquid hydrocarbons secondary cracking gas mixed altogether [23]. Carbon and hydrogen isotopic composition of methane and ethane indicate that the Longmaxi shale is in high over maturity stage ($R_O > 2.0\%$).

The hydrogen isotope of shale gas in the Longmaxi Formation, Sichuan Basin, is centralized $\delta D_{CH4} = -133‰$ to

−151‰. It shows that the parent material belongs to the typical marine sedimentary environment [24]. Methane carbon and hydrogen isotopes correlation can distinguish the origin of gas [25]. $\delta^{13}C_1$ and δD_{CH4} in Fig. 4b show that the shale gas' methane is thermogenic (Fig. 4b). $\delta^{13}C_2$ is controlled by parent material kerogen carbon isotope composition; it is the most important gas source index [26−28]. The Silurian shale gas' ethane carbon isotope is lighter than −28‰. Hence, shale gas in this area belongs to liquid hydrocarbon cracking gas. This is consistent with the conclusion that the residual gas came from liquid hydrocarbons secondary cracking [23].

Longmaxi shale gas presents a carbon isotopic reversal: $\delta^{13}C_1 > \delta^{13}C_2$ (Fig. 2), this is similar to the North American shale gas. There are different inducements for the carbon isotope reversal mechanism such as the mixture of different gas sources, secondary cracking of oil and gas or diffusion, the reaction of water to oil and gas, etc. Carbon isotope reversals can be used to indicate overpressure and shale gas reservoir with high yield [5,6,8,29].

Shale gas has two origins, namely biogenic and pyrolysis product. The two type of shale gas is characterized by positive sequence distribution of carbon isotopes. Liquid hydrocarbons secondary cracking gas always has an antitone sequence (i.e., isotopic reversals) order. The Sichuan Basin shale has high maturity (R_O = 1.85%−4.2%) and high dry coefficient (99.38%−99.67%), C_{3+} content is extremely low. Longmaxi shale is in the high over mature stage, thus, gaseous hydrocarbon begins to crack [2,7,29]. Carbon isotope reversals in the Weiyuan and Changning district are mainly caused by the secondary cracking of oil and gas.

5.3. The factors of carbon isotopic composition difference

The Weiyuan and Changning districts' shale gas has apparent differences in carbon isotope characteristics (See Chapter 4.3). Shale gas carbon isotope composition is controlled by hydrocarbon source rock types, gas migration [30,31], mixture of gas with various origin [4,7], water−rock reaction [5,29,32] and other factors.

The Longmaxi shale in Weiyuan-Changning area was mainly of type I and II_1 kerogen. They have the same type of organic matter [2,11,33]. Therefore, the source rock type can't be the main factor for carbon isotope differences in the two areas.

Shale gas, for the most part, are adsorbed gas, free gas, and dissolved gas stored in the shale pore and fracture. Sichuan Basin is within a strong tectonic activity area and fracture development. Most of the shale experienced multiple tectonization that resulted to shale gas diffusion [33,34]. Tectonic movement in the Weiyuan and Changning district is different as well. The Weiyuan region has experienced strong subsidence from the Triassic to the Early Cretaceous, but in the Late Cretaceous, a tectonic uplift took place. Strata temperature and pressure had changed greatly and it affected shale gas enrichment and preservation [35,36]. Shale gas wells in the Weiyuan district is roughly 1520−3000 m. However, the depth of the Changning district wells was more than 3500 m [10]. The process of mining caused gas diffusion that leads to early shale gas to have lighter carbon isotope [37]. Nevertheless, carbon isotopic data have no significant changes between 2012's and 2014's samples [2]. This shows that the gas diffusion cannot cause any difference between the Weiyuan and Changning shale gas.

The ratio of ^3He to ^4He demonstrates that there is no atmosphere and that the mantle source gas is mixed in shale gas [38]. It's mainly thermal degradation gas and liquid hydrocarbons secondary cracking gas mixture. The Weiyuan Longmaxi shale is thicker, lower in organic content, and shallower in terms of buried depth compared to the Changning district. Liquid hydrocarbon cracking methane is lighter than residual kerogen cracking methane. Higher organic content and higher maturity provide the material basis and conditions for oil and gas secondary cracking in Changning district. So most of organic and oil were cracking in Changning and less asphaltene left [9,39,40]. The higher the molecular weight the smaller the activation energy needed to alkane cracking, hence, it is easier to crack; chemical bonds between lighter isotopes rupture easily. In the late cracking stage of oil and gas, the low molecular weight of alkane gradually enriches heavier isotopes (^{13}C, D) in the process of evolution [41,42]. The permeability of the Changning shale is higher than that in the Weiyuan shale. Some free gas may be lost due to osmosis; residual shale gas obtained heavy carbon isotope composition [43]. It follows that the difference in thermal evolution between the Weiyuan and the Changning could lead to liquid secondary hydrocarbon cracking gas mixture ratio that's different. Thusly, the differences of carbon isotope composition may be related to liquid hydrocarbons secondary cracking gas mixing ratio.

6. Conclusions

(1) Sichuan basin's Longmaxi shale gas has high CH_4 content, low C_{2+} content, and high dry coefficient. It's one of the driest gas in the world. Non-hydrocarbon gas content such as N_2, CO_2, and trace He was low. ($\delta^{13}C_1$ = −27.2‰ to −36.8‰, $\delta^{13}C_2$ = −33.7‰ to −41.9‰) The shale gas carbon isotopes are reversals. ($\delta^{13}C_{CO_2}$>−8‰; $^3He/^4He$ = 0.01−0.03 Ra)

(2) Geochemical characteristics between the shale gas from the Weiyuan and Changning districts have noticeable contrast. Hydrocarbon gas content (94.14%−98.73%) in the Weiyuan shale gas is lower than that in the Changning shale gas (98.89%−99.03%). Not to mention, $\delta^{13}C_1$ and $\delta^{13}C_2$ is lighter by 8‰ and 6‰, respectively, in the Weiyuan shale gas than in the Changning shale gas.

(3) The Sichuan Basin's Longmaxi shale gas is a mixture of cracking gasses that were produced in various thermal evolution stage, including kerogen initial cracking gasses, liquid hydrocarbons secondary cracking gas, and gaseous hydrocarbons secondary cracking gas. There were traces of small amounts of carbonate mineral decomposition of CO_2. Different geological and geochemical conditions lead to carbon isotope reversal made a big disparity between the Weiyuan and Changning districts.

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Conflict of interest

The authors declare no conflicts of interest.

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