Geochemical Characteristics and Sedimentary Environment of the Upper Permian Longtan Coal Series Shale in Western Guizhou Province, South China

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China’s marine-continental transitional facies shale gas resources are abundant with shale gas resources of about 19.8 trillion cubic meters, while the exploration and development of these shale gas resources are still in the initial stage. The Upper Permian Longtan coal series shale is one of the most important transitional shales in the Yangtze platform, China. In this study, the comprehensive methods of mineralogy and organic geochemistry are used to discuss the characteristic of organic matter and sedimentary environment of the Longtan coal series shale in western Guizhou Province, South China. The results show that (1) the total organic carbon (TOC) content of this shale ranges in 0.6%-28.21%, mainly in 3%-12%, indicating a "good-excellent" hydrocarbon source rock, and its vitrinite reflectance ($R_0$) ranges from 1.48% to 2.93%, indicating a high-overmature organic matter; (2) the organic matter in this shale is multiorigin, and most of them come from the terrestrial higher plant while the rest come from the plankton; (3) type index (TI) of organic matter is from -65 to 41, indicating most of the kerogens which are II-III types; and (4) the sedimentary environment of this shale is dominated by suboxic-anoxic fresh water environment, which provides a favorable condition for the preservation of organic matter. In addition, the warm and humid climate during the Late Permian in the Yangtze platform promotes plant growth, and as a result, the Longtan coal series shale is rich in organic matter and has great potential of shale gas exploration and development.

1. Introduction

Shale gas has become an important part of natural gas production growth in China [1, 2]. In 2020, China has achieved shale gas production of $200 \times 10^8$ m$^3$, and it was mainly produced from four major shale gas fields (they are Jiaoshiba, Changning, Weiyuan, and Zhaotong shale gas fields) [2]. However, the commercial development of shale gas in China is limited to marine strata in the Sichuan Basin and its periphery. The exploration and development of marine-continental transitional facies shale gas have not made great progress and are still in the early evaluation stage [3]. Large-scale marine-continental transitional facies shale gas resources are enriched in the Upper Carboniferous Taiyuan and Lower Permian Shanxi Formations in Ordos, Qinshui, Southern North China, and Bohai Bay Basins and Upper Permian Longtan Formation in the Yangtze platform. The Longtan Formation is rich in shale gas resources, accounting...
for a quarter of the total shale gas resources in China, and has great potential of hydrocarbon exploration and development [4, 5].

The marine-continental transitional facies shale gas develops in delta, estuary, barrier island, tidal flat, lagoon, and other environments. Organic-rich shale is more common in lagoon phase, and its sedimentary model is barrier island-lagoon sedimentary model. Influenced by terrigenous clastic materials and sea level change, organic-rich shale often intercalates with coal and tight sandstone and changes laterally, with high organic matter abundance and complex organic matter composition (covering kerogens of type I, type II, and type III) [3, 5–9]. These characteristics provide a favorable hydrocarbon-generating material basis and preservation conditions for marine-continental transitional shale gas, but increase the difficulty of studying the organic matter enrichment mechanism and sedimentary environment of this kind of shale.

The Longtan coal series shale in Guizhou Province is one of the significant transitional fine grain rocks in the Yangtze platform, which is rich in organic matter, and the recoverable shale gas resources are about 3107.73 × 10⁹ m³ [8, 10–13]. Influenced by weathering products of Kangdian ancient land and seawater intrusion, there is little research on the occurrence characteristics and sources of organic matter in this coal series shale, which restricts the exploration and development process of shale gas.

In this study, the source and sedimentary environment of organic matter in the Longtan coal series shale in southwestern Guizhou Province were studied by combining the analyzing methods of organic geochemistry and mineral petrology, which could provide theoretical reference for the exploration and development of this kind of shale gas resources.

2. Geological Background

Guizhou Province is located in the southeastern margin of Upper Yangtze Block, which rose to land at the end of the Middle Permian and experienced long-term denudation. During the Late Permian, the basement subsidence and seawater intrusion occurred again, resulting in the coal-bearing series in continental, marine-continental transitional facies, and marine facies [14]. Because the Kangdian rift zone revived at the end of the Middle Permian, the Kangdian ancient land rose to generate a palaeogeographic pattern of higher west and lower east in the Upper Yangtze platform. Thus, the Kangdian ancient land was the main terrigenous supply area in the Upper Yangtze platform during the late Permian coal accumulation period [14, 15]. At the same time, seawater intruded from the east and southeast, which caused the Upper Permian coal measure strata in the Upper Yangtze platform to be affected by both continental input and seawater, and sedimentary systems such as ancient land (denudation area), alluvial plain river, delta, tidal flat-lagoon, carbonate platform, and deep water basin were distributed in turn from west to east (Figure 1) [12, 16, 17]. The Longtan Formation is the most significant coal-bearing strata of the Upper Permian, which belongs to marine-continental transitional facies. Xuanwei Formation, Wujiaaping Formation, and Longtan Formation are deposited at the same time (Figure 2). In contrast to the Longtan Formation, the Xuanwei Formation belongs to continental sediments and the Wujiaoping Formation is mainly marine sediments. The coal-bearing properties of the Xuanwei and Wujiaoping Formations are obviously lower than that of the Longtan Formation.

3. Samples and Experiments

3.1. Sample Collection. In this study, 81 fresh core samples of the Longtan coal series shale in Guizhou Province were collected. Among them, 63 samples were collected from well W2 in Pu’an County (see Figure 1), and 18 samples were from well W4, Zhijin County.

3.2. Experiments. For the collected shale samples, the experiments about the total organic carbon (TOC) content, vitrinite reflectance, organic maceral and mineral compositions, chloroform asphalt “A” extraction, group component separation, and saturated hydrocarbon gas chromatography-mass spectrometry (GC-MS) were conducted.

The total organic carbon (TOC) content was analyzed by TL851-5A sulfur and carbon analyzer. The analysis of mineral composition was completed on D/MAX2000 X-ray diffractometer. The chloroform asphalt “A” extraction and group component separation experiments follow two oil fractometer. The chloroform asphalt “A” extraction and group component separation experiments follow two oil and gas industry standards (SY/T 5118-2005 and SY/T 5119-1995).

The gas chromatography-mass spectrometry analysis was completed on Agilent 7890 GC-MS, and the carrier gas was helium with a purity of 99.99%. During this analysis, the conditions were set as (1) the injector temperature was 300°C, and the chromatographic column was a 30 m × 0.25 mm × 0.25 μm HP-5MS elastic quartz capillary column; (2) the initial temperature was 50°C, and after 3 minutes, it was heated to 320°C with a rate of 3°C/min; (3) the flow rate of carrier gas was 1 mL/min, lasting for 20 min. The method of data acquisition was multi-ion detection.

In addition to the above samples and experiments, this paper also collates the preliminary analysis results of organic geochemical parameters of the Longtan coal series shale, Guizhou Province, including well W1, well W3, and well W5 (Figures 1 and 3), and discusses the organic matter source and sedimentary environment of the Longtan coal series shale combined with the experimental results in this study.

4. Results and Discussion

4.1. Organic Geochemical Characteristics

4.1.1. Types of Organic Matter. According to the morphology of organic matter and its contact relationship with minerals, the occurrence of organic matter in the Longtan coal series shale can be divided into four types, and they are banded organic matter, massive organic matter, dispersed organic matter, and interwoven organic matter (Figure 4). The source of organic matter in source rocks is closely related to kerogen types. Type I kerogen mainly comes from lower
plankton, such as algae and fungi, while type III kerogen mainly comes from terrestrial higher plants. Type II kerogen is a mixed source of lower plankton and higher plants. The kerogen type index, such as TI index, is a significant method to judge the kerogen type of source rocks. $\text{TI} \geq 80$ indicates type I kerogen, $40 \leq \text{TI} < 80$ is a main character of type II kerogen, TI value ranges in 0-40 indicating type II kerogen, and type III kerogen generally has TI value less than 0 [18]. The TI values of the Longtan coal series shale samples range from 41 to 65 (32-39 for W2 well and 41-65 for W4 well, Figure 3), indicating that II-III kerogens are the main organic matter components of this shale.

4.1.2. Abundance of Organic Matter. Organic matter is the material basis of hydrocarbon generation in source rocks, and its abundance is a key factor determining the hydrocarbon generation capacity of source rocks. Geochemical indicators for evaluating the abundance of organic matter mainly include TOC content, chloroform asphalt “A”, hydrocarbon generation potential ($S_1 + S_2$), and total hydrocarbons [19]. Among these indicators, chloroform asphalt “A”, hydrocarbon generation potential, and total hydrocarbon can effectively reflect the original hydrocarbon generation ability of source rocks in the low maturity evolution stage. With the increase of thermal evolution degree and the continuous hydrocarbon generation and expulsion, the mass fraction of organic carbon remaining in source rocks in the high-overmature evolution stage is low. Thus, it is difficult to accurately and objectively evaluate original hydrocarbon generation capacity of high-overmature source rocks by hydrocarbon generation potential and total hydrocarbon [19, 20]. In contrast, TOC content has high stability
during thermal maturation and can effectively reflect the organic matter abundance of high-overmatured source rocks [18]. The Longtan coal series shale of the Upper Permian in Guizhou Province is generally high-overmature [12]. In this study, TOC content was used as a key parameter evaluating the organic matter abundance of this shale, combined with chloroform asphalt “A”, hydrocarbon generation potential, and total hydrocarbon.

The TOC content of shale samples in W2 (Pu’an County) well ranges in 0.61%-12%, with an average of...
3.34%, and which is 1.12%-17.24% (averaging 5.34%) in these samples from W4 well (Zhijin County) (Figure 3). Previous studies recognized that the TOC content of coal series shale in W1 well, Xingren County, ranges from 0.6% to 11.72%, with an average of 3.43% [12], and the TOC content of coal series shale in W3 well, Shuicheng County, is as high as 2.18%-28.21% (averaging 7.7%) [7]. The TOC content of coal shale in W5 of Qianxi County is between 1.29% and 14.8%, with an average of 5.27% [10]. The above results indicate that the TOC content in the Longtan coal series shale in Guizhou Province is relatively high, and this shale belongs to "good" or "excellent" source rocks according to the evaluation standard of organic matter abundance of coal series shale [21] (Figure 5).

The total hydrocarbon content of the shale sample in this study ranges from 32.79% to 47.37%, indicating that it is an excellent source rock. However, the content of chloroform asphalt "A" in these samples is between 0.0014% and 0.0084%, with an average of 0.00368%, which is much lower than the limit of hydrocarbon generation potential of coal series source rocks (0.15%). According to the total hydrocarbon content, the Longtan coal series shale studied here belongs to nonhydrocarbon source rocks. The range of hydrocarbon generation potential is 0.1097-2.7018 mg/g, implying that most of the shale samples in this study belong to inferior source rocks, and a few of them are nonsource rocks. The reason for the low content of chloroform bitumen “A” and hydrocarbon generation potential in the Longtan Formation coal series shale is that the shale has a high thermal evolution degree, which generally reaches a high-overmaturity evolution stage [12]. During this stage, a large number of liquid hydrocarbons are cracked to generate gaseous hydrocarbons and then lead to a decrease in hydrocarbon generation potential.

Considering the high stability of TOC content, the Longtan coal series shale in Guizhou Province is mainly categorized as "good" and "excellent" source rock according to TOC content. In addition, the TOC content has a good positive correlation with hydrocarbon generation potential (Figure 5(a)), indicating that the higher the TOC content, the greater the hydrocarbon generation potential.

4.1.3. Organic Thermal Maturity. Vitrinite reflectance ($R_o$) and biomarker compounds are significant indicators of thermal evolution of source rocks, and the maturity of organic matter of shale gas in the Longtan Formation coal series shale was analyzed in this study based on these indexes.

The $R_o$ values of well 2 range in 2.26%-2.58% (Figure 3), with an average of 2.41%, and the $R_o$ values of W4 are from 1.46% to 2.52%, averaging 1.89%. These results indicate that the Longtan Formation coal series shale in Guizhou Province is in a high-overmaturity evolution stage. Previous studies have also shown that this shale is in the high-overmaturity evolution stage, such as the $R_o$ values of the Xingren W1 well.
are 1.92%-2.93% [11, 12], and which range in 1.48%-1.84% in the Shuicheng W3 well [8] and 1.89%-2.74% in the Qianxi W5 well [10]. Based on previous studies and experimental results in this paper, it can be inferred that (1) shale gas in the Longtan Formation coal series shale in Guizhou Province is in a high-overmature evolution stage; (2) the maturity of organic matter in the zone of Pu’an-Qinglong-Zhenfeng-Xingyi is the highest, which is basically in the evolution stage of overmaturity ($R_o ≥ 2\%$). The organic matter in the zone of Weining-Panxian-Zhijin-Nayong is mainly high maturity ($1.3% < R_o < 2.0\%$), and some of them are overmature [12].

The odd-even predominance (OEP) of saturated hydrocarbon of the Longtan Formation coal series shale ranges from 0.82 to 1.21 (averaging 1.04), and even carbon number dominance is not obvious. The carbon preference index (CPI) ranges from 1.12 to 1.51, with an average of 1.26, indicating that source rocks have all entered the mature stage (Figure 6(a)). Compared with $R_o$, some biomarker compounds (Table 1) reflect that the maturity of the Longtan Formation coal series shale samples is low. For example, the steranes $C_{29}ααα20S/(20S + 20R)$ and $C_{29}ββ/(20R + 20S)$ in the samples range in 0.27-0.42 (averaging 0.37) and 0.22-0.38 (averaging 0.31), respectively, which are significantly higher than the hydrocarbon generation threshold and did not reach their thermal evolution equilibrium. This result indicates that the organic matter is in the mature stage. The $Ts/(Tm + Ts)$ ratios range from 0.4 to 0.69, with an average of 0.5, and the content of $C_{31}/(22R + 22S)$ range in 0.57-0.62 (averaging 0.59) indicates that the organic matter evolution degree of the Longtan

Figure 5: (a) Plot of TOC content vs. $S_1 + S_2$ and (b) plot of chloroform bitumen “A” vs. total hydrocarbon of the Longtan coal series shale.
Formation coal series shale is close to the peak stage of hydrocarbon generation. The biomarker compound index is greatly affected by maturity. The above indexes have a high accuracy in the immature stage of organic matter, and this accuracy decreases when organic matter enters into high-overmature stage [19, 20, 22, 23]. Therefore, based on Ro, combined with CPI-OEP diagram to judge the maturity of organic matter in this study, the results show that the Longtan Formation coal series shale is in the high-overmature stage.

4.2 Organic Matter Source. According to biomarkers data, the content and distribution of n-alkanes are of great significance to reveal the source of organic matter. The characteristics of n-alkanes in the Longtan Formation coal series shale samples include (1) the carbon number distributes in nC14-nC35; (2) the carbon peaks are mainly distributed among nC15-nC18 (Figure 7), followed by nC24, nC25, and nC21, indicating the multiple sources of organic matter in the sample; (3) mudstone has higher nC21/nC22, and the ratio ranges in 0.5-8.4 (averaging 2.72), implying that light
hydrocarbon components occupy an absolute advantage; and (4) \((nC_{21} + nC_{22})/(nC_{28} + nC_{29})\) is between 0.78 and 2.36 (averaging 1.34) indicating a significant low carbon advantage. These characteristics comprehensively reflect that the organic matter in the Longtan Formation coal series shale has various sources.

The Longtan Formation coal series shale samples contain abundant terpenoids. Pentacyclic triterpenoids are the richest one, followed by tricyclic diterpenes and long-chain triterpenoids, and tetracyclic terpenes and gammaceranes are less compositions (Table 1). It is generally believed that the hopanes are derived from microbial bacteria, and the high abundance of Epimedium is also related to the strong bacterial activity during the deposition period. The content of hopane compounds in the samples in this study is relatively high, and \(C_{30}\) hopane is the dominated one. Octane was detected from \(C_{31}\) to \(C_{35}\), indicating that organic matter is contributed by lower organisms such as algae. Tricyclic terpanes mainly come from the cell membrane of protozoa or low aquatic organisms such as algae, which are closely related to the saline water environment. The abundance of tricyclic terpanes in some samples is low, and the main peak is located in \(C_{15}\) to \(C_{18}\), reflecting a large amount of organic matter come from higher plants. High abundance of tricyclic terpanes was also detected in some samples, implying that some organic matters come from lower aquatic organisms.

The main steranes detected in the Longtan Formation coal series shale samples are regular steranes \(C_{27}, C_{28}, \) and \(C_{29}\) and progesterone steranes, and there is also a small amount of rearranged sterane. The average relative contents of \(C_{27}, C_{28}, \) and \(C_{29}\) were 37.98%, 22.76%, and 39.25%, respectively (Table 1). The high \(C_{29}\) content indicates that organic matter mainly comes from terrestrial higher plants, and the input of low aquatic organisms is relatively weak. The ternary diagram of regular steranes \(C_{27}, C_{28}, \) and \(C_{29}\) is one of the methods to classify the parent material types of organic matter, and as shown in Figure 8(a), the organic matter of the Longtan Formation coal series shale is rich and has a mixed source.

4.3. Sedimentary Environment. Geochemical indicators including \(TS/2 \ast TOC\), isoprenoids, and steroids are effectively used to reveal sedimentary environment. Among them, \(TS/2 \ast TOC\) is a good indicator to distinguish the difference of salinity in marine and terrestrial water, and the larger the value, the higher the salinity of the reaction water. The \(TS/2 \ast TOC\) value of the Longtan Formation coal series shale ranges from 0.014 to 1.08 (sample number is 36) (Figure 3) [8]. About 77.78% of the samples were deposited in fresh water with a \(TS/2 \ast TOC\) value less than 0.38, and only a small amount of the samples indicate salt water. The biomarker compounds contain small amounts of pregnane and gammacerane (Figure 7), also indicating that the Longtan Formation coal series shale was mainly deposited under fresh water condition. This fresh water condition may be the result of strong terrigenous input.

The original substance of pristane and phytane is phytol, which is influenced by water oxidation-deoxidation conditions and microbial differences. In general, pristane indicates the oxidation environment and phytane indicates the reduction environment, so the ratio of pristane to plant (Pr/Ph) can be used as an indicator to judge the oxidation-deoxidation state of the sedimentary environment [24–26]. Pr/Ph ≤ 1 denotes an oxygen-containing environment and anoxic environment, and this ratio is higher than 1 when oxygen-containing conditions appear. In general, this ratio
is close to 1 indicating alternation of oxygen-containing environment and anoxic environment [18, 24]. The Pr/Ph of the Longtan Formation coal series shale ranges from 0.58 to 1.25 (sample number is 18), with an average of 0.865, indicating that the water was mainly in an anoxic environment and oxygen content fluctuated during the deposition period. The results of Zhang et al. (2020) [8] show that the Longtan Formation coal series shale has a high sulfur content, with an average of 3.73%, proving that it is mainly deposited in an anoxic water environment. Based on previous studies and experimental results in this study, the relationship between Pr/nC17 versus Ph/nC 18 is used to judge the sedimentary environment, which indicates that this coal series shale was deposited under subanoxic to

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**Figure 8:** (a) Ternary diagram of regular steranes (C27–C28–C29) (the basemap is from [31]) and (b) ternary diagram of minerals of the Longtan coal series shale.

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**Figure 9:** Organic matter enrichment model of the Longtan coal series shale.
anoxic conditions. Especially, the water body in Shuicheng County is mainly an anoxic environment, while in Pu’an and Zhijin Counties is mainly an anoxic and suboxic environment. Combined with the tidal flat-lagoonal sedimentary background of the Late Permian in the study area [13, 27], the Longtan Formation was supplied by the provenance from the western Kangdian ancient land during the sedimentary period, which was mainly composed of clay minerals and terrigenous clastic quartz, and the lithology included siliceous shale, clayey shale, and mixed shale (Figure 8(b)). Among them, shale samples from W4 are clay shale or siliceous shale with very few carbonate minerals (averaging 1.33%). The carbonate mineral content of shale samples from W2 (averaging 15.27%) is much higher than that of W4. The reason may be that seawater invaded from the southeast during this period (Figure 1). Moreover, because the influence of seawater was greater in W2 in the south, carbonate mineral content is higher there. Therefore, under the comprehensive influence of terrigenous detrital injection and marine transgression, the organic matter of the Longtan Formation coal series shale came from both terrestrial higher plants and marine low organisms, which has a mixed source. During the Late Permian, the Upper Yangtze platform was in a warm-humid palaeoclimate background, and plants flourished, providing a rich primitive material basis for the enrichment of organic matter [14, 15, 27]. The suboxic-anoxic water environment in this block provided superior conditions for preserving organic matter (Figure 9) and leading to the abundance of organic matter in this coal series shale (Figures 3, 4, and 5) and the great potential of shale gas resources.

5. Conclusions

In this study, by combined methods of organic geochemistry and mineral petrology, the sedimentary environment and origin of organic matter in the Upper Permian Longtan coal series shale in western Guizhou Province were studied, and following conclusions were recognized.

(1) The coal series shale in the study area has a high abundance of organic matter, with a TOC content of 0.6%-28.21%, most of which are “good” or “excellent” source rocks, and the organic matter is in the high-overmaturity evolution stage ($R_o$ value is 1.48%-2.93%). Under the influence of high thermal evolution degree, the chloroform pitch “A” and hydrocarbon generation potential in the organic matter of this coal series shale are relatively low.

(2) The analyzing results of organic microscopic components, such as n-alkanes, isoprenoids, regular steranes, and terpenoids, show that the organic matter of the coal series shale of the Longtan Formation in Guizhou Province has multiple sources. The main source of this shale is terrestrial higher plants, and the kerogen in this shale is mainly II$_1$-III type.

(3) The analyzing results of TS/2 ∗ TOC, isoprenoids, and steroids show that the depositional environment of coal series shale in the Longtan Formation in the study area is dominated by suboxic-anoxic environment, which provides more favorable conditions for the preservation of organic matter.

(4) During the deposition of the Longtan Formation, the warm and humid paleoclimate background led to the flourishing of organisms, which provided a rich original material basis for the enrichment of organic matter, coupled with favorable conditions for preserving organic matter. The coal series shale of the Longtan Formation in the study area was rich in organic matter, and it has a great potential for shale gas exploration and development.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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