



Geochemical Characteristics and Genesis of Cambrian Shale Gas in the Southern Margin of Hannan Ancient Uplift

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The geological characteristics of shale and the gas composition and carbon isotopic variation from the shale are very important indicators for the shale gas study. This article analyzed the geological characteristics of Cambrian Niutitang shale and focused on the gas composition and carbon isotopic characteristics of the shale gas from the Cambrian Niutitang Formation. We can see that the total organic carbon content ranges from 0.41 to 4.29%, with an average of 1.65%, which is mainly type I and II₁. The thermal maturity of sample ranges from 1.98 to 2.53%, with an average of 2.30%, which is in the postmature stage of thermal evolution. The Cambrian Niutitang Formation shale gas in the southern margin of the Hannan ancient uplift is the high-quality hydrocarbon gas methane that takes an absolute majority with a content ranging from 89.60 to 99.19% with an average of 96.46%. The wetness of the gas from the study area ranges from 0.06 to 0.42%, with only 0.25% on an average, which is defined as typical dry gas. The distribution of carbon isotope values has partial “reverse” characteristics that are $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ and $\delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$. The natural gas of Niutitang Formation in the study area belongs to thermogenic gas. At the same time, it is found that some data points are beyond the range of thermogenic gas, which is mainly due to the low-humidity and heavy carbon isotope value of methane caused by the high maturity of source rock. In the study area, the Niutitang Formation natural gas carbon isotope values are located in Zone III with the characteristics of mixed reversal gas in the $\delta^{13}\text{C}_1$ - $\delta^{13}\text{C}_2$ part.

Keywords: geochemical characteristics, chemical composition, carbon isotopic composition, shale gas, Niutitang formation, Hannan ancient uplift

INTRODUCTION

Cambrian Niutitang Formation organic-rich shale is a set of main shale strata in southern China, and shale gas has been found and broken through in many areas. This set of shale strata is also widely developed in the southern margin of Hannan ancient uplift and is an important field of shale gas survey and exploration in the future.

The gas composition of shale gas wells mined in China and North America shows that shale gas is mainly methane, containing a small amount of ethane and propane, and other non-hydrocarbon gas components are less (Zumberge et al., 2009, Zumberge et al., 2012). The composition and relative content of hydrocarbon gas are obviously closely related to the thermal evolution of organic matter.

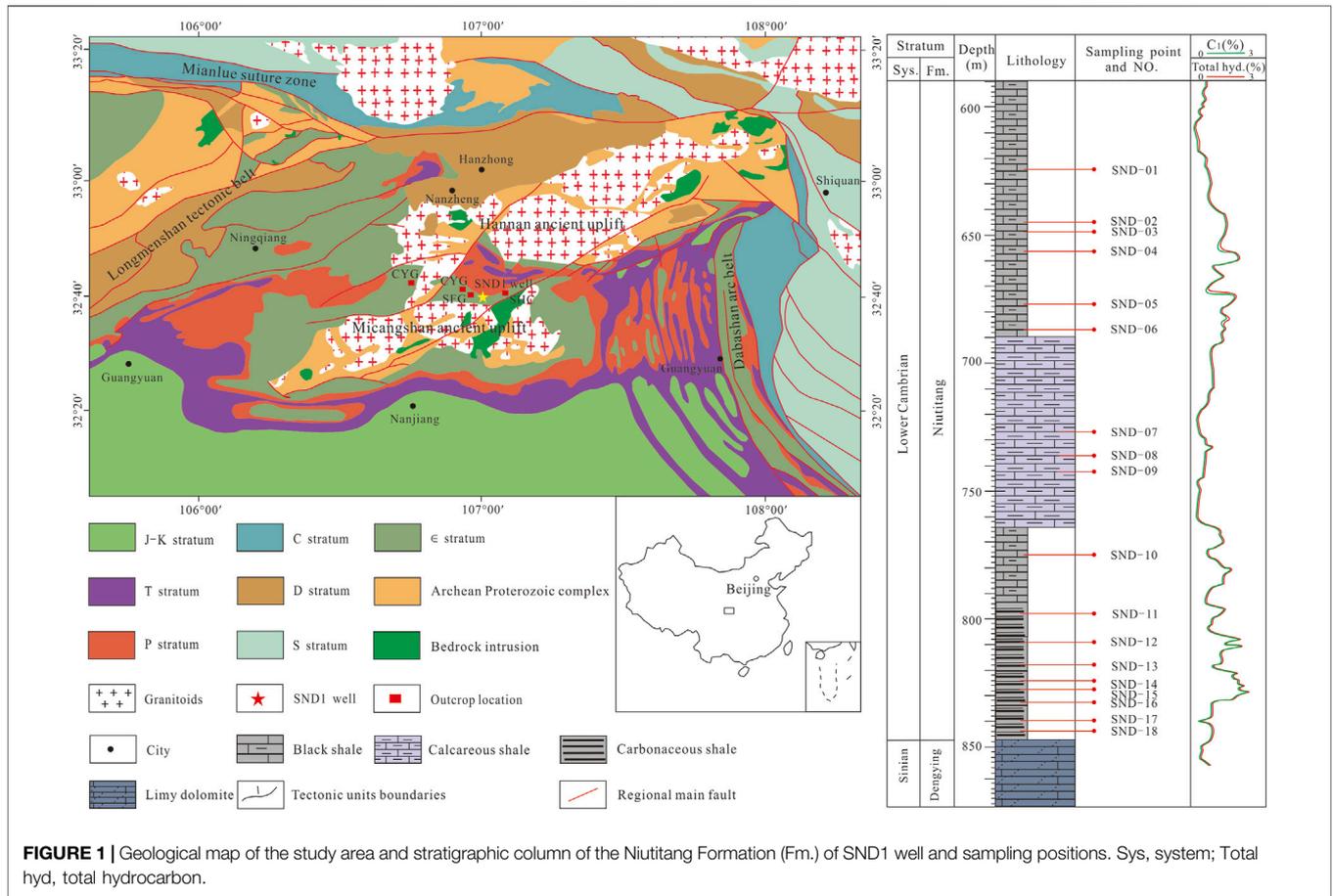


FIGURE 1 | Geological map of the study area and stratigraphic column of the Niutitang Formation (Fm.) of SND1 well and sampling positions. Sys, system; Total hyd, total hydrocarbon.

Shale gas is mostly dry gas in high-overmature shale, while the carbon isotope inversion has become a typical feature of some shale gas fields and attracted more and more attention (Ellis et al., 2003; Xia and Tang, 2012). One of the reasons is that most of the gas wells with carbon isotope inversion are medium- and high-production wells (Han et al., 2013).

In order to understand the formation conditions and characteristics of natural gas in Cambrian Niutitang Formation of SND1 well in the study area, it is necessary to conduct in-depth research on the geochemical characteristics and natural gas genesis of Cambrian Niutitang Formation in the study area (Dai et al., 2003). In order to clarify the origin of natural gas in Niutitang Formation in this area, a reliable judgment can be made by studying the carbon isotope series and inversion of alkane gas. At the same time, a strong judgment can be further made for the origin of natural gas in this area according to the relationship between carbon isotope of alkane gas and alkane gas components and the relationship between the methane carbon isotope and hydrogen isotope (Whiticar, 1999; Liu et al., 2016).

This article analyzed the geological characteristics of Cambrian Niutitang shale and focused on the gas composition and carbon isotopic characteristics of the shale gas from the Cambrian Niutitang Formation to obtain deep insights into the genesis of shale gas, the reasons for isotopic reversal, and shale gas enrichment mechanism (Li et al., 2020).

GEOLOGICAL BACKGROUND

The Micangshan–Hannan uplift is tectonically located at the northwestern margin of the Upper Yangtze Plate, adjacent to the Longmenshan tectonic belt in the west, and separated by the Dabashan arc belt in the east (Tian et al., 2021). The study area, Huijunba syncline is between Micangshan uplift and Hannan uplift, whose western section is relatively open, and gradually converges into an arc toward the northeast (Chen et al., 2018). The tectonic line of Huijunba syncline is nearly east–west trending, which consists of several suborder anticlines (Liu et al., 2021). In the study area, the Early Paleozoic strata are fully developed, whereas the Devonian and Carboniferous strata are absent in the Late Paleozoic strata, and the Permian and Triassic strata are mainly exposed. The Lower Cambrian Niutitang Formation was mainly formed in a shallow shelf environment and partly in a coastal or supratidal environment, which is exposed only in the margin of the uplift (Yu et al., 2011; Liu et al., 2021). The average thickness of the shale in the Niutitang Formation is mainly more than 100 meters, which has the characteristics of high total organic carbon content, low thermal maturity, and shallow burial depth (Tian et al., 2019). The lithology of Niutitang Formation shale mainly consists of black shale and calcareous mudstone, which acted as the favorable shale gas reservoir section (Figure 1).

TABLE 1 | Organic geochemical characteristics and gas content of the Niutitang Formation shale gas in the study area.

Location	Sample No.	TOC (%)	Ro (%)	Organic matter type	Gas content (m ³ /t)
SND1 well	SND1-01	0.75	2.38	I	2.03
	SND1-02	2.52	2.46	II ₁	3.05
	SND1-03	1.95		I	1.56
	SND1-04	1.63	2.50	I	1.52
	SND1-05	0.81		II ₁	2.13
	SND1-06	1.56		II ₁	0.94
	SND1-07	0.48		I	0.94
	SND1-08	0.43		II ₁	0.83
	SND1-09	0.45		II ₁	1.14
	SND1-10	0.45		II ₁	5.28
	SND1-11	1.67		I	1.61
	SND1-12	2.91		I	1.3
	SND1-13	4.29	2.41	I	2.54
	SND1-14	4.16		I	1.53
	SND1-15	3.40		I	0.95
	SND1-16	3.12	2.53	II ₁	0.95
	SND1-17	1.89	2.36	I	0.93
	SND1-18	2.38	2.42	I	1.88
GWS outcrop	GWS-01	1.02	2.17	I	
	GWS-02	1.04	2.12	I	
	GWS-03	1.20	2.42	I	
	GWS-04	0.97	2.09	I	
	GWS-05	0.88	2.01	II ₁	
CY outcrop	CYG-01	1.23	2.34	II ₁	
	CYG-02	0.41	1.98	II ₁	
	CYG-03	1.32	2.31	II ₁	
	CYG-04	1.35	2.40	I	
SFG outcrop	SFG-01	2.09	2.37	I	
XH outcrop	XHC-01	0.79	2.03	I	
	XHC-02	2.29	2.31	I	

SAMPLES AND METHODS

Sampling

We studied the Niutitang Formation black shales from SND1 well and outcrop samples in the southern Shaanxi region. The Niutitang Formation in SND1 well is about 280 m thick (Figure 1). A total of 30 core and outcrop samples were collected for thermal maturity (Ro, %), total organic carbon (TOC, %), and organic matter type test, and 18 core samples of SND1 well were collected for the gas content test (fielding desorption test), gas composition, and organic carbon isotope studies.

Geochemical Characteristics

Total organic carbon abundances were measured using a LECO CS230 carbon and sulfur analyzer adopting dry combustion in Yangtze University. The samples were ground to less than 200 mesh size and washed with acid (HCl) to expel carbonate minerals at 60°C for 24 h, then distilled water was used to eliminate treated HCl, and samples were oven-dried at 50°C for 24 h. The organic matter was measured using a Zeiss Axio Scope.A1/J&M Msp 200 as a complement to vitrinite reflectance (VRo) and bitumen reflectance (BRo) measurements that are more conventionally used for maturity analysis.

Chemical Composition

The chemical compositions (CH₄, C₂H₆, C₃H₈, CO₂, and N₂) were determined using a 7890A gas chromatograph (GC) equipped with a thermal conductivity detector and a flame ionization detector.

Stable Carbon and Hydrogen Isotopes

The carbon and hydrogen isotopes data were determined using a 7890A gas chromatograph and an IsoPrime 100 Gas temperature isotope mass spectrometer by the GC/TC/IRMS system method. The detection ambient temperature is 22°C, and the humidity is 65%.

Gas Content

A total of 18 samples from SND1 well were analyzed in the field, and the residual gas content was measured in the laboratory, and the lost gas content was calculated by the linear regression analysis method. During the gas content test process, core samples were moved into a transparent sealed tank filled with saturated salt water, and then the sealed tank was placed in a constant temperature water bath of 60°C for gas resolution at reservoir temperature (55°C). The shale was resolved for 72 h to ensure that the gas in the shale was fully resolved. After the analysis is completed, the gas is collected, and the volume of the gas is measured.

RESULTS

Organic Geochemical Characteristics

Organic matter abundance (TOC) is not only the material basis of shale gas production but also affects the total gas accumulation in shale gas reservoirs. The organic carbon content ranges from 0.41 to 4.29%, with an average of 1.65%. Specifically, the average of TOC for outcrop and well samples is 1.22 and 1.94%, respectively. Kerogen microscopy identification and kerogen carbon isotope results show that the organic matter in the Niutitang shale is mainly type I, and some samples are type II₁. The thermal maturity of sample ranges from 1.98 to 2.53%, with an average of 2.30%. Therefore, the shale of Niutitang Formation is in the postmature stage of thermal evolution (Table 1). Compared with the characteristics of high maturity of marine shale in Niutitang Formation in southern China, the maturity of samples in this study is relatively moderate, which is speculated to be related to the proximity of Hannan uplift, which is more favorable for the preservation of shale gas (Zhai et al., 2018; Xu et al., 2020a).

Gas Content of Shale

The field analytical gas content of SND1 well is between 0.04 m³/t and 0.91 m³/t, with an average of 0.40 m³/t. The total gas content is 0.83–5.28 m³/t, with an average of 1.73 m³/t. The total gas content is not very high which may be caused by shallow burial depth and poor preservation conditions (Table 1).

Characteristics of Gas Composition

The natural gas of the Cambrian Niutitang Formation in the southern margin of the Hannan ancient uplift is the high-quality

TABLE 2 | Component and isotope properties of the Niutitang Formation shale gas in the study area.

Sample No.	Strata	Gas component, (%)				Wetness (%)	$\delta^{13}\text{C}$ (‰), V-PDB				δD (‰), V-SMOW	
		CH ₄	C ₂ H ₆	N ₂	CO ₂		CH ₄	C ₂ H ₆	C ₃ H ₈	Kerogen	CH ₄	C ₂ H ₆
SND1-01	Є1n	98.40	0.27	0.79	0.54	0.28	-34.80	-37.60	Nd	-30.66	-234	-180
SND1-02	Є1n	96.85	0.28	1.22	1.65	0.29	-35.40	-38.30	Nd	-30.34	Nd	Nd
SND1-03	Є1n	97.46	0.29	1.14	1.10	0.30	-35.40	-38.30	-36.30	-30.41	Nd	Nd
SND1-04	Є1n	96.69	0.27	1.66	1.39	0.28	-36.00	-38.40	Nd	-30.76	Nd	Nd
SND1-05	Є1n	99.19	0.26	0.23	0.32	0.26	-35.50	-37.60	Nd	-30.11	Nd	Nd
SND1-06	Є1n	97.34	0.23	1.05	1.38	0.23	-35.70	-38.30	-37.60	-30.28	Nd	Nd
SND1-07	Є1n	97.34	0.26	1.61	0.78	0.27	-35.40	-38.40	-37.90	-30.28	Nd	Nd
SND1-08	Є1n	92.68	0.14	1.33	5.86	0.15	-36.80	-37.70	Nd	-30.05	-247	-142
SND1-09	Є1n	98.03	0.18	1.11	0.67	0.18	-37.30	-38.30	-38.20	-30.60	Nd	Nd
SND1-10	Є1n	89.60	0.05	1.94	8.42	0.06	-37.60	-37.10	Nd	-30.60	-234	-210
SND1-11	Є1n	97.52	0.41	0.54	1.52	0.42	-31.30	-34.80	-34.30	-33.28	Nd	Nd

Nd, not determined.

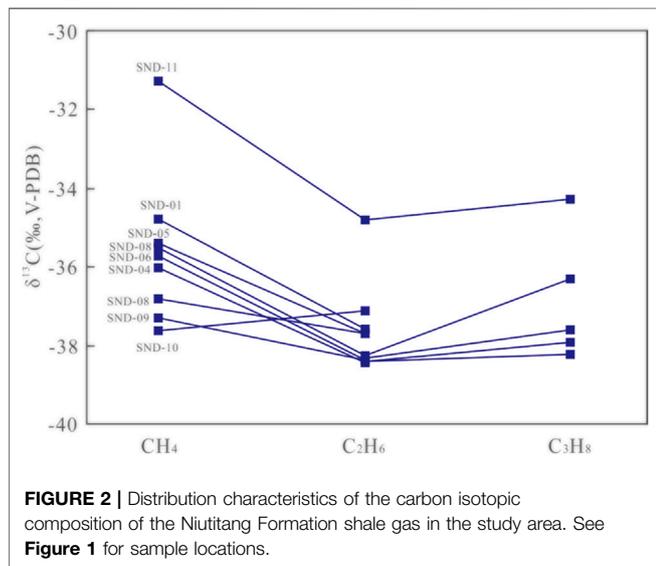


FIGURE 2 | Distribution characteristics of the carbon isotopic composition of the Niutitang Formation shale gas in the study area. See **Figure 1** for sample locations.

hydrocarbon gas methane that takes an absolute majority with a content ranging from 89.60 to 99.19% with an average of 96.46%, which is similar to that of the Fuling (average of 98.16%), Changning (average of 98.69%), and Weiyuan (average of 98.01%) areas (Liu, 2015; Wu et al., 2015; Feng et al., 2016). The ethane content is extremely low with 0.24% on an average, which is similar to that of Fuling (average of 0.69%), Changning (average of 0.49%), and Weiyuan (average of 0.46%) areas (Liu, 2015; Wu et al., 2015; Feng et al., 2016; Xu

et al., 2020b). Almost no propane and other heavy hydrocarbon components were present. The wetness ((C₂-C₅)/(C₁-C₅)) of the gas from the study area ranges from 0.06 to 0.42%, with only 0.25% on an average, which is defined as typical dry gas. The content of non-hydrocarbon gases such as CO₂ and N₂ is very low, and the average content accounts for only 2.15 and 1.15%, respectively. No hydrogen sulfide and other gases were detected in the shale gas of Niutitang Formation in the study area (Table 2).

Carbon Isotopic Composition

The carbon isotopic value of methane ($\delta^{13}\text{C}_1$) of natural gas from Niutitang Formation shale in the study area ranges between -37.6‰ and -31.3‰ with an average of -35.56‰. The carbon isotopic value of ethane ($\delta^{13}\text{C}_2$) of natural gas ranges between -38.4‰ and -34.8‰ with an average of -37.7‰. The carbon isotopic value of propane ($\delta^{13}\text{C}_3$) of natural gas ranges between -38.2‰ and -34.3‰ with an average of -36.86‰ (Table 2). The distribution of carbon isotope values of methane, ethane, and propane has partial “reverse” characteristics that are $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ and $\delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$ (Figure 2).

DISCUSSION

Discrimination of Thermogenic Gas

The genetic types of natural gas can be divided into inorganic genetic gas, organic genetic gas, and mixed genetic gas. Inorganic gas is generally related to the deep activities of the earth and usually has the following distinguishing features: 1) the carbon

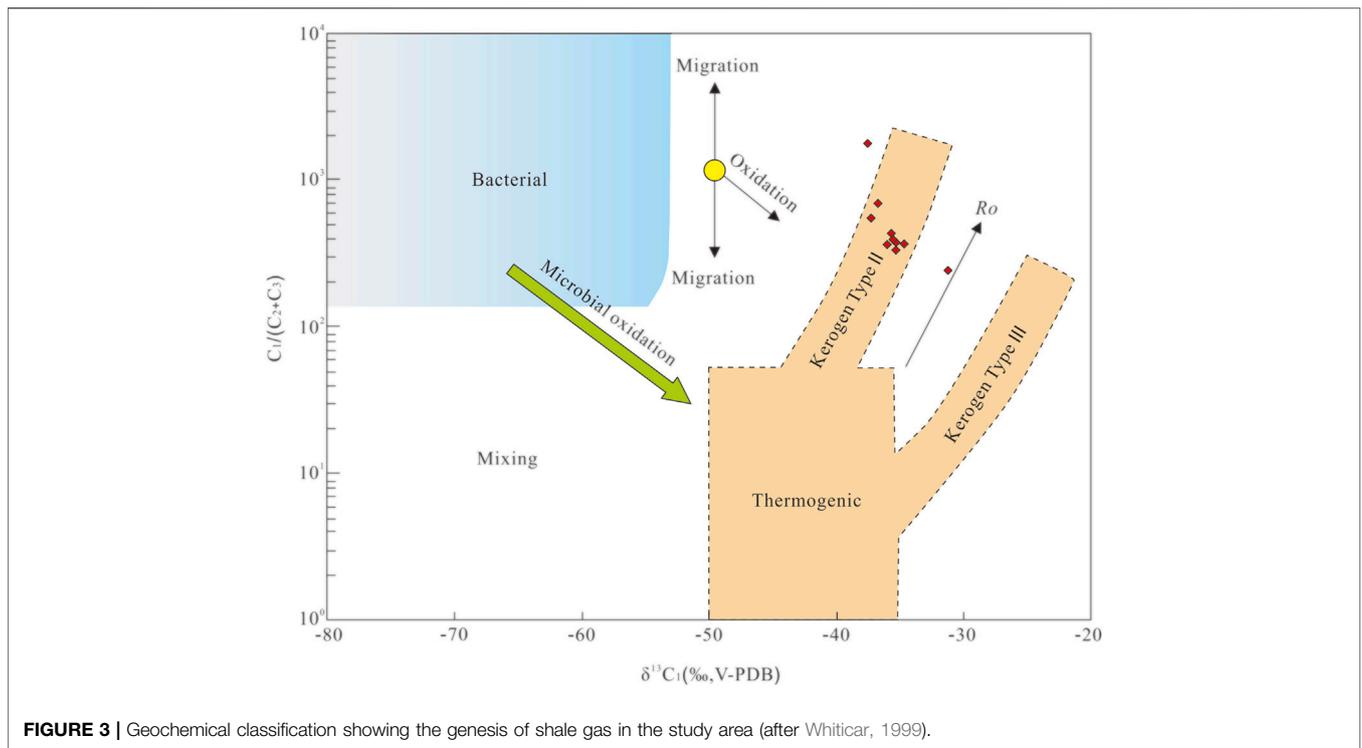


FIGURE 3 | Geochemical classification showing the genesis of shale gas in the study area (after Whiticar, 1999).

TABLE 3 | Identification items of carbon isotopes and composition (after Dai et al., 1992).

Subject	Oil-type gas	Coal-type gas
$\delta^{13}C_1/\text{‰}$	$-30 > \delta^{13}C_1 > -55$	$-10 > \delta^{13}C_1 > -43$
$\delta^{13}C_2/\text{‰}$	$\delta^{13}C_2 < -29$	$\delta^{13}C_2 > -28$
$\delta^{13}C_3/\text{‰}$	$\delta^{13}C_3 < -27$	$\delta^{13}C_3 > -25.5$

isotopic composition characteristics of inorganic genetic gas with $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$; 2) the carbon isotope value of methane is generally more than -30‰ (Dai et al., 2008) or -25‰ and -20‰; 3) the carbon dioxide content is more than 60%; and 4) the carbon isotope content of carbon dioxide is more than -8‰ (Dai et al., 2008). Although the distribution of carbon isotope values of methane, ethane, and propane has partial “reverse” characteristics that are $\delta^{13}C_1 > \delta^{13}C_2$ and $\delta^{13}C_2 < \delta^{13}C_3$ (Figure 2), due to the $\delta^{13}C_1$ is far less than -30‰ and the CO₂ content is far less than 60%, which shows the characteristics of the alkane gas in Niutitang Formation shale in the study area with organic genetic gas.

The organic gas can be divided into biogenic gas, pyrolytic gas, and cleavage gas according to the thermal maturity of organic matter. According to $\delta^{13}C_1$ - C_1/C_{2+3} parameters, Whiticar compiled the genetic identification chart of natural gas (Whiticar, 1999). Put the $\delta^{13}C_1$ value and the calculated C_1/C_{2+3} value from the Table 2 into the chart, and it is judged that the natural gas of Niutitang Formation in the study area belongs to thermogenic gas. At the same time, it is found that some data points are beyond the range of thermogenic gas, which is mainly due to the low-humidity (average 0.25%) and heavy methane

carbon isotope value (average -35.56‰) caused by the high maturity of source rock (average Ro = 2.30%) (Liu et al., 2016; Zhang et al., 2016; Gou et al., 2019). Therefore, the shale gas of Niutitang Formation in the study area is organic high-temperature pyrolysis gas (Figure 3).

Discrimination of Oil Type Gas

Organic thermogenic natural gas is mainly divided into oil-type gas and coal-type gas (Dai et al., 1992). Some scholars listed the carbon isotope identification indicators of alkane gas with condensate oil and crude oil or their homologous components (Table 3). These indicators are common indicators in gas source correlation with high reliability. The carbon isotope of natural gas in the study area is with $-37.60\text{‰} \leq \delta^{13}C_1 \leq -31.30\text{‰}$, $-38.40\text{‰} \leq \delta^{13}C_2 \leq -34.80\text{‰}$ and $-38.20\text{‰} \leq \delta^{13}C_3 \leq -34.30\text{‰}$, which is characterized by oil-type gas. Put the $\delta^{13}C_1$ and $\delta^{13}C_2$ value into the chart (Gang et al., 1997), and the data points also fall within the oil-type gas range (Figure 4).

Using $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ values from a large amount of oil-type gas and coal-type gas in many oil and gas fields around the world, the predecessor compiled and improved the chart for distinguishing the coal-type gas and oil-type gas (Dai et al., 2014a; Feng et al., 2016). Put the value from the Table 2 into the chart and found that the carbon isotope values of Niutitang Formation natural gas in the study area are within the Zone III which represents the mixed reversal gas zone in the $\delta^{13}C_1$ - $\delta^{13}C_2$ part (Figure 4). However only a few data points are within the Zone III, while most other data points are not within any gas zone, but close to the mixed reversal gas zone in the $\delta^{13}C_1$ - $\delta^{13}C_3$ part (Figure 4). According to the investment results, the $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ values of natural gas from Niutitang Formation in the

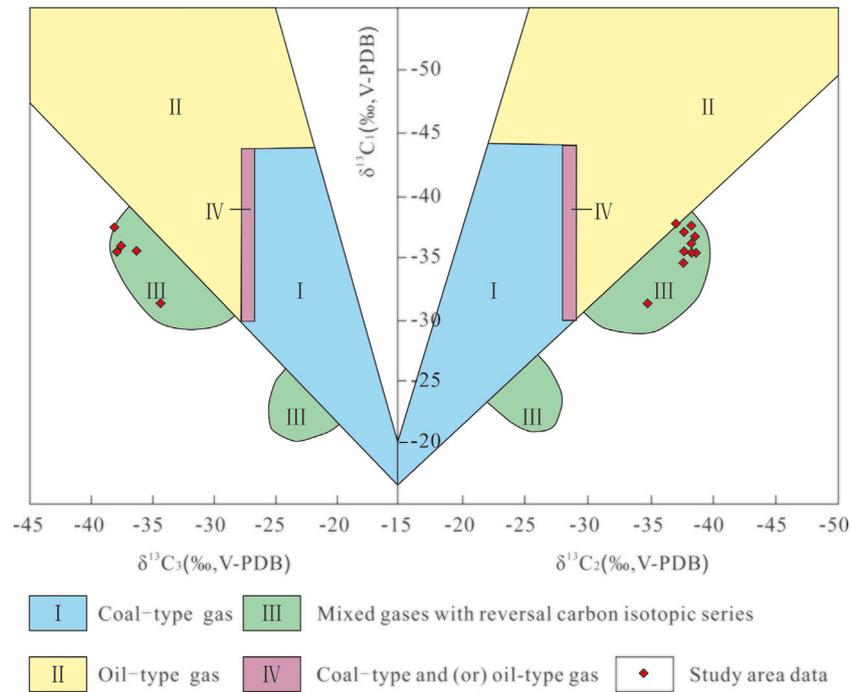


FIGURE 4 | Identification chart of $\delta^{13}C_1$ - $\delta^{13}C_2$ - $\delta^{13}C_3$ for the Niutitang Formation shale gas in the study area (after Dai et al., 1992).

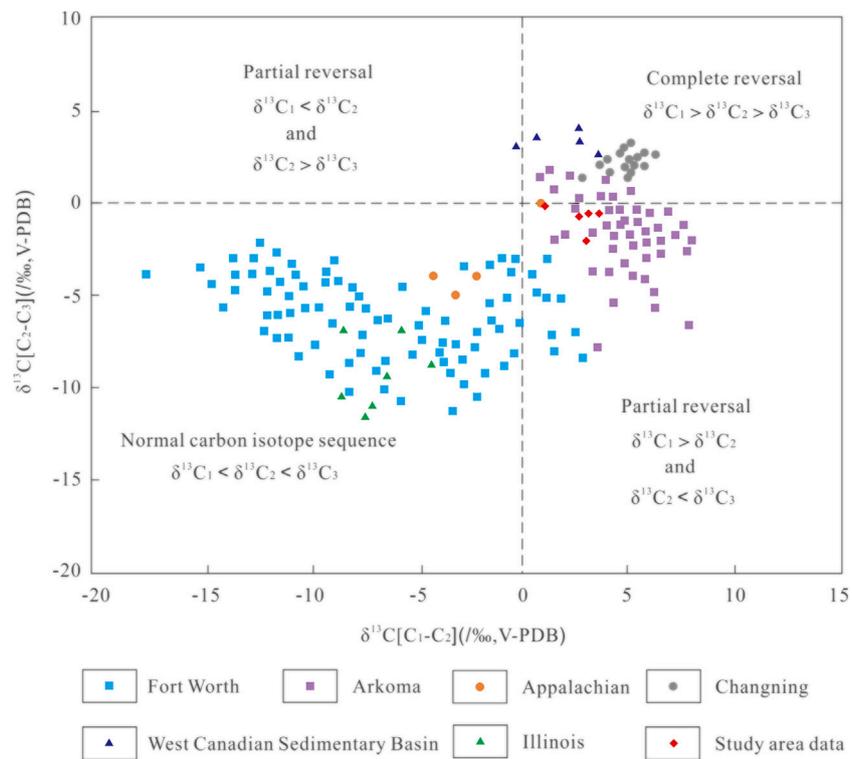
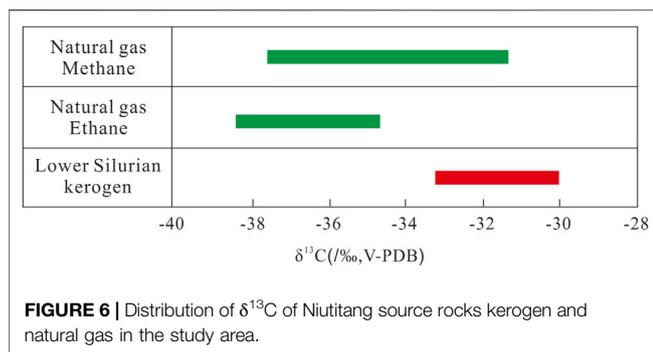


FIGURE 5 | Reversal distribution mode of carbon isotopic composition of shale gas (modified from Zumberge et al., 2012; Tilley and Muehlenbachs, 2013; Hao and Zou, 2013; Liu, 2015; Wu et al., 2015; Feng et al., 2016).



study area are not located in Zone I and IV, which generally reflects that the gases are not coal-type gas. At the same time, it also shows that the natural gas data points of Niutitang Formation in the study area are not completely included in the I-V gas zone in the chart, which may indicate that the carbon isotope of shale gas has its particularity with conventional natural gas.

Partial Reversal of Carbon Isotopic Composition

Generally, the primary negative carbon isotope sequence is $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$. However, in recent years, including natural gas in the study area, more and more phenomena of carbon isotope reversal have been discovered such as $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ pervasively exists in organic origin gas (Figure 5). This phenomenon is common in these areas such as the Longmaxi Formation shale gas in Changning, Fuling, and Weiyuan areas of Sichuan Basin, China (Dai et al., 2014b; Feng et al., 2016; Qin et al., 2017), the Songkan Formation and Niutitang Formation shale gas in the middle Yangtze area, China (Zhang et al., 2018), the Permian shale gas in the north of South China (Liu et al., 2018), the Mississippian Barnett and Fayetteville shale gas from the Fort Worth and Eastern Arkoma basins, North America (Zumberge et al., 2012; Li et al., 2020), and Horn River shale gas at the western edge of the Western Canada basin (Tilley et al., 2011; Li et al., 2020).

There has always been controversy about the origin of carbon isotope inversion. The main viewpoints are as follows: 1) the mixing of gases in different periods of homology (Zumberge et al., 2012; Hao and Zou, 2013). For example, high-maturity natural gas is mixed with early residual ^{12}C -rich ethane, resulting in lighter carbon isotopic composition of ethane and $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ partial inversion. 2) The mixture of kerogen pyrolysis gas and asphalt, retained oil, wet gas pyrolysis gas in the high-evolution stage, and the pyrolysis gas produced by retained oil or asphalt will produce lighter ethane (^{12}C -rich) (Tang et al., 2000; Xia and Tang, 2012; Hao and Zou, 2013; Tilley and Muehlenbachs, 2013; Xia et al., 2013). 3) Water and other substances participate in the redox reaction (Burruss and Laughrey, 2010; Zumberge et al., 2012; Gao et al., 2014). 4) Isotope fractionation caused by hydrocarbon expulsion and diffusion. Methane rich in ^{12}C will be preferentially lost in the diffusion process, resulting in the enrichment of ^{13}C in residual methane and the heavier carbon

isotope composition (Qin et al., 2016, 2017). There is no consensus on the cause of carbon isotope inversion, but it may not be caused by one factor but by multiple factors.

According to the previous discussion on the genesis of shale gas, we believe that the carbon isotope inversion of shale gas in Niutitang Formation in the study area is mainly caused by the mixing of natural gas produced by the degradation of highly mature kerogen and residual crude oil pyrolysis gas. With the increase of maturity, crude oil begins to crack gradually, crude oil-cracking gas accounts for an increasing proportion in the mixture, and the carbon isotopes of methane and ethane begin to lighten gradually (Xia et al., 2013). However, due to the high $\text{C}_2 +$ content in oil-cracked gas, ethane is enriched in a large number of light isotopes (^{12}C) faster. With the continuous improvement of maturity, the light carbon isotopes of methane and ethane are enriched. Therefore, the carbon isotope of methane is heavier than that of ethane, and the carbon isotope is reversed.

However, only the secondary cracking of moisture may not be completely reversed. Previous thermal simulation tests in the closed system show that carbon isotope inversion is unlikely to occur in pure thermogenic shale gas (Qu et al., 2016), so other factors must play a role. Other factors may include the reaction of ethane with water and ferrous metals under Rayleigh fractionation. In addition, high ground temperature conditions may also be one of the important influencing factors.

Natural Gas Sources

The study confirmed that the shale of the Cambrian Niutitang Formation in the study area is rich in natural gas, and the source of natural gas is not only related to the discovered natural gas whether it is shale gas or not but also has an important impact on the next exploration deployment. It is found that there are mainly two sets of source rocks in the study area, namely Lower Cambrian Niutitang Formation black carbonaceous shale and Lower Silurian Longmaxi Formation black graptolite shale.

According to the relevant data of formation pressure, there is a certain overpressure in the Cambrian Niutitang Formation in the study area, while other overlying strata do not develop overpressure (Chen et al., 2018). Therefore, the natural gas generated by these sets of source rocks cannot migrate downward to Niutitang Formation and form overpressure. According to the drilling logging and geological profile survey results, the thickness of the shale of Niutitang Formation in the study area is more than 100 m, and the average value of organic carbon reaches 1.65%. Kerogen macerals are mainly type I-II₁, which have good hydrocarbon generation potential and have reached the overmature stage, indicating that Niutitang Formation shale itself has the potential to produce a large amount of oil and gas.

According to the variation law of the carbon isotope value of gas and source rock, the highly mature natural gas should come from the source rock with slightly higher carbon isotope value (1–3‰). The test data of 6 Niutitang Formation source rocks in the study area show that the kerogen type is mainly I-II₁, and the value of $\delta^{13}\text{C}_1$ is between -33.28‰ and -30.05‰ , which is similar to the natural gas in the Niutitang Formation reservoir (Figure 6). It indicates that the natural gas of Niutitang Formation should come from its own stratigraphic source

rock. The natural gas in the Niutitang Formation of the study area is oil-type gas. The natural gas components show the characteristics of high-methane content (89.60–99.19%), large drying coefficient, and no H₂S (Table 2), which is consistent with the characteristics of source rocks of Niutitang Formation.

CONCLUSION

The following conclusions are drawn from this study:

- 1) The shale of the Cambrian Niutitang Formation in the southern margin of Hannan ancient uplift is developed with large thickness, high organic carbon content, and moderate thermal evolution, which indicate the geological conditions for shale gas hydrocarbon generation and accumulation are favorable.
- 2) The natural gas of the Cambrian Niutitang Formation in the southern margin of the Hannan ancient uplift is high-quality hydrocarbon gas.
- 3) The distribution of carbon isotope values of methane, ethane, and propane has partial “reverse” characteristics that are $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$, $\delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$. The natural gas of Niutitang Formation in the study area belongs to thermogenic gas.
- 4) The carbon isotope inversion of shale gas in Niutitang Formation in the study area is mainly caused by the mixing of natural gas produced by the degradation of highly mature kerogen and residual crude oil pyrolysis gas.

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DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

TG contributed as the major author of the manuscript. XC conceived the project and analyzed the samples. MG and CW collected the samples. SB and DS assisted in the compilation of some chapters. All authors contributed to the article and approved the submitted version.

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Conflict of Interest: TG, XC, MG, CW, SB, and DS were employed by the company Oil and Gas Survey.

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