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Effect of methane cracking on carbon isotope reversal and the production of over-mature shale gas

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Abstract: The geochemical statistics indicate that the wetness (C_2-C_5/C_1-C_5) of over-mature shale gas with carbon isotope reversal is less than 1.8%. The magnitude of carbon isotope reversal ($\delta^{13}C_1$-$\delta^{13}C_2$) increases with decreasing wetness within a wetness range of 0.9% ~1.8% and then decreases at wetness < 0.9%. The experimental result demonstrates that CH_4 polymerization proceeding to CH_4 substantial cracking is an important factor involved in isotope reversal of over-mature shale gas. Moreover, $\delta^{13}C_1$-$\delta^{13}C_2$ decreases with an increase in experimental temperature prior to CH_4 substantial cracking. The values of $\delta^{13}C_1$ and $\delta^{13}C_2$ tend to equalize during CH_4 substantial cracking. The $\delta^{13}C_1$-$\delta^{13}C_2$ of mud gas investigated at different depths during shale gas drilling in Sichuan Basin increases initially, then decreases with further increase in the depth and finally tends to zero, with only a trace hydrocarbon gas being detectable. Thus, the approximately equal value between $\delta^{13}C_1$ and $\delta^{13}C_2$ for over-mature shale gas and very low wetness could potentially serve as useful criteria to screen CH_4 substantial cracking. Two geochemical indices to indicate CH_4 substantial cracking in geological setting are proposed according to the variation production data with geochemistry of over-mature shale gas in Sichuan Basin, China.

Keywords: over-mature shale gas; Magnitude of isotope reversal; CH_4 polymerization; CH_4 cracking; Mud gas

1. Introduction

Geological explorations in the 21st century have resulted in the discovery of extensive reserves of shale gas with isotopic reversal [1–3]. These expeditions elucidated that shale gas with isotopic reversal developed in areas where the maturity of source rock was much greater than 2.0% R_o [2, 4].

In recent years, substantial research has been conducted to unravel the mechanism of isotopic rollover and reversal of over-mature natural gas. However, the specific procedures involved in this phenomenon remains to be not understood completely. Over the past two years, a novel approach was proposed which implied that isotopic reversal of over-mature shale gas was related to CH_4 polymerization occurring in the early stage of CH_4 cracking [5, 6]. Chen, B. et al. [5] proved that shale gas with carbon isotope reversal could be produced via a CH_4 pyrolysis experiment conducted in a closed gold tube system. Furthermore, Mi, J.K. et al. [6] also demonstrated that the CH_4 polymerization could form a heavy hydrocarbon gas (C_2–C_5) with depleted $\delta^{13}C$ by continuous heating at 450–800 °C, while performing the CH_4 thermal cracking experiment at a heating rate of 20 °C per hour . They further hypothesized that the combination of methyl formed in the early CH_4 cracking stage (termed CH_4 polymerization) was a crucial factor for isotope reversal in over-mature shale gas and that the magnitude of carbon isotope reversal ($\delta^{13}C_1$-$\delta^{13}C_2$) was inversely proportional to the degree of CH_4 cracking. In other words, the $\delta^{13}C_1$-$\delta^{13}C_2$ would mirror the degree of over-mature natural gas cracking, to some extent. Zumberge,

J. et al. [1] found that the high production of shale gas occurs only at low wetness values (<5%) corresponding to isotopic reversal and the biggest producers tend to have more negative ethane carbon isotope compositions. If the hypothesis that carbon isotopic reversal of over-mature gas is relative with CH_4 cracking. There should be a genetic relationship between CH_4 cracking and the $\delta^{13}C_1$-$\delta^{13}C_2$ in over-mature shale gas.

CH_4 is the most stable hydrocarbon component and the chief composition in natural gas [7]. CH_4 thermal stability or the natural gas geochemistry corresponding to CH_4 substantial cracking in geological setting is very important to determine the largest depth of natural gas exploration [8]. The present study investigated the geochemical data of several hundred isotopically "abnormal" shale gas. Then, a CH_4 pyrolysis experiment was conducted to investigate the carbon isotope variation of hydrocarbon gas generated in CH_4 cracking process. The similar variations in $\delta^{13}C_1$ and $\delta^{13}C_2$ of mud gas with increasing depth in three shale gas production wells and in that of gaseous products with increasing experimental temperature in CH_4 cracking experiment indicates that CH_4 polymerization and CH_4 substantial cracking would happen in geological setting. Finally, two geochemical indices to indicate CH_4 substantial cracking are proposed according to the experimental result of CH_4 pyrolysis experiment, $\delta^{13}C_1$ and $\delta^{13}C_2$ variation of mud gas with increasing depth and variation of shale gas production as a function of geochemical composition in Sichuan Basin. The scope of this work is to offer new insight into geochemistry to aid the exploration of over-mature shale gas.

2. Isotope reversal range variation of over-mature natural gas with the wetness

Previous exploration has proven that the shale gas with isotope reversal possesses very low wetness [2,3,8]. The relationship between wetness and $\delta^{13}C_1$-$\delta^{13}C_2$ for isotopic reversal natural gas obtained from gas fields in the US and China is shown in Figure 1. It is evident that $\delta^{13}C_1$-$\delta^{13}C_2$ variation with decreasing wetness of over-mature shale gas can be represented by parabolic curve. The wetness of shale gas with isotope reversal is less than 1.8%. The $\delta^{13}C_1$-$\delta^{13}C_2$ increases initially with decreasing wetness within wetness range of 0.9% ~1.8% and then decreases at wetness < 0.9%.

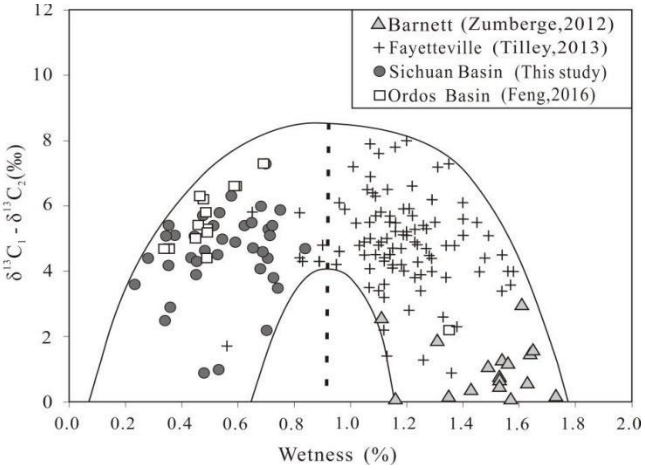

Figure 1. Relationship between wetness and $\delta^{13}C_1$-$\delta^{13}C_2$ of the shale gas with isotope reversal

Several researchers have attempted to unravel the mechanism underlying the isotopic reversal of over-mature natural gas since it was extensively encountered in shale gas. Their interpretations on the same can be classified into four types. (1) The isotopic reversal of shale gas at over-mature stage is caused by mixing of primary gas from kerogen cracking and secondary gas from the cracking of remained hydrocarbons [2,3,9]. (2) The redox reactions between water and CH_4 at 250–300 °C generate isotopically light carbon dioxide and hydrogen, which further interact and form isotopically light ethane (C_2H_6) and finally cause the isotopic reversal of the shale gas [1, 8]. (3) Isotope fractionation mechanism during gas desorption from depressurized late-mature shale leads to isotope reversal in the residual gas produced from shale formation [4]. (4) CH_4 polymerization prior to its substantial cracking causes the isotopic reversal of over-mature natural gas [5,6].

(1) Mixing mechanism：In all mixing model, one end member employed in mixing process was characterized by high wetness (wetness >20% generally), while another one was a dry gas (wetness < 5%). For instance, the wetness of the two end members that were selected as primary gas and residual cracking gas by Xia X.Y. et al.[9] for their mixing model were 2.44% and 63.6%, respectively. The 63.6% wetness of residual cracking gas was so high that it rarely exists naturally in geological settings, especially in a shale system with over maturity. Oil-prone kerogen pyrolysis experiment results under hydrous and anhydrous conditions in a closed system illustrated that mixing between primary and cracking gases would not yield isotopic reversal, only isotopic rollover [10,11]. While the wetness of two end members involved in a mixing model are fixed, the geochemistry of gases involved in a mixing process is variable in a geological setting. Thus, the interpretation on isotope reversal of over-mature shale gas by mixing mechanism does not hold true.

(2) Mechanism of oxidation-reduction reactions between CH_4 and H_2O: In geological settings, as the geological temperature attains the range at which CH_4 can react with water (i.e., 250–300 ^oC), C_2H_6 reacts with water prior to CH_4 owing to the comparatively lower activation energy. The reaction between C_2H_6 and water would result in the residual C_2H_6 possessing heavier carbon isotope. Thus, the model of carbon isotopic reversal will not occur.

(3) Isotope fractionation mechanism during the uplift and depressurization of shale：The initial gas generated in the shale exhibits a normal isotope trend, with $\delta^{13}C_1<\delta^{13}C_2$. After the generation of the new gas essentially ceases at high maturities (VR>2%) and the uplift as well as depressurization are initiated, methane enriched in ^{12}C desorbs from the source rock more rapidly than CH_4 enriched in ^{13}C. Consequently, the residual CH_4 becomes enriched in ^{13}C more rapidly than the residual C_2H_6, which leads to isotope reversal of the residual gas present in rocks [4]. Thus, the gas stored in conventional reservoirs should exhibits a normal isotope trend in view of this fractionation mechanism. However, the natural gases with isotopic reversal were found both in marine conventional gas carbonate reservoir in Sichuan Basin, China [12] and in coal-derived tight reservoirs [13–15]. Therefore, the isotope fractionation mechanism of shale gas might be just a speculation and requires more concrete evidence.

(4) CH_4 polymerization mechanism: In theory, the ultimate product of CH_4 thermal cracking is C and H_2. However, CH_4 does not crack into carbon and H_2 directly during the cracking process, but a gradual dehydrogenation one [5,16,17]. In CH_4 cracking process, a methane molecular dehydrogenate and form a methyl radical (CH_3•) and a hydrogen radical (H•) initially. If two H• combine and form H_2, two CH_3• can also combine to produce C_2H_6. There are two kinds of methane molecules ($^{12}CH_4$ and $^{13}CH_4$) in natural gas. $^{12}CH_3$–H is characterized by preferential bond cleavage, while $^{13}CH_3$–H is not. Thus, the preferentially formed CH_3• is depleted in ^{13}C. $^{12}CH_3$• combination leads to depletion of ^{13}C in heavy gas, and further causes the carbon isotopic reversal of over-mature gas.

Natural gas with the isotopic reversal feature was originally considered to be of abiogenic origin before shale gas with similar features was identified. The abnormal isotopic feature of abiogenic hydrocarbon gas was thought to be caused by polymerization of CH_4 formed by Fischer–Tropsch synthesis between H_2 and CO_2 (or CO) as well [18–20]. However, the hypothesis that CH_4 polymerization leads to isotope reversal in over-mature gas requires further validation with more experimental data.

3. Carbon isotopic variation of hydrocarbon gas products in CH_4 pyrolysis experiment

The modern petrochemical industry has demonstrated that higher hydrocarbons can be generated via CH_4 polymerization in a presence of bifunctional catalysts [16,17]. However, in geological settings with sparse metallic catalysts, whether heavy gases depleted in ^{13}C and generated by CH_4 polymerization can form naturally or not must be experimentally proven. In this study, a CH_4 pyrolysis experiment was conducted without any catalysts in a gold tube system.

To quantify the CH_4 content in products at different temperatures, a mixing gas of N_2 and CH_4 was used in the CH_4 cracking experiment. N_2 was selected as the reference gas in this experiment, as it is the most stable diatomic molecule with a decomposition temperature greater than 3000 ^{o}C, thus ensuring that it could not crack at the highest temperature (800 ^{o}C) used in this experiment. The gas mixture was purchased from Zhaoge Gas Company, Beijing, China, whereby the CH_4 and N_2 (v/v) mixing ratio was 89.67% and 10.33%, respectively. The carbon isotopic value of CH_4 was -26.07% and no other hydrocarbon components were detected in the gas mixture via gas chromatography (GC).

The experiments were performed in a gold tube with a length, outer diameter and thickness of 100, 5.5 and 0.25 mm, respectively. Prior to loading the gas mixture, one end of the tube was sealed by argon-arc welding. To load gas into the gold tube, a special device was developed to connect a vacuum pump and the open tube mouth. In a typical gas loading procedure, the air in the tube was first removed by the vacuum pump to a pressure less than 1 kPa. Then, the open mouth of the tube was closed by a pincer after the mixing gas was injected into the tube from a gas cylinder. Finally, the open end of tube was sealed by argon-arc welding while the tube was immersed in ice water. The pressure of gas injected in the tube was approximately 4 atm in this experiment, which was monitored via a pressure gauge on the gas cylinder. The external fluid pressure was maintained at a constant value of 50 MPa throughout the experiment. Experimental temperature was programmed as follows: the tube was first heated from 20 ºC to 300 ^{o}C in 1 h and held for 30 min, then heated at a rate of 20 ^{o}C/h till the target temperature was arrived. Subsequently, the autoclave heating was terminated, and the tubes were moved to room temperature for analysis.

Duplicate gold tubes were used at every temperature point in case of breakage. Moreover, additional tubes were also used as replicates for gas analysis and quantification.

Identification and quantification of individual hydrocarbon and non-hydrocarbon gas components were carried out using a two-channel Wasson-Agilent 7890 series gas chromatograph. The heating program for the GC oven heated from room temperature to 68 ºC (held isothermal for 7 min), then to 90 °C (at a rate of 10 ºC/min and then held isothermal for 1.5 min.), and finally to 175 ºC (at a rate of 15 ºC /min then held isothermal for 1.5 min). An external standard was used for the chromatographic calibration. Certified gas standards were prepared at a precision of better than ± 0.1 mol% for each component made by BAPB Inc, United State.

The stable carbon isotopes of the hydrocarbon gases were determined by using an Isochrom II GC-IRMS coupled with a Poraplot Q column with helium as the carrier gas. The heating started from an initial temperature at 30 ºC (isothermal for 3 min) with heating at 15 ºC /min to 150 ºC, and held isothermal for 8 min. The measurement of $\delta^{13}C$ for each component was repeated at least twice to ensure that the error of each component was less than 0.3‰. The $\delta^{13}C$ values for each component presented in this work were the average value of two measurements. Trace carbon isotopes of other hydrocarbon gases were not measured in this study.

The geochemistry of gaseous products of CH_4 cracking experiments at different temperatures has been summarized in Table 1. Besides the original components (CH_4 and N_2), heavy hydrocarbon gases (including alkane and alkene) as well as H_2 were formed during the experiment, at different temperatures. The heavy hydrocarbon gases were generated solely via the CH_4 polymerization, as no heavy hydrocarbon gases were present in the original mixing gas. The CH_4 content clearly decreased with increasing temperature (Figure 2, a). However, the CH_4 content decreased slowly below 700 ^{o}C, and a steep decline in

CH_4 content occurred above 700 °C. The percentages of C_2H_6 and H_2 were high in the newly formed components and in the same order of magnitude ($\times10^{-1}$ %). The content of all heavy gases increased initially and then decreased with the increase in temperature (Figure 2, b, c). The corresponding temperatures at which the contents of C_2H_6 and other heavy alkane gas components reached their maximum values were 750 °C and 675°C, respectively. The highest observed percentage of total heavy gas was 1.05% at 750 °C.

The variation in C_2H_6 content with increasing temperature could be classified under three increasing segments (slow, moderate, and intense) as well as a decreasing segment. The slow increase in C_2H_6 content below 575 °C (Figure 2, b) indicated that CH_4 polymerization was weak. Similarly, the moderate increase in C_2H_6 content within a temperature range of 575 °C to 650 °C suggested that CH_4 polymerization increased, while the intense increase in the C_2H_6 content within a temperature range of 650 °C to 750 °C indicated that CH_4 polymerization increased sharply. The decrease in C_2H_6 content above 750°C (Figure 2, b) was relative to the cracking of C_2H_6 formed by CH_4 polymerization.

Table 1. Components and carbon isotopes of gaseous products at different temperatures

Temp (°C)	**Contents (% vol)**									**$\delta^{13}C$ (‰)**	
	CH_4	C_2H_6 ($\times10^{-1}$)	C_2H_4 ($\times10^{-3}$)	C_3H_8 ($\times10^{-2}$)	C_3H_6 ($\times10^{-3}$)	iC_4H_{10} ($\times10^{-3}$)	nC_4H_{10} ($\times10^{-3}$)	H_2 ($\times10^{-1}$)	N_2	CH_4	C_2H_6
450	89.65	0.01	0	0	0	0	0	0	10.35	-26.08	/
475	89.55	0.01	0	0.03	0	0	0	0	10.45	-25.94	/
500	89.53	0.01	0	0.04	0	0	0	0.01	10.47	-25.71	/
525	89.48	0.01	0	0.04	0	0	0	0.06	10.51	-25.71	-33.78
550	89.44	0.02	0	0.04	0	0	0	0.15	10.54	-25.84	-33.51
575	89.31	0.15	0	0.11	0	0	0	0.21	10.66	-25.74	-33.22
600	89.21	0.39	0	0.2	0	0	0	0.35	10.71	-26.01	-32.74
625	89.12	0.69	0.14	0.37	0.31	0	0.27	0.7	10.74	-25.69	-32.47
650	89.06	1.08	0.19	0.56	0.38	0.24	0.37	1.07	10.72	-25.97	-30.26
675	88.66	3.08	2.33	5.19	2.89	1.68	2.56	2.26	10.75	-25.81	-27.47
700	88.41	4.50	1.14	3.97	0.96	0.97	1.62	3.38	10.76	-25.83	-26.02
725	87.25	9.53	1.05	3.75	0.83	0.9	1.39	5.03	11.25	-25.66	-25.11
750	86.25	10.11	0.86	3.41	0.61	0.62	0.98	7.02	12	-25.28	-24.82
775	85.02	8.6	0.58	2.63	0.36	0.45	0.68	8.12	13.28	-25.04	-24.68
800	82.34	7.2	0.22	0.75	0.14	0.24	0.3	9.1	16.02	-24.60	-24.50

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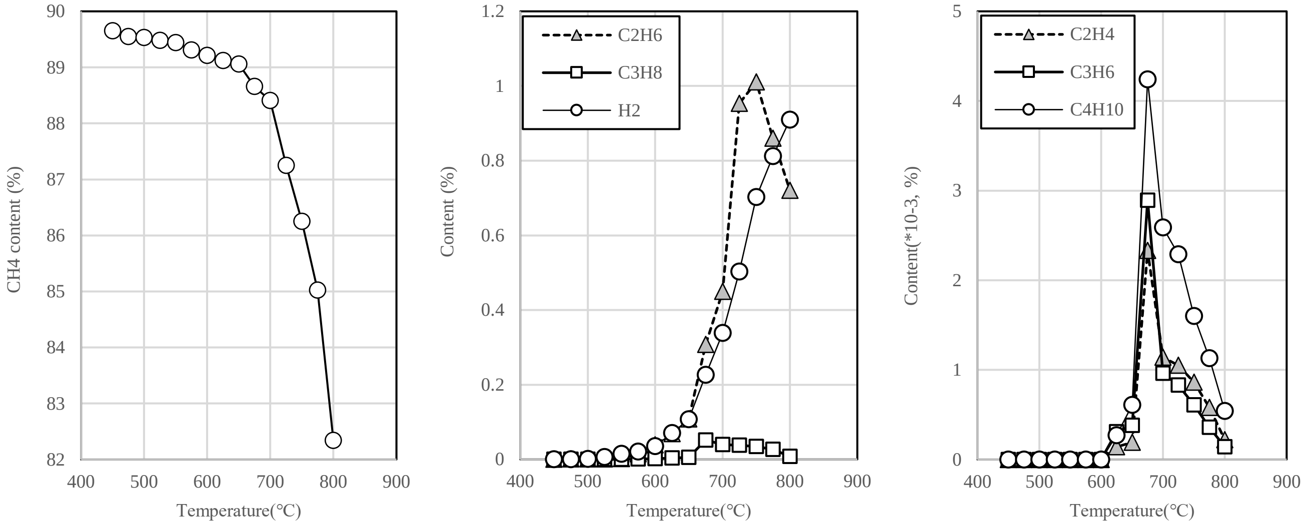

(a) (b) (c)

Figure 2. Concentration variation of gaseous components with increasing temperature

The temperature of 750 °C at which C_2H_6 content began to decrease, was higher than that of 700 °C, at which CH_4 content began to decrease rapidly. This appeared to conflict with the general knowledge in chemistry that the thermal stability of C_2H_6 is lower than that of CH_4. Shuai et al. (2006) observed via a coal pyrolysis experiment in a confined system that the generation and cracking of C_2H_6 could co-exist at high temperatures [21]. Their experiment result indicated that C_2H_6 cracking began at 500 °C in a coal pyrolysis experiment with a same heating rate of 20 °C/h as that in our experiment. In theory, the ultimate products of CH_4 cracking is C and H_2. However, CH_4 does not produced C and H_2 directly in the cracking process, but a gradual dehydrogenation process. The reactions involved in the process include to CH_4 polymerization to form heavy hydrocarbon gas, dehydrogenation of the heavy hydrocarbon gas to produce unsaturated heavy gas and the further dehydrogenation of the unsaturated heavy hydrocarbon gas to generate C and H_2 [5,16,17]. Therefore, all the aforementioned reactions (include to CH_4 polymerization and heavy gas further dehydrogenation or cracking) could not stop as CH_4 does not convert into C and H_2 completely. Although the content of CH_4 decreases obviously at the highest experimental temperature of 800 °C, C_2H_6 does not disappears in experimental products. In other words, C_2H_6 cracking and C_2H_6 formation *vs* CH_4 polymerization could co-exist at high temperatures of our experiment. In the temperature range of 700– 750 °C, the ratio of C_2H_6 formation *vs* CH_4 polymerization was greater than that of C_2H_6 cracking, which was attributed to the increasing of C_2H_6 content in this temperature range. Correspondingly, the higher ratio of C_2H_6 cracking *vs* that of C_2H_6 formation via CH_4 polymerization caused the decrease in the content above 750 °C. In this study, the whole process of CH_4 cracking is divided into two stages: early cracking stage and substantial cracking stage. The early CH_4 cracking stage includes all the reaction prior to solid C formation. Whereas, the substantial CH_4 cracking stage refers from solid C appearance to CH_4 complete conversion into solid C.

The decrease in content of other heavy gas above 675 °C (Figure 2, c) was also caused by their cracking. The same cracking temperature of 675 °C for C_3H_8 and C_4H_{10} did not mean that they shared same thermal stability as well. Instead, the temperature interval 650–675 °C used in this experiment might cover the temperature point at which C_4H_{10} contents began to decrease.

The inner wall of the tubes heated to different temperatures has been depicted in Figure 3. The color of the inner wall of the tube was brown at 725 °C, and became black with increasing temperature. The brown and black solid deposited on inner walls above 725 °C was identified as carbon via energy spectrum analysis. The temperature at which the solid C formed was consistent with that at which CH$_4$ began to decrease sharply. Consequently, the appearance of solid carbon on the tube inner wall at 725 ^{o}C indicated that the substantial cracking of CH$_4$ began in the temperature range of 700–725 ^{o}C.

Zhang et al (2013) had reported that the lowest temperature of solid C generated by CH$_4$ cracking is 400 ^{o}C in a isothermal Fischer–Tropsch experiment [22]. The lowest temperature (725 ^{o}C) of solid C generated in our non-isothermal CH$_4$ cracking experiment is higher than that of solid C appearance in Zhang et al (2013) isothermal Fischer–Tropsch experiment. This difference in temperature corresponding to solid C appearance is attributed to the compensation between temperature and isothermal duration as well as the catalyst effect in Zhang et al (2013) isothermal experiment. Nevertheless, the hydrocarbon gas shares a feature of carbon isotopic reversal before solid C appearance in the two experiments. This also indicates the CH$_4$ polymerization happen before CH$_4$ substantial cracking.

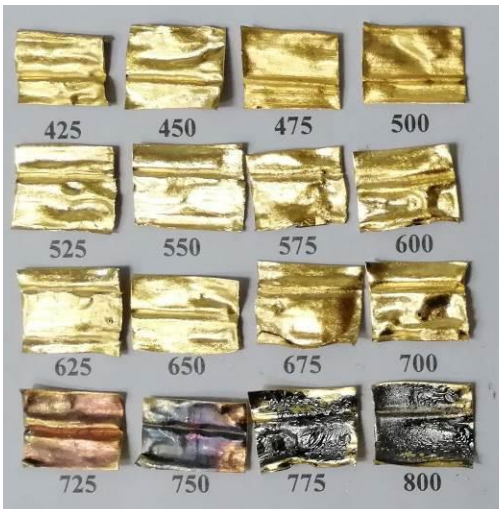

Figure 3. Inner wall photo of tube heated to different temperatures

As presented in Table 1 and Figure 4, $\delta^{13}C_1$ and $\delta^{13}C_2$ generally increased with increasing temperature (Figure 3). The variation in $\delta^{13}C_2$ with increasing temperature could be divided into three segments: gradual increase in $\delta^{13}C_2$ below 625 ^{o}C; rapid increase from 625 to 725 ^{o}C; and slow increase above 725 ^{o}C. The variation of $\delta^{13}C_1$ was not observable within the analytic error (±0.5‰) below 725 ^{o}C. This is consistent with the slight decrease in CH$_4$ content (1.26%) below 725 ^{o}C. The distribution between $\delta^{13}C_1$ and $\delta^{13}C_2$ showed a distinct reversal trend for ($\delta^{13}C_1 > \delta^{13}C_2$) below 725 ^{o}C, while it was normal ($\delta^{13}C_1 < \delta^{13}C_2$) above 725 ^{o}C.

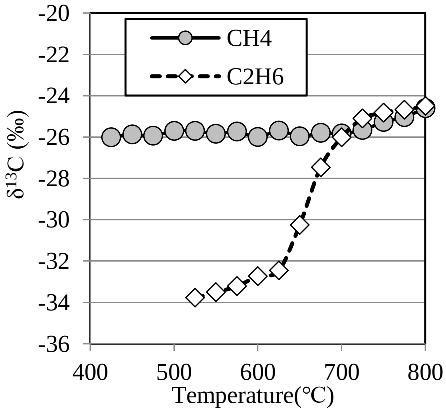

Figure 4. Variations of $\delta^{13}C_1$ and $\delta^{13}C_2$ with increasing temperature

The experiment CH$_4$ results cracking indicated that CH$_4$ polymerization leading to heavy gas formation had occurred at 450 ^{o}C. However, the CH$_4$ polymerization was so weak that no obvious decrease in CH_4 content—and consequently, a trace heavy gas was observed below 600 °C. CH_4 polymerization increased noticeably within the temperature range of 600–750 °C, resulting in increased heavy gas content. The generation of non-saturated heavy gas above 600 °C indicated that saturated heavy gas had begun to undergo cracking and further caused rapid isotopic reversal of $\delta^{13}C_2$. Nevertheless, C_2H_6 content continued to increase and carbon isotopic distribution exhibited a reversal below 725 °C (Figure 4). This was attributed to the relatively higher ratio of the CH_4 polymerization to form heavy gas than that of heavy gas cracking, i.e., a high ratio of C_2H_6 cracking compared to C_2H_6 formation, caused by the decrease in C_2H_6 content above 725 °C. The values of $\delta^{13}C_1$ and $\delta^{13}C_2$ tended towards becoming equal as CH_4 began to substantial crack at 700–725 °C.

The CH_4 cracking experiment elucidated that methane cracking could be divided into two stages, early cracking and substantial cracking. The combination of methyl depleted in $\delta^{13}C$, which formed in the early CH_4 cracking stage, produced heavy hydrocarbon gas with light isotopic composition. The methyl combination could be looked as CH_4 polymerization. CH_4 polymerization is an important underlying factor for isotope reversal in over-mature gas. Moreover, $\delta^{13}C_1$-$\delta^{13}C_2$ decreased with an increase in experimental temperature prior to CH_4 substantial cracking. The values of $\delta^{13}C_1$-$\delta^{13}C_2$ tended to become zero during the process of CH_4 substantial cracking. Thus, $\delta^{13}C_1$-$\delta^{13}C_2$ could potentially be interpreted as a factor to predict the degree of CH_4 cracking.

4. Carbon isotope variation of mud gas *vs.* the depth during shale gas drilling

As mentioned above, the CH_4 cracking experiment proved that $\delta^{13}C_1$-$\delta^{13}C_2$ in over-mature shale gas could be used as an index to extrapolate the degree of CH_4 cracking. Nevertheless, the experimental conclusion requires further validation of the practical data obtained from shale gas exploration. Generally, shale gas collected from a gas field is often a mixture of the gases obtained at different depths from the entire reservoir. The carbon isotopic composition of shale gas does not display any variations in $\delta^{13}C_1$ and $\delta^{13}C_2$ with increasing depth. In reality, the mud gas from varying depths during shale drilling is the original shale gas stored in shale. Thus, the carbon composition of mud gas from different depths could reveal whether the trend of $\delta^{13}C_1$ and $\delta^{13}C_2$ variation with increasing depth—similar to that observed during the CH_4 cracking experiment with increasing temperature—exists in geological settings.

Sichuan Basin is a petroliferous gas basin located in the southwest of China. A large amount of shale gas have been produced in both the Cambrian Qiongzhusi Formation and the Silurian Longmaxi Formation in the basin. Both these clusters of shale gas attain over maturity [23,24]. Moreover, a majority of the shale gas extracted from these formations bears a feature of isotope reversal [25].

Niu et al had presented the carbon isotope composition variation with depth of mud gases obtained from the three shale gas wells (DY5, JY10-10, SY3, Figure 5) [26]. In the three wells, the $\delta^{13}C_1$ of mud gas increased with increasing depth. Contrastingly, the $\delta^{13}C_2$ of mud gas initially decreased with increasing depth, followed by a sharp increase. All the mud gas observed in the interval segment exhibited isotope reversal. With increasing depth, $\delta^{13}C_1$-$\delta^{13}C_2$ of mud gas increases initially, then decreases and ultimately reaches zero. The vertical variation in $\delta^{13}C_1$-$\delta^{13}C_2$ for mud gas was fairly consistent with the conclusion derived from the CH_4 cracking experiment that $\delta^{13}C_1$-$\delta^{13}C_2$ decreased with increasing CH_4 cracking degree.

The CH_4 cracking experiment results indicated that CH_4 polymerization had occurred at 450 °C (Easy R_o=1.49%). At this maturity level, the C_2H_6, which existed originally in over-mature shale gas, could not undergo substantial cracking in geological settings. With a rise in geological temperature or maturity level, CH_4 polymerization also increases and more C_2H_6 depleted in $\delta^{13}C$ is formed. The latter cause depletion of $\delta^{13}C$ in the original C_2H_6, further resulting in isotope reversal in natural gas. With the increase in C_2H_6 formation via polymerization, the $\delta^{13}C_1$-$\delta^{13}C_2$ in natural gas escalates as well. The cracking of C_2H_6 formed via CH_4 polymerization occurs at a greater depth or higher temperature and causes a rapid increase in $\delta^{13}C_2$. At this stage, CH_4 cracking and polymerization attain a dynamic equilibrium, while the $\delta^{13}C_1$ and $\delta^{13}C_2$ tend to become equal. Thus, the vertical variation in $\delta^{13}C_1$-$\delta^{13}C_2$ in mud gases with increasing depth is in concurrence with the conclusions derived from the CH_4 cracking experiment. Moreover, the vertical variations of $\delta^{13}C_1$ and $\delta^{13}C_2$ with increasing depth is consistent with the results presented in Figure 1, which reflects the relationship between $\delta^{13}C_1$-$\delta^{13}C_2$ and the wetness of over-mature shale gas.

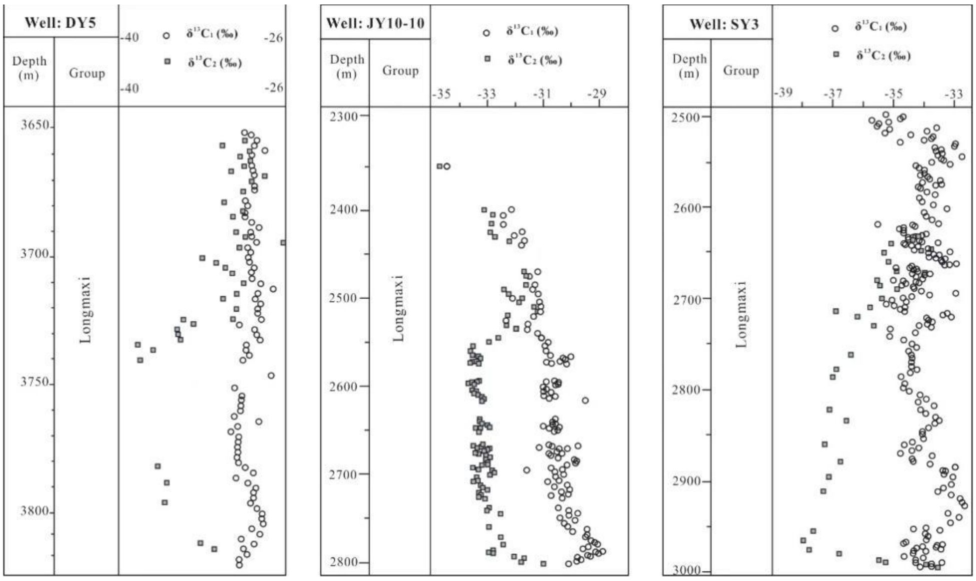

Figure 5. $\delta^{13}C_1$ and $\delta^{13}C_2$ variation of mud gases with increasing depth (cited from reference [26],with some modifyiles)

The quantity of mud gas is very low in the segment of the three wells, where $\delta^{13}C_1$ nearly equals $\delta^{13}C_2$. In addition, hardly any hydrocarbon gas was detected in the deeper segment below the layer where $\delta^{13}C_1$ nearly equals $\delta^{13}C_2$. Thus, it is evident that the phenomenon of very low gas content and approximately equivalent $\delta^{13}C_1$ and $\delta^{13}C_2$ should be caused by CH_4 substantial cracking.

5. Production of shale gas *vs.* $\delta^{13}C_1$ - $\delta^{13}C_2$ and wetness

Since natural gas is primarily composed of CH_4, especially for over-mature gas. Thus, the content and production of shale gas would decrease when CH_4 undergoes substantial cracking in geological settings. The experimental result of CH_4 pyrolysis indicates that $\delta^{13}C_1$ and $\delta^{13}C_2$ trend to be equal as CH_4 substantial cracking. Based on this assumption, the production of over-mature shale gas would diminish with decreasing $\delta^{13}C_1$-$\delta^{13}C_2$. Figure 6 depicts the relationship between production and $\delta^{13}C_1$-$\delta^{13}C_2$ in shale gas sourced from different wells of the Longmaxi Formation in Sichuan Basin, China. Both the average production per month and the accumulated production of shale gas from different wells generally showed a decrease with the reduction in $\delta^{13}C_1$-$\delta^{13}C_2$. It also indicates that natural gas (CH_4) cracking impacts the production of shale gas quite significantly. The nonlinear relationship between the production of shale gas and $\delta^{13}C_1$-$\delta^{13}C_2$ is attributable to the fact that shale gas production is controlled by diverse geological factors and development of engineering methods, such as the physical property of shale, pore evolution with increasing maturity, total organic carbon, type of organic matter, and fracturing method. Nevertheless, CH_4 cracking is undoubtedly a crucial factor that affects shale gas production, according to the production data of shale gas in the Sichuan Basin. The shale gas from Longmaxi Formation in Sichuan basin, China, bears a feature of $\delta^{13}C_1$-$\delta^{13}C_2$ > 1‰ (Figure 6).

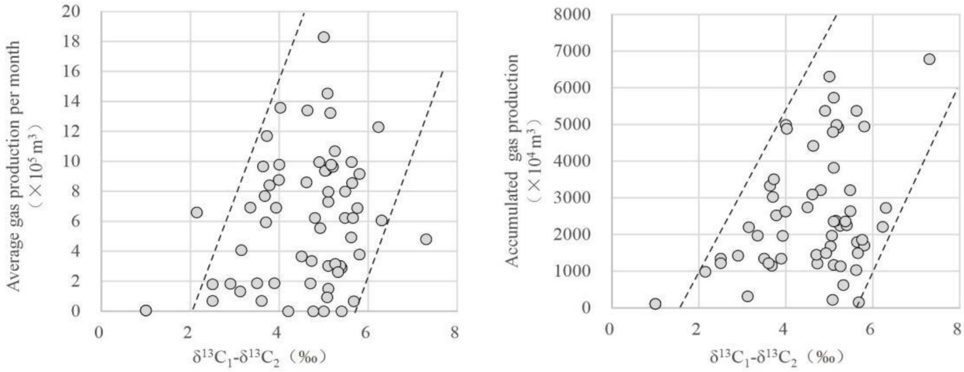

Figure 6. Relationship between $\delta^{13}C_1$ - $\delta^{13}C_2$ and the production of shale gas in Longmaxi Formation of Sichuan basin

The wetness of the shale gas with isotope reversal in the Sichuan Basin is less than 0.9% (Figure 1). Moreover, there is a positive relationship between the wetness and the $\delta^{13}C_1$-$\delta^{13}C_2$ of the shale gas found in this location. The relationship between the wetness and the production of shale gas in the Longmaxi Formation of the Sichuan Basin has been presented in Figure 7. Both the average production per month and the accumulated production present a decreasing trend with a decline in the wetness of shale gas from different wells. The statistics in Figure 7 demonstrates that the wetness of the shale gas produced in the Sichuan Basin is more than 0.2%.

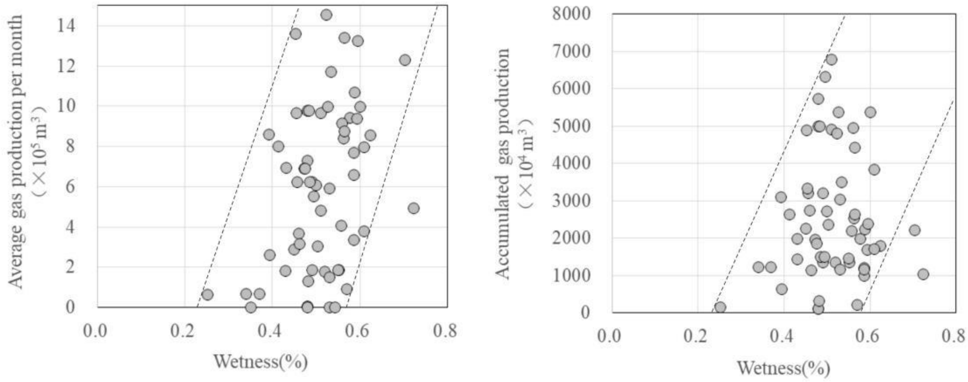

Figure 7. Relationship between the wetness and the production of shale gas in Longmaxi Formation of Sichuan basin

6. Conclusions

Geochemical statistics indicate that the wetness of shale gas with carbon isotope reversal is less than 1.8%. Furthermore, $\delta^{13}C_1$-$\delta^{13}C_2$ presents a parabolic variation with decreasing wetness. $\delta^{13}C_1$- $\delta^{13}C_2$ increases with decreasing wetness at the wetness range of 0.9% ~1.8%, and declines with decreasing wetness at wetness < 0.9 %. The CH_4 experiment cracking suggests that the polymerization occurring in the early CH_4 cracking stage is an important mechanism involved in the isotope reversal in over-mature gas. Moreover, $\delta^{13}C_1$-$\delta^{13}C_2$ exhibited a decrease with the increase in experimental temperature, prior to CH_4 substantial cracking. The values of $\delta^{13}C_1$ and $\delta^{13}C_2$ tend to become equal during the process of CH_4 substantial cracking. Thus, $\delta^{13}C_1$-$\delta^{13}C_2$ can be adopted as an index to interpret the degree of CH_4 cracking. The geochemical data of mud gas obtained during shale gas drilling in Sichuan Basin suggest that the value of $\delta^{13}C_1$-$\delta^{13}C_2$ increases initially, followed by a decrease with increasing depth and finally tending towards zero, with only a trace or no hydrocarbon gas being identifiable. The $\delta^{13}C_1$ and $\delta^{13}C_2$ variation with increasing depth of mud gas is consistent with that of gaseous products formed in CH_4 cracking experiment with increasing experimental temperature. The actual statistics of production and geochemistry of shale gas in the Longmaxi Formation of the Sichuan Basin show that production of shale gas declines with the decreasing $\delta^{13}C_1$-$\delta^{13}C_2$ value and wetness. According to the results obtained from the CH_4 cracking experiment and geochemical data of over-mature shale gas exploration and development in Sichuan Basin, we suggest that shale gas exploration in deeper layer must be undertaken with great care when the wetness and $\delta^{13}C_1$-$\delta^{13}C_2$ are less than 0.2% and 1‰, respectively.

Acknowledgments

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