Composition of Formation Water and Natural Gas as an Indicator of Shale Gas Preservation Conditions: A Case Study of the Marine Shale of the Niutitang Formation in the Cengong Block in Northern Guizhou, China

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ABSTRACT: Shale gas (SG) wells in the Wufeng–Longmaxi Formation in northern Guizhou differ considerably in their production capacities. Preservation conditions are a crucial factor affecting the formation of SG reservoirs. In this study, the formation water (FW) in four wells in northern Guizhou was analyzed to determine the type; the Cl/Mg, Ca/Mg, and Na/Cl coefficients (C_{Cl/Mg}, C_{Ca/Mg}, and C_{Na/Cl}, respectively), and the coefficient of desulfurization (C_d); the SG in these wells was tested to identify its composition and the sources of its components. The results show the following: wells TX1 and CY1 contain two types (CaCl$_2$ and NaHCO$_3$) of FW, each with low C_{Na/Cl}, low C_d, high C_{Ca/Mg}, and high C_{Cl/Mg}, suggesting a high level of FW retention. The FW in wells TM1 and CD1 is of NaHCO$_3$ type and is characterized by high C_{Na/Cl}, high C_d, low C_{Ca/Mg}, and low C_{Cl/Mg}, indicating a high level of connectivity between the FW and surface water. Nonhydrocarbon gases account for a high proportion of SG in composition; with a 15N value between $-8.7$ and $-4.2$‰, $N_2$ accounts for approximately 20% of SG in wells TX1 and CY1, respectively. This result indicates the ammonification of organic matter (OM) during pyrolysis and hydrocarbon generation as sources of $N_2$. In contrast, with a 15N value between $-3.6$ and 0‰, $N_2$ accounts for over 70% of SG in wells TM1 and CD1, respectively, indicating the atmosphere, the ammonification of OM, and the presence of poor preservation conditions due to a high level of connectivity between the shale bed and the atmosphere acted as the sources of $N_2$. The metamorphism coefficients of FW in conjunction with the SG composition and the sources of nonhydrocarbon gases can serve as auxiliary indicators of the quality of SG preservation conditions.

1. INTRODUCTION

Characterized by low porosity and low–ultralow permeability, shales are frequently considered as a special type of rock with an integrated source–reservoir–caprock system. Advancements in horizontal wells and staged fracturing technologies have continually increased the production of shale gas (SG). Consequently, SG has become an essential part of unconventional oil and gas resources. Generally, with high total organic carbon (TOC) content, a high degree of thermal evolution, and large thicknesses, marine shales in the southern region of China constitute the primary strata for current SG development projects. As a result of multiple tectonic movements after formation, Lower Palaeozoic marine shales are noted for their high structural strength, the presence of faults, and markedly varying in situ stress conditions. The vast difference in SG preservation conditions between areas causes significant differences between SG wells in different parts of the same region regarding their production capacity. These differences also hinder the exploration and efficient development of SG. Various methods for assessing the preservation of SG are currently available. Earlier research has identified two key factors that affect SG preservation: the temporal and spatial match between tectonic movements and the hydrocarbon (HC) generation stage after the formation of a shale bed, as well as the damage caused by the faults that form from intense tectonic movements to the roof and floor of the shale bed. Assessment of the preservation conditions in a formation has been primarily centered on factors such as fault development and sealing capacity, the time and extent of uplift, and the integrity of the roof and floor. In addition, according to the degree of influence of different factors, the
corresponding preservation assessment systems have been established.\textsuperscript{28,29} Tang evaluated the preservation conditions of the Longmaxi Formation marine shale in the southeastern Sichuan Basin by assigning values to factors such as roof and floor conditions, structural locations, fracture development, fracture spacing, and stratum thickness. Among them, fault development and roof and floor conditions are assigned the highest value;\textsuperscript{30} Zhang believes that tectonic action affects the preservation conditions of SG from three aspects: time, intensity, and formed tectonic style, among which tectonic strength plays a decisive role.\textsuperscript{31}

In recent years, the progress of SG exploration has resulted in an inaccurate analysis of SG preservation conditions, becoming an important step in SG assessment. Researchers in China and abroad have begun to assess preservation conditions using factors such as SG composition, the sources of its components, and the formation water (FW) type.\textsuperscript{32−34} These factors are examined from preservation quality.\textsuperscript{35−41} Generally, the SG composition and FW properties vary profoundly with preservation conditions. The presence of poor preservation conditions leads to a high level of connectivity between the target layer and the surface, allowing for exchange between the SG and the atmosphere as well as facilitating the surface water to infiltrate along the channels and exchange particles with the connate FW, which in turn alters the FW properties and the SG composition. Therefore, the quality of SG preservation conditions can be quantified based on the composition of FW and SG.\textsuperscript{42} Buried at depths greater than 1000 m, the Niutitang Formation in the study area is exposed and eroded by weather only in the Tongluo–Baiguo area. With the Sinian Dengying Formation and Cambrian Mingxinsi Formation as its direct roof and floor, respectively, this formation is distributed continuously in the transverse direction and thickness over 30 m. In addition, the ultrathick low-permeability shale in the Jindingshan Formation can serve as a high-quality caprock that effectively reduces the damage caused by FW infiltration into the SG reservoir.\textsuperscript{43,44} FW and gas exchange occur mainly through the faults that cut through the roof. Thrust faults from multiple periods have developed at the top surface of the Niutitang Formation in the Cengong area. The entire study area is divided and confined by these thrust faults. The target layer has a gentle structure. The four wells selected in this study are located on both sides of the strike-slip fault in the central region of the study area, whose sealing capacity plays a direct role in their preservation conditions.\textsuperscript{45−47}

This study examines the marine shale belonging to the Lower Paleozoic Niutitang Formation from the Cengong area in northern Guizhou. The difference in connectivity between the Niutitang Formation and the surface between different areas is analyzed through factors, including the types of ions in the FW, the FW type, the SG composition, and the sources of nonhydrocarbon gases. On this basis, the SG preservation conditions and the optimal areas for SG exploration in the Niutitang Formation in northern Guizhou are analyzed.

2. OVERVIEW OF REGIONAL GEOLOGY

Situatated at the junction of Qiandongnan Prefecture and the cities of Tongren and Huaihua in Guizhou and with its main body located within Cengong County, the Cengong area forms part of the southeastern area of the Yangtze Plate and the southern area of the western Hunan–Hubei trough-like fold belt from the perspective of the regional tectonic structure.\textsuperscript{48} During the sedimentation of the Niutitang Formation, the

![Figure 1. Tectonic location and the comprehensive stratigraphic column of the Cengong Block.](https://doi.org/10.1021/acsomega.1c06745)
surface structure formed a geological pattern characterized by a high elevation in the northwest and a low elevation in the southeast. Global transgressive events have deepened the sedimentary water bodies in the study area. This area is generally noted for the presence of a deep-water continental shelf sedimentary environment as well as organic matter (OM)-rich and siliceous shales that are steadily distributed in the horizontal transverse direction and are, on average, approximately 60 m in thickness. The Niutitang Formation has undergone superimposition and reformation due to multiple tectonic movements. The glacially deposited Nantuo Formation of the Nanhua System is the oldest formation exposed at the surface. The Niutitang Formation is buried at depths greater than 1000 m and outcrops only in the northeastern study area. This formation is structurally strong on both sides and weak in the middle. A large number of north-northeast-trending thrust faults have developed above the Niutitang Formation and are clustered in the northwestern and southeastern regions of the study area. The strike-slip fault developed in the middle of the Niutitang Formation divides the study area into eastern and western areas. The formation in the eastern area is relatively flat and deformed to a relatively small extent with a high gas content. The formation to the west of the strike-slip fault is heavily deformed and has low gas content.

The Niutitang Formation is characterized by “three highs and two lows”, namely, a high content of highly brittle minerals, a high TOC content (1.9–7.9%), a high degree of thermal evolution (2.2–2.4%), low porosity (1.4–2.2%), and low permeability. The OM in the shale consists primarily of type I kerogens and some type II kerogens. The pores in the shale are predominantly composed of organic pores and, to a lesser extent, inorganic pores. The pressure coefficient of the Niutitang Formation ranges from 0.93 to 1.21, suggesting the presence of atmospheric pressure conditions. Vertically, the Niutitang Formation is in conformable contact with the underlying Sinian Dengying Formation and the overlying Mingxinsi Formation, which constitute its direct roof and floor. In contrast to the Longmaxi Formation in the Sichuan Basin, where the shale has successfully developed (high TOC content, high over mature evolution, and formation over-pressure), the Niutitang Formation in the study area has a slightly lower degree of thermal evolution and a low-pressure coefficient. The SG flow was obtained during four wells in the early exploration, of which the gas content of well TX1 is between 1.18 and 2.77 m³/t, while well TM1 was ignited successfully. Still, the gas production time is short, and the gas content is below 0.5 m³/t, reflecting the difference in their preservation conditions (Figures 1 and 2).

3. FLUID SAMPLING AND TESTING CONDITIONS

FW samples were collected from four wells (TM1, TX1, CD1, and CY1). To ensure the comparability of FW ions during the sampling process, water samples with long flowback time and small changes in ion type and concentration are selected as sampling and analysis targets. The SG samples collected from the SG wells in northern Guizhou were used during the analysis. Specifically, high-pressure cylinders, degassed with vacuum pumping, were used to collect the SG samples. The cylinders were washed multiple times on-site before the
The N isotope values of N2 in the SG samples were calculated using the N isotope values of N2 in the atmosphere as a standard. In addition, the C isotope values of CO2 were tested using an ICS-5000 multifunctional ion chromatograph (IC) system (Thermo Fisher Scientific, USA) equipped with electron ionization (EI) power supply and a Trace GC Ultra gas chromatography system. During the test, a gas with an ultrahigh purity of above 99.99%, passivated through a passivation tube, was used as the carrier gas. The EI power supply could supply energy ranging from 0 to 150 eV and emit a current up to 35 μA. The ion source was heated between 125 and 350 °C.

3.1. Composition Testing of the SG Samples. The composition of the SG samples was tested using an ISQ gas chromatograph-mass spectrometer (Thermo Fisher Scientific, USA). This IC system was tested using a MAT253 gas isotope ratio mass spectrometer (Carlo Erba, Italy). The sample was maintained at 200 °C for 15 min. The N isotope values of N2 in the SG samples were calculated using the N isotope values of N2 in the atmosphere as a standard. In addition, the C isotope values of CO2 were calculated.

3.2. Isotopic Testing of the SG Samples. N isotopes were tested using a MAT253 gas–isotope ratio mass spectrometer (Finnigan, Germany). During the test, the temperature at the gas inlet was 200 °C. The sample was injected at a split ratio of 20:1 and heated to 80 °C at a rate of 15 °C/min and continuously to 200 °C at a decreased rate of 5 °C/min. The sample was maintained at 200 °C for 15 min. The N isotope values of N2 in the SG samples were calculated using the N isotope values of N2 in the atmosphere as a standard. In addition, the C isotope values of CO2 were calculated.

3.3. Testing of the Concentrations of Ions in the FW Samples. The concentrations of ions in the FW samples were tested using an ICS-5000 multifunctional ion chromatograph (IC) system (Thermo Fisher Scientific, USA). This IC system can supply a pump flow of up to 10 mL/min and a pressure of up to 31 MPa, with high-capacity separation. During the test, a fully compatible reversed-phase reagent was used in addition to highly acidic and alkaline eluents. During the experiment, the temperature of the cylinder was set at 30 °C, the flow rate of the cation pump was 0.25 mL/min, and the current of the suppressor was set at 20 mA with the concentration of methyl sulfonic acid at 15 mM. The flow rate of the anionic pump was 0.38 mL/min, and the current of the suppressor with a potassium hydroxide concentration of 30 mM was 29 mA. The testing was completed at the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation at Southwest Petroleum University.

4. RESULTS

4.1. Types of Ions and Degrees of Mineralization in the FW Samples. The types of ions and the degrees of mineralization in FW can be ascribed to the combined action of geological and hydrological changes. Analysis of the FW samples collected from different wells in terms of the types and concentrations of ions as well as the degree of mineralization reveals the following: identical types of ions were found in the FW samples collected from different wells in the Niutitang Formation. The major cations included K+, Ca2+, Na+, and Mg2+. Na+ accounted for a predominant proportion of the ions in FW, with an average concentration of 341.28 mg/L. The average concentrations of Ca2+, K+, and Mg2+ were 87.96, 62.38, and 21.67 mg/L, respectively. The major anions included Cl−, HCO3−, and SO42−, of which HCO3− was the highest in concentration, averaging 1059.38 mg/L, followed by Cl− and SO42−, the average concentrations of which were 415.63 and 48.00 mg/L, respectively. The FW samples collected from different wells differed considerably in terms of the concentrations of ions and the degree of mineralization.

The degrees of mineralization of the FM samples collected from wells TM1, TX1, CD1, and CY1 were found to be in the ranges of 1860.97–2001.41 mg/L (average: 1932.93 mg/L), 2201.3–2704 mg/L (average: 2473.70 mg/L), 1633.90–1699.90 mg/L (average: 1661.25 mg/L), and 1706.50–2445.30 mg/L (average: 2077.38 mg/L), respectively (Table 1).

4.2. Natural Gas Composition. The SG test results reveal a pronounced variation in the wells’ natural gas composition. The gas samples collected from wells with a high gas content (i.e., wells TX1 and CY1) consisted primarily of HC gases, the majority being CH4 mixed with an extremely small quantity of NHC gases. NHC gases in these wells were composed mainly of N2 and CO2 as well as a certain amount of He and Ar.

CH4, N2, and CO2 were found to account for 78.39–80.64% (average: 79.44%), 14.82–17.53% (average: 16.34%), and 2.37–2.62% (average: 2.49%) of SG in well TX1, respectively, and 74.67–78.04% (average: 76.39%), 21.58–23.87% (average: 22.88%), and 0.26–0.47% (average: 0.34%) of SG in well CY1, respectively. The SG in wells TM1 and CD1 was found to contain mainly NHC gases and only a small amount of HC gases. CH4, N2, and CO2 were found to account for 2.53–
5.42% (average: 3.99%), 93.41–95.87% (average: 94.76%), and 0.22–0.47% (average: 0.32%) of SG in well TM1, respectively, and 15.84–20.47% (average: 18.7%), 78.12–83.25% (average: 79.9%), and 0.26–0.41% (average: 0.34%) of SG in well CD1, respectively. The SG in each of these two wells was found to contain an extremely small quantity of C2H6.

Table 2 summarizes the detailed composition of the gas samples collected from each well.

| Sample | CH4/% | C2H6/% | C3H8/% | N2/% | CO2/% | Other gases/% |
|--------|-------|--------|--------|------|-------|--------------|
| TX1    | 80.64 | 1.53   | 0.04   | 14.82| 2.54  | 0.43         |
| TX1    | 78.57 | 1.28   | 0.07   | 17.53| 2.37  | 0.18         |
| TX1    | 80.16 | 1.44   | 0.01   | 15.55| 2.62  | 0.22         |
| TX1    | 78.39 | 1.15   | 0.03   | 17.47| 2.44  | 0.52         |
| TM1    | 3.84  | 0.12   | 0.01   | 95.22| 0.34  | 0.47         |
| TM1    | 5.42  | 0.24   | 0.0    | 93.41| 0.22  | 0.71         |
| TM1    | 2.53  | 0.19   | 0.02   | 95.87| 0.47  | 0.92         |
| TM1    | 4.16  | 0.27   | 0.02   | 94.53| 0.26  | 0.77         |
| CD1    | 15.84 | 0.45   | 0.03   | 83.25| 0.33  | 0.10         |
| CD1    | 20.47 | 0.33   | 0.04   | 78.12| 0.26  | 0.78         |
| CD1    | 19.87 | 0.47   | 0.02   | 78.88| 0.41  | 0.35         |
| CD1    | 18.62 | 0.39   | 0.03   | 79.33| 0.37  | 1.26         |
| CY1    | 76.52 | 0.05   | 0      | 23.04| 0.26  | 0.13         |
| CY1    | 74.67 | 0.18   | 0      | 23.87| 0.47  | 0.81         |
| CY1    | 78.04 | 0.04   | 0.01   | 21.58| 0.28  | 0.05         |
| CY1    | 76.33 | 0.08   | 0      | 23.04| 0.36  | 0.19         |

4.3. Gas Isotopes. The C and N isotope test results regarding the HC and NHC components in the SG samples collected from the different wells reveal the following. The δ13N (ratio of heavy/light isotopic abundances of nitrogen in gas components) values of the SG samples collected from wells TX1 and CY1 ranged from −8.7 to −4.6‰ (average: −6.6‰) and from −8.7 to −2.4‰ (average: −4.7‰), respectively. In addition, the δ13C (ratio of heavy/light isotopic abundance of carbon in gas components) values of the HC components of the SG samples collected from these two wells ranged from 35.7 to 38.2‰ (average: 37.3‰) and 36.4 to 37.2‰ (average: 36.8‰), respectively. In contrast, the δ13C values of their NHC components ranged from 12.4 to 15.9‰ (average: 14.3‰) and 11.6–15.7‰ (average: 12.8‰), respectively. For the SG samples collected from wells TM1 and CD1 (noted for high N2 content and low HC gas content in their SG), their δ13N values ranged from −2.1 to 0‰ (average: −0.53‰) and −3.6–0‰ (average: −0.9‰), respectively. Moreover, the δ13C values of the HC components of the SG samples collected from these two wells ranged from 31.8 to 35.1‰ (average: 33.0‰) and 32.7–37.3‰ (average: 34.5‰), respectively, while the δ13C values of their NHC components ranged from 1.8 to 5.2‰ (average: 14.3‰) and 2.9–7.3‰ (average: 4.2‰), respectively. The δ15N values of the SG differed notably by the well. At the same time, the δ13C ranges of the SG from different wells were essentially similar, suggesting that the NHC components of the SG from different wells have different origins (Table 3).

Table 3. Isotopic Analysis of the SG in the Niutitang Formation

| Sample | δ13C(CH4)/‰ | δ13C(C2H6)/‰ | δ13C(C3H8)/‰ | δ15N/N2/‰ | δ34S/COS/‰ |
|--------|-------------|-------------|-------------|------------|-------------|
| TX1    | 35.7        | 36.4        | 35.9        | −4.6       | 12.4        |
| TX1    | 37.4        | 37.4        | 38.2        | −8.7       | 15.9        |
| TX1    | 38.2        | 38.5        | 37.9        | −5.1       | 14.7        |
| TX1    | 37.9        | 37.6        | 37.5        | −5.9       | 14.3        |
| TM1    | 31.8        | 32.2        | 32.7        | 0          | 1.8         |
| TM1    | 31.8        | 31.8        | 0           | 0          | 1.8         |
| TM1    | 33.4        | 33.7        | 33.5        | −2.1       | 5.2         |
| TM1    | 35.1        | 34.9        | 35.5        | 0          | 4.7         |
| CD1    | 37.3        | 37.5        | 37.7        | 0          | 3.6         |
| CD1    | 35.4        | 36.1        | 35.9        | −3.6       | 7.3         |
| CD1    | 32.7        | 33.3        | 33.2        | 0          | 2.9         |
| CD1    | 32.7        | 32.9        | 33.1        | 0          | 2.9         |
| CY1    | 36.6        | 36.9        | 36.9        | −2.4       | 11.6        |
| CY1    | 36.4        | 96.6        | 96.6        | −2.4       | 11.6        |
| CY1    | 37.2        | 37.7        | 37.4        | −8.1       | 12.1        |
| CY1    | 36.9        | 37.0        | 37.0        | −5.9       | 15.7        |

5. DISCUSSION

5.1. Preservation Conditions Reflected by FW Characteristics. Based on the difference in the connectivity of a formation, its water connection system can be divided transversely and longitudinally into a free exchange zone (FEZ), a hindered exchange zone (HEZ), and a nonexchange zone (NEZ), of which the FEZ has the highest level of connectivity with the surface water, followed by the HEZ and NEZ. However, the NEZ has the best preservation conditions for a shale formation, followed by HEZ and FEZ. The types and concentrations of ions in FW can reflect the fluid environment. On this basis, some parameters have been derived from analyzing the level at which a formation is sealed, which is then further used to reflect its SG preservation conditions. These FW parameters mainly include the CI/Mg, Ca/Mg, and Na/Cl coefficients (CI/Cl, Mg/Mg, and Na/Cl, respectively), the coefficient of desulfurization (COS), and the FW type.68 The conditions reflected by different parametric indexes differ to some extent.

Determining the level of connectivity between an oil and gas reservoir and the surface based on the FW type is an approach commonly used in oil production. Generally, well-sealed formations contain CaCl2- and MgCl2-type water, while poorly sealed formations contain Na2SO4- and NaHCO3-type water. Analysis of the FW types in the SG wells at different horizons within the Sichuan Basin reveals that while wells containing CaCl2-type FW are high in both gas content and production capacity, the FW in SG wells in some shallow, broad, and gentle structures is of NaHCO3 type. Therefore, assessment of the SG preservation conditions in a formation based on water type alone is incapable of producing an unequivocal conclusion; obtaining this information requires supplementary analysis of the level at which the formation is sealed using indices that reflect the differences in the level at which its water is retained and sealed (e.g., CI/Cl, Mg/Mg, Na/Cl, and Cd). Cd reflects the level of metamorphism and the activity of FW.69 The average Cd value for normal seawater is 0.85. A low Cd value indicates well-sealed FW. Cd can be used to quantitatively reflect the level of metamorphism of subsurface brine,69 often with a threshold value of 3. A high Cd value indicates well-sealed formation. Based on the difference between the CI/Cl values for the formations in the successfully developed Jingbian gas
field, a $C_{\text{Cl} / \text{Mg}}$ value above 8.5 often indicates a large reserve of oil and gas in the area (Table 4).71

Table 4. FW Preservation Index of Niutitang Formation in the Cengong Area

| advantageous zone level | $C_{\text{Na}/\text{Cl}}$ | $C_{\text{J}}$ | $C_{\text{Cl}/\text{Mg}}$ | $C_{\text{Ca}/\text{Mg}}$ | FW          |
|-------------------------|---------------------------|--------------|-------------------------|-------------------------|-------------|
| conserved area           | <0.65                     | <1           | >8.5                    | >3                      | CaCl$_2$    |
| sub-favorable area       | 0.65–0.75                 | 1–4          |                         |                         | CaCl$_2$, MgCl$_2$ |
| weak conserved area      | 0.75–0.85                 | 4–40         | <8.5                    | <3                      | NaHCO$_3$, Na$_2$SO$_4$ |
| nonreserved area         | >0.85                     | >40          |                         |                         | NaHCO$_3$   |

Table 5 summarizes the parametric characteristics of FW, which were calculated based on the measured concentrations of the ions in the FW samples collected from different wells. These results show the following: there are two types (NaHCO$_3$ and CaCl$_2$) of water in the Niutitang Formation. Both types are present in wells CY1 and TZ1, suggesting that the FW originated from deep metamorphism and the atmosphere. In contrast, only NaHCO$_3$-type FW is currently in wells CD1 and TM1, indicating meteoric freshwater in a continental sedimentary environment as its source. Relatively low $C_{\text{Na}/\text{Cl}}$ and $C_{\text{J}}$ values and relatively high $C_{\text{Cl} / \text{Mg}}$ and $C_{\text{Ca} / \text{Mg}}$ values were found for the FW samples collected from the wells with a relatively high gas content (i.e., wells TX1 and CY1). Specifically, the $C_{\text{Cl} / \text{Mg}}$ ranges of 9.03–23.95, 9.59–20.73, 7.82–9.87, and 6.57–9.31 and the $C_{\text{Na} / \text{Cl}}$ ranges of 0.47–1.03, 0.83–1.52, 2.84–4.47, and 2.93–3.03 were found in the FW samples collected from wells TX1, CY1, TM1, and CD1, respectively. Higher $C_{\text{J}}$ values were generally found in the FW samples collected from well TM1 than those collected from TX1 and CY1. Specifically, $C_{\text{J}}$ ranges of 14.60–19.81 and 7.54–17.18 were found in the FW samples collected from wells TM1 and CD1, respectively, suggesting that the formation is poorly sealed. The analysis of parameters such as the type, $C_{\text{Na} / \text{Cl} / \text{Mg}}$ and $C_{\text{Ca} / \text{Mg}}$ of FW shows the following common conclusion: the four wells located in the study area have all been scoured by surface water. The FW in each area has undergone an exchange with the surface water, and the FW has been retained at higher levels in wells TX1 and CY1 than in wells CD1 and TM1. The surface water has scoured and damaged the SG reservoir to a relatively small extent in the areas where wells TX1 and CY1 are located. As a result, the shale in these areas contains a certain gas content and potential for commercial development.

5.2. Sources of Natural Gas. The composition analysis of the gases in the successfully developed highly mature SG reservoirs in and around the Sichuan Basin reveals that these SG reservoirs primarily contain HC gases (mostly CH$_4$) and some NHC gases (including mainly N$_2$ and CO$_2$, a small number of inert gases). The types and concentrations of NHC gases are often used to analyze the gas reservoir quality.72,73 The NHC components of the SG in northern Guizhou consist mainly of N$_2$ and, to a small extent, CO$_2$. In addition, the N$_2$ content varies notably between wells. Published studies show that the HC components of the SG originate primarily from the OM during the pyrolysis and HC generation process, while N$_2$ and CO$_2$ originate from four types of sources, namely, the atmosphere, pyrolysis and HC generation, crustal metamorphism, and the deep mantle. When the shale is connected to the atmosphere directly or through faults, the nitrogen in the shale is mainly the atmospheric source. As the OM in the shale evolves and generates HCs, its microbial degradation or ammonification at the high maturity stage can also lead to the formation of N$_2$, which is an endogenic gas and cannot be used to determine the quality of SG preservation conditions. Therefore, accurate quality analysis of SG preservation conditions cannot be achieved using the content of NHC gases as the sole indicator. More importantly, it requires an examination of their sources as a supplement.

The deepening of SG research has gradually allowed for the development of methods that determine the genesis of natural gas based on its atomic composition and its associated gases and the production of plots to facilitate the identification of gases such as HC gases, CO$_2$, and N$_2$. The N$_2$ sources are identified primarily through the analysis of its $^{15}$N content. The $^{15}$N content differs remarkably between N$_2$ from organic and atmospheric origins. N$_2$ formed from the ammonification of OM is associated with $^{15}$N values between −10 and −1‰, and pyrolysis of OM is related to $^{15}$N values above 5‰ whereas N$_2$ of an atmospheric origin contains no $^{15}$N. CO$_2$ sources are frequently determined based on a cross-plot of the content of CO$_2$ and its $^{13}$C component, which can be divided into four regions indicative of different origins, namely, an organic origin, an inorganic origin, a combination of organic–inorganic origins, and mixed inorganic gases.

The test results for the samples collected from the four wells reveal a large variation in the composition of natural gas and the isotopic content of the NHC components within a well (Table 5). The samples collected from wells TX1 and CY1 contained mostly HC gases and some N$_2$ and CO$_2$. Analysis of the CO$_2$ content and its C isotope component in the samples collected from each well in combination with the CO$_2$ source analysis plot reveals that all the sample points distributed within the region indicate an organic origin. The N$_2$ content ranged from 10 to 20% and below 10% in the samples collected from wells TX1 and CY1, respectively. In addition, isotopic analysis reveals $^{15}$N values between −8.7 and −4.6‰ for N$_2$ and $^{13}$C values between 12.4 and 15.9‰ for CO$_2$ in the samples collected from well TX1. According to the N$_2$ source analysis plot, the N$_2$ in wells TX1 and CY1 originated primarily from the ammonification of OM during the highly mature stage.

In contrast, the samples collected from wells CD1 and TM1 in the same study area contained a small content of HC gases and a high content of N$_2$. Specifically, N$_2$ accounted for over

Table 5. Characteristics of Water in the Niutitang Shale Formation in the Cengong Area

| sample | FW       | $C_{\text{Cl} / \text{Mg}}$ | $C_{\text{Ca} / \text{Mg}}$ | $C_{\text{J}}$ | $C_{\text{Na} / \text{Cl}}$ |
|--------|----------|-----------------------------|-----------------------------|--------------|-----------------------------|
| TM     | NaHCO$_3$| 7.82–9.87/8.57              |                            |              |                             |
| TX     | CaCl$_2$, NaHCO$_3$| 9.03–23.95/18.06          |                            |              |                             |
| CD     | NaHCO$_3$| 6.57–9.31/8.21              |                            |              |                             |
| CY     | CaCl$_2$, NaHCO$_3$| 9.59–20.73/14.58          |                            |              |                             |
90 and 70–84% of SG in wells TM1 and CD1, respectively. Therefore, the SG in these two wells can be classified as N2-rich SG. Isotopic analysis reveals a similarity in the content of \(^{15}\)N between 85% of the samples collected from wells TM1 and CD1 and the atmosphere. The test results for a few samples show that the N\(_2\) in these two wells originated from the ammonification of OM and that the CO\(_2\) was of an organic origin. Based on the content as well as the isotopic content of the two NHC gases, the preservation conditions in wells TX1 and CY1 in the study area are better than those in wells CD1 and TM1.

5.3. Comprehensive Analysis of Preservation Conditions. As discussed earlier, the four wells in the study area differ considerably in their gas composition and FW characteristics. While the FW properties and gas composition can, to some extent, reflect the connectivity between a shale bed and the surface, analysis of FW properties or gas composition alone is incapable of producing an unequivocal conclusion. Therefore, SG preservation conditions should be comprehensively analyzed based on the FW properties and gas composition in conjunction with the actual geological conditions.

A comprehensive analysis of the FW sample properties as well as the content and sources of each component of the gas samples collected from different wells in the study area reveals the following: FW and gas source analysis results for both wells TX1 and CY1, which are located on the right side of the strike-slip fault in the study area, indicate the presence of good preservation conditions. Analysis of the regional tectonic structure and the development characteristics of the faults reveals that well TX1 is located in the relatively stable central region of the study area where the formations dip at small angles and are distant from large faults; small faults are also absent around the well TX1. These conditions are favorable to the preservation of SG. The SG content in this well is greater than 2.5 m\(^3\)/t. In contrast, well CY1 is relatively close to a fault and surrounded by a number of small faults.

Consequently, the preservation conditions in well CY1 are inferior to those in well TX1. The SG content in well CY1 is approximately 1.2 m\(^3\)/t.\(^{72,73}\) The gas composition test results reveal a high N\(_2\) content in both wells. However, the analysis identifies the ammonification of OM as the source of N\(_2\) in these two wells. FW analysis shows the following: Both wells TX1 and CY1 contain NaHCO\(_3\)-type water, suggesting a certain level of connectivity between their formation and meteoric water. However, the levels of metamorphism of the FW in these two wells are relatively high within the study area.

Moreover, both wells contain a high SG content, the NHC components of which were found to have originated from HC generation and the ammonification process, suggesting that a certain level of connectivity between the FW and the surface within this broad and gentle area had a limited destructive effect on the SG reservoirs. Therefore, good SG preservation conditions are present in the areas where wells TX1 and CY1 are located. In comparison, both wells CD1 and TM1, located on the left side of the strike-slip fault, contain an SG content greater than 1.0 m\(^3\)/t and an N\(_2\) content greater than 70%. The N\(_2\) in these two wells originated primarily from the atmosphere, while the FW is of the NaHCO\(_3\) type and is mineralized to a low degree. These findings suggest a high level of connectivity between the formation and the atmosphere, which is inimical to SG preservation. Based on the analysis of factors affecting the preservation, such as structure, roof, and floor differences, the main reason for the gas-bearing difference of SG wells on both sides of the strike-slip fault is the sealing difference between the roof and floor of wells CD1 and TM on the left side of the strike-slip fault. Well TM1 has no complete roof and floor conditions, while well CD1 has a complete roof, and both wells are at a relatively high point. FW and SG exchange and escape through the incomplete roof, resulting in poor gas-bearing properties of shale.

6. CONCLUSIONS

(1) The Niutitang Formation in the Cengong area contains two water types (CaCl\(_2\) and NaHCO\(_3\)). Characterized by low C\(_{Na/Ct}\), high C\(_{Ca/Mg}\) and high C\(_{o}\), the FW in wells TX1 and CY1 is of CaCl\(_2\) type and is retained at a high level. In comparison, characterized by high C\(_{Na/Ct}\), low C\(_{Ca/Mg}\) and low C\(_{o}\), the FW in wells TM1 and CD1 is of NaHCO\(_3\) type and undergoes an intense exchange with surface water.

(2) The SG in the Niutitang Formation contains a high N\(_2\) content, which originated from two main sources: the atmosphere and the ammonification of OM. With a \(^{15}\)N value between −8.7 and −4.2‰, N\(_2\) accounts for approximately 20% of SG in wells TX1 and CY1 and was formed from OM’s ammonification during the pyrolysis HC generation process. With a \(^{15}\)N value of −3.6 to 0‰, N\(_2\) accounts for more than 70% of SG in wells TM1 and CD1, and it originated from the atmosphere and the ammonification of OM. A high level of connectivity with the atmosphere results in poor preservation conditions in the shale beds in these two wells.

(3) Combined with the analysis results of FW and gas components and sources, the preservation conditions of TX1 well and CY1 well are relatively good, and CaCl\(_2\)-type water, an indicator of good preservation conditions, is present in both wells TM1 and CD1. However, the SG in these two wells contains a high content of atmospherically derived N\(_2\). Therefore, when the FW properties and the SG composition are supplementarily analyzed to determine the quality of the SG preservation conditions, the FW type and the content of NHC gases should not be used as sole indicators. Instead, they should be combined with the tectonic conditions as well as the levels of retention and metamorphism of the FW and the sources of NHC gases to make a reasonable evaluation.

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Notes
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