Reconstructing the Climatic–Oceanic Environment and Exploring the Enrichment Mechanism of Organic Matter in the Black Shale across the Late Ordovician–Early Silurian Transition on the Upper Yangtze Platform Using Geochemical Proxies

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ABSTRACT: Black shale deposited in the transitional period from the Late Ordovician to Early Silurian is the most important source rock and shale gas reservoir in the Yangtze region of South China. However, the source of these sediments is still controversial. In this paper, the changes in total organic carbon (TOC), total sulfur (TS), organic carbon isotopes (δ13Corg), biomarkers, trace elements, and rare earth elements in the Ordovician–Silurian boundary strata of the XK-1 well in northern Guizhou Province, South China, have been systematically studied. The paleoenvironmental and paleoclimatic conditions of the Late Ordovician to Early Silurian and their relationship with organic matter enrichment in the Upper Yangtze Platform have been reconstructed. The distribution of biomarkers reflects that the Late Ordovician–Early Silurian shale was deposited in the marine environment and was highly contributed by marine plankton/algae and microorganisms. Paleoclimatic proxies (Sr/Cu, δ13Corg) show that the global climate system experienced significant changes from a warm-humid climate to a brief period of cold-dry climate and then back to a warm-humid climate during the Ordovician–Silurian transition. This warm and humid climate condition helps to improve the biological productivity within the photic zone of the water column during deposition. In addition, the low oxygen (reduction) conditions during the deposition of the Late Ordovician–Early Silurian deposits are characterized by low Pr/Ph values (0.39–0.79) and relatively high elemental ratios of V/Ni (1.40–5.77) and V/(V + Ni) (0.58–0.85). This paleoredox condition contributes to the preservation of organic matter during deposition of the Late Ordovician–Early Silurian deposits. Therefore, it is demonstrated that the climate and ocean fluctuated greatly during the Late Ordovician–Early Silurian transition period, and this fluctuation provided necessary control factors for marine anoxia, primary productivity, and subsequent organic-rich black shale deposition in the Upper Yangtze region during the Late Ordovician and Early Silurian intervals.

1. INTRODUCTION

The Late Ordovician–Early Silurian is an important turning point in the evolution of biology, climate, and environment in geological history.1–4 During this transition, many abnormal geological events occurred, such as a mass extinction of organisms, large-scale glacial events, sea level rise and fall, extensive volcanic activities, oceanic anoxic events, large-scale fluctuation of carbon isotopes, and an extensive deposition of organic-rich shale.5–13 Among them, the widely distributed black shale is considered the most important Paleozoic source rock and shale gas reservoir, and it has been deposited throughout the basin and even globally, such as the hot shale deposited in the Middle East, North Africa, and South China.14–16 The formation of black shale rich in organic matter is a complex process that reflects the interaction of various climatic and marine factors, such as continental weathering, sea level change, biosphere change, biological productivity, oxygen content in bottom water, and the hydrological environment.14,17,18 Among these factors, conservation and biological productivity play important roles in organic matter accumulation.4,5 The preservation model emphasizes that hypoxia is an important factor in increasing the accumulation of organic matter. In contrast, productivity models support higher organic carbon fluxes caused by the high biological productivity of surface water that controls organic enrichment.20,21 Therefore, the enrichment mechanism of organic matter in black shale has been controversial.22–25

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In South China, the black shales across the Ordovician−Silurian boundary are distributed all over the Upper Yangtze Platform, especially the black shales of the Lower Ordovician Wufeng Formation and the Upper Silurian Longmaxi Formation, which have been the focus of exploration and development in recent years. In fact, several studies have elaborated on the shale reservoir characteristics and shale gas accumulation process of these deposits. Many of these studies have shown that organic matter plays an important role in controlling a range of shale reservoir properties, including the nanoscale pore volume that serves as a natural gas reservoir space. In addition, organic carbon content has an important effect on the adsorption capacity and potential permeability of natural gas. It is of great significance to study the sedimentary environment and organic matter enrichment mechanism of shale gas to predict the favorable areas for shale gas exploration and development. Therefore, an in-depth understanding of the black shale organic matter enrichment mechanism provides a good geological basis for shale gas exploration and development.

2. GEOLOGICAL BACKGROUND

The Yangtze block and the Cathaysia block jointly formed the South China Plate during the Late Ordovician and Early Silurian. At the end of the Ordovician period, the Yangtze Plate was covered by the extensive surface Sea (Yangtze Sea), bordering on the China Sea to the southeast. From Late Ordovician to Early Silurian, the upper Yangtze plate was in compression, and many uplifts began to rise around the Yangtze, such as the central Sichuan uplift in the northwest, the Central Guizhou uplift in the south, and the Xuefeng uplift in the southeast. Surrounded by these ancient lands and uplifts, the upper Yangtze plate evolved from an extensive sea area to a restricted sea area during the Middle Ordovician, forming a large area of a sedimentary environment with low energy, undercompensation and anoxic. At the same time, due to the impact of global transgression, several settling centers of organic-rich shale deposits have formed in the upper Yangtze region.

The Ordovician and Silurian boundary strata of the Yangtze Platform are the Wufeng Formation, Guanyinqiao Formation, and Longmaxi Formation, respectively. The Wufeng Formation and Longmaxi Formation are mainly composed of black shale rich in organic matter and graptolite, while the Guanyinqiao Formation is mainly composed of limestone or sandy to silty mudstone with abundant benthos. In this study, the XK-1 well is located in Xishui County in northern Guizhou Province (Figure 1a). The Ordovician−Silurian boundary succession at XK-1 commences with the Baota Formation composed of gray nodular limestone, which is overlain by the carbonaceous and siliceous shales of the Wufeng Formation (7.20 m thick). Moving upward is the overlying Guanyinqiao Formation.

Figure 1. (a) Paleogeography of the Upper Yangtze Basin in the early Silurian and XK-1 well location (modified from Huang et al., 2020) and (b) stratigraphic columns of the XK-1 well.
composed of limestone (0.70 m thick). It is further overlain by the Longmaxi Formation covered with black shale, gray black carbonaceous mudstone, and dark gray calcareous mudstone with a thickness greater than 130 m (Figure 1b).
3. RESULTS

3.1. TOC, TS Contents, and Organic Carbon Isotopic Signatures. The TOC, TS, and δ13Corg values of the Late Ordovician—Early Silurian samples are shown in Table 1. The TOC content of the XK-1 well varied greatly, ranging from 0.28 to 8.03% with an average value of 3.05%. The highest values were found within the ~20 m thick black shale interval located at the bottom of the core (>2.00%). The TS of XK-1 ranged from 0.17−2.63%, averaging 1.20% and exhibiting a positive correlation with TOC (Figure 2). The δ13Corg values for XK-1 were in the range of −30.6 to −28.0‰ (mean = −28.9‰) and displayed a strong negative correlation with TOC (Figure 2).

In most of the studied samples, C29-norhpane was generally low concentrations of tricyclic terpanes (Figure 4a), which ranged between C20 and C26, tricyclic terpanes, and the tricyclic terpane ratios were calculated (Table 1).

As shown in Table 1, the study samples were mainly composed of C27 regular steranes (Figure 4b), in which the proportion of C27 (mean = 39%) was higher than that of C29 (mean = 33%) and C28 (mean = 28%) steranes. The ratios of C29/C27 regular steranes were calculated, and the results are listed in Table 1.

3.3. Trace and Rare Earth Elements. Certain trace elements, including V, Ni, Sr, and Cu, were detected in the analyzed Ordovician—Silurian samples (Table 2). The contents of V and Sr were relatively high, with average contents of 201.01 and 145.592 ppm, respectively, while the average contents of Ni and Cu were 62.14 and 50.49 ppm, respectively. The ratios of Sr/Cu, V/Ni, and V/(V+Ni) were calculated, and the results are listed in Table 2.

Table 3 presents the rare earth compositions of the Late Ordovician—Early Silurian samples. The light rare earth elements, such as La, Ce, Pr, Nd, Sm, and Eu, were relatively enriched; their average contents were 122.87, 91.13, 71.06, 55.32, 31.33, and 16.92 μg/g, respectively. The average contents of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were 21.59, 17.87, 14.07, 12.94, 12.57, 11.60, 11.20, and 10.68 μg/g, respectively, showing the relative depletion of heavy rare earth elements. In addition, the ratios of LREE/HREE, (La/Yb)N, (La/Sm)N, (Gd/Yb)N, (Gd/Yb)N, (Gd/Yb)N, and (Ce/Yb)N were calculated, and the results are listed in Table 3.

4. DISCUSSION

4.1. Origin of Organic Matter. Lipid biomarkers are commonly used to identify sources, inputs, and depositional environments of organic compounds, such as land and ocean.

In this study, algae and microorganisms are the main inputs of organic matter in the sediment deposition process. This discovery is based on the distribution of n-alkanes and is characterized by the predominance of low-molecular-weight compounds (nC14−nC17), as shown in Figure 3. In addition, the Pr value that is higher than the Ph value also indicates that a large amount of algal organic matter was input during the deposition process of the Late Ordovician—Early Silurian samples. These characteristics are consistent with the low values of the Pr/Ph, Pr/nC17, and Ph/nC18 ratios, which are typical of marine organic matter input (Figure 5).

The high contribution rate of marine organic matter input in the samples from the Late Ordovician to Early Silurian is also reflected in the presence of a large number of tricyclic terpenoids in the m/z 191 mass fragment map (Figure 4a). Compared with tetraacyclic terpanes, tricyclic terpanes have advantages (Figure 4a), and the ratio of C24TeT/C23TeT is 3.13−5.00 (Table 1), which is consistent with the high contribution of marine organic matter. This result is further supported by the relatively low C24TeT/C30 hopane and C24/C23 tricyclic terpane ratios and high C24TeT/C30 hopane and C24/C26 tricyclic terpane ratios (Table 1).

The distribution of C27−C29 regular steranes in the m/z 217 mass fragments of all samples may also indicate the origin of organic matter and the sedimentary environment of the Late Ordovician—Early Silurian samples (Figure 4b). As shown in the m/z 217 mass fragment diagram, the saturated hydrocarbon component is characterized by a higher abundance of C27 regular steranes than C28 and C29 regular steranes (Figure 4b and Table 1). This result also indicates higher levels of marine planktonic-bacterial organic matter, such as the regular sterane ratio ternary diagram (Figure 6) and the high C27/C29 regular sterane ratios (Table 1).

4.2. Paleo-Weathering and Paleoclimate. When rocks undergo intense weathering, heavy rare earth elements are more likely to dissolve and migrate than are light rare earth elements.
Therefore, high $\sum$LREE/$\sum$HREE values indicate strong paleo-weathering conditions. In addition, the ratios of (La/Yb)$_N$, (La/Sm)$_N$, (Gd/Yb)$_N$, and (Ce/Yb)$_N$ were positively correlated with LREE enrichment and ancient weathering.

The $\sum$LREE/$\sum$HREE ratios of the Late Ordovician—Early Silurian samples ranged from 2.24 to 4.73 (average 3.51) (Table 3), indicating LREE enrichment. The (La/Yb)$_N$ ratio is represented by the slope of the normalized REE distribution curve of chondritic meteorites (Figure 7), which represents the degree of inclination of the graph. The (La/Yb)$_N$ values varied between 6.58 and 14.72 (with an average of 11.18) (Table 3), indicating that the curve tilted to the right and that the sample was rich in light rare earth acid rocks (Figure 7). The (La/Sm)$_N$ ratio representing the fractionation degree of LREEs was positively correlated with the $\sum$LREE. The $\sum$LREE/$\sum$HREE ratios of the Late Ordovician—Early Silurian samples ranged from 2.24 to 4.73 (average of 3.51) (Table 3), indicating LREE enrichment. The (La/Yb)$_N$ ratio is represented by the slope of the normalized REE distribution curve of chondritic meteorites (Figure 7), which represents the degree of inclination of the graph. The (La/Yb)$_N$ values varied between 6.58 and 14.72 (with an average of 11.18) (Table 3), indicating that the curve tilted to the right and that the sample was rich in light rare earth acid rocks (Figure 7). The (La/Sm)$_N$ ratio representing the fractionation degree of LREEs was positively correlated with the $\sum$LREE. The (Gd/Yb)$_N$ values ranged from 1.16 to 3.78 (with an average of 1.95), and the (Ce/Yb)$_N$ ratios ranged from 5.04 to 10.81 (with an average of 8.28) (Table 3), indicating that the Late Ordovician—Early Silurian samples were depleted in HREEs (Figure 7). In summary, the REE results (Table 3) showed that the samples were deposited under moderate weathering conditions and had a period of intense weathering.

The paleoclimate affected the intensity of chemical weathering and debris flow in the source area and ultimately determined the mineral composition and chemical composition of the sediments. The ratio of strontium to copper is a common method used to study the sedimentary paleoclimate. A Sr/Cu ratio greater than 5.0 indicates a hot and arid climate, while a low Sr/Cu ratio in the range of 1.3–5.0 indicates a warm and humid climate. In the XK-1 well, the Sr/Cu ratios exhibit significant fluctuations across the Ordovician—Silurian boundary (Figure 2). More specifically, the Sr/Cu ratios of the Wufeng Formation generally vary between 1.78 and 2.49 (Figure 2 and Table 2). Further upward, the Sr/Cu ratio declines to 0.65 in the Guanyinqiao Formation (Figure 2 and Table 2). Then, the Sr/Cu ratio increases again, varying between 1.91 and 4.90 in the Longmaxi Formation (Figure 2 and Table 2). These results indicate that the paleoclimatic changes of the Late Ordovician and Early Silurian can be divided into three stages: from a warm-humid climate to a brief period of cold-arid and then back to warm-humid conditions.
The variation range of the δ^{13}C_{org} record in the XK-1 well is as high as 2.6‰. After the positive shift of the Guanyinqiao Formation (~28.2‰), a fast negative shift of almost the same size occurred on the Ordovician–Silurian boundary (Figure 3). A similar degree of 13C positive deviation is also reported in other sections, including Dob’s Linn in Scotland,66 Mirny Creek in the Omulev Mountains in Russia,66 Anticosti Island in Canada,67 Oklahoma in the United States, and Pandivere in Estonia.48 This global fluctuation of the δ^{13}C_{org} isotope reflects a large disturbance in the carbon cycle. Although the cause of 13C drift remains uncertain, it appears to be related to environmental changes caused by climate or glaciation. Yan et al. (2009)69 believed that the lower value of δ^{13}C_{org} below the Guanyinqiao Formation may be due to higher photosynthetic activity at high pCO2 level. The gradual increase in organic matter burial may lead to the removal of 13C from the carbon reservoir, leading to a positive shift in 13C and further climatic cooling. The subsequent dramatic negative shift in δ^{13}C_{org} indicates a warming climate, leading to accelerated carbon fixation at high pCO2 levels. This variation in the δ^{13}C_{org} isotope, combined with the Sr/Cu ratio, indicates that the global climate system underwent significant changes during the Late Ordovician. Similarly, Finnegan et al. (2011)70 suggested that during the Ordovician–Silurian transition, tropical ocean temperatures were ~32–37 °C, with the exception of the short-lived Late Ordovician Hirnantian cooling of ~5 °C.

### 4.3. Paleoredox Conditions

The redox environment is important for understanding organic matter accumulation and black shale deposition, but there are few empirical limitations of the competitive environment model.69,70 Sedimentary facies and fossils are useful indicators used to reveal the change in the oxidation state of the bottom water column. According to the changes in the sedimentary facies of the Ordovician–Silurian boundary, the black shale of the Wufeng Formation and Longmaxi Formation is distributed in most areas of the Yangtze region, which are generally benthos, indicating that the water body is in an anoxic or at least partially anoxic state.71 Comparatively speaking, the Guanyinqiao Formation has many types of facies, such as argillaceous siltstone, argillaceous limestone, and shell-like limestone. The sedimentary environment can also be limited by the results of organic carbon isotopes.72 Phytoplankton is the most common carbon-fixing plant in the marine environment, and its δ^{13}C_{org} values are between ~24 and ~18‰.73 The value of δ^{13}C_{org} in modern environmental sediments, such as those in the Black Sea, is approximately ~24‰.49 In the study of Late Ordovician–Early Silurian samples, δ^{13}C_{org} was found to be negatively correlated with TOC content (and positively correlated with TS content) (Figure 2), indicating that organic matter was well preserved after burial. The value of δ^{13}C_{org} of the sample from the XK-1 well is between ~30.6 and ~28.0‰, which is obviously lighter than that in modern environmental

| sample ID | depth (m) | V (ppm) | Ni (ppm) | Cu (ppm) | Sr (ppm) | V/Ni | V/(V + Ni) | Sr/Cu |
|-----------|-----------|---------|----------|----------|----------|------|------------|-------|
| XK-6      | 16.05     | 95.74   | 33.28    | 41.54    | 203.35   | 2.88 | 0.74       | 4.90  |
| XK-11     | 24.56     | 103.23  | 37.69    | 48.28    | 198.28   | 2.74 | 0.73       | 4.11  |
| XK-14     | 31.08     | 113.31  | 41.35    | 46.99    | 206.78   | 2.74 | 0.73       | 4.40  |
| XK-17     | 38.59     | 111.81  | 40.50    | 48.12    | 194.49   | 2.76 | 0.73       | 4.04  |
| XK-21     | 45.95     | 69.46   | 29.76    | 42.57    | 185.68   | 2.33 | 0.70       | 4.36  |
| XK-24     | 53.78     | 105.04  | 41.53    | 39.25    | 144.40   | 2.53 | 0.72       | 3.68  |
| XK-28     | 61.08     | 102.27  | 42.66    | 65.63    | 256.28   | 2.40 | 0.71       | 3.91  |
| XK-33     | 68.86     | 100.26  | 37.48    | 28.73    | 117.69   | 2.68 | 0.73       | 4.10  |
| XK-36     | 75.62     | 133.07  | 47.90    | 43.83    | 157.62   | 2.78 | 0.74       | 3.60  |
| XK-39     | 82.21     | 116.44  | 43.34    | 29.90    | 114.27   | 2.69 | 0.73       | 3.82  |
| XK-42     | 90.52     | 81.66   | 34.68    | 39.42    | 116.13   | 2.35 | 0.70       | 2.95  |

Table 2. Trace Elements of the Late Ordovician to Early Silurian Samples in XK-1 Well
### Table 3. Rare Earth Elements of the Late Ordovician to Early Silurian Samples in the XK-1 Well

| Sample ID | ID     | Sample ID | ID     | Depth (m) | La (μg/g) | Ce (μg/g) | Pr (μg/g) | Nd (μg/g) | Sm (μg/g) | Eu (μg/g) | Gd (μg/g) | Tb (μg/g) | Dy (μg/g) | Ho (μg/g) | Er (μg/g) | Tm (μg/g) | Yb (μg/g) | Lu (μg/g) |
|-----------|--------|-----------|--------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| XK-6      | 16.05  | XK-11     | 24.56  | 16.05     | 142.42    | 107.94    | 81.09     | 59.08     | 30.65     | 14.94     | 14.48     | 15.23     | 13.26     | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      |
| XK-11     | 30.08  | XK-14     | 31.08  | 30.08     | 16.27     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-14     | 38.89  | XK-17     | 31.08  | 38.89     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-17     | 45.96  | XK-21     | 31.08  | 45.96     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-21     | 52.78  | XK-28     | 31.08  | 52.78     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-28     | 59.57  | XK-33     | 31.08  | 59.57     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-33     | 66.36  | XK-39     | 31.08  | 66.36     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-39     | 73.15  | XK-46     | 31.08  | 73.15     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-46     | 80.14  | XK-54     | 31.08  | 80.14     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-54     | 87.03  | XK-63     | 31.08  | 87.03     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-63     | 94.02  | XK-70     | 31.08  | 94.02     | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-70     | 101.09 | XK-75     | 31.08  | 101.09    | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-75     | 108.09 | XK-77     | 31.08  | 108.09    | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-77     | 115.13 | XK-79     | 31.08  | 115.13    | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-79     | 122.12 | XK-81     | 31.08  | 122.12    | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |
| XK-81     | 129.13 | XK-82     | 31.08  | 129.13    | 10.26     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      | 4.24      | 4.33      | 10.01     | 9.43      | 0.99      |

*Note: Where N refers to the chondrite-normalized value.*
An abnormally low value of δ¹³C<sub>org</sub> can be interpreted as extreme hypoxia in the marine environment, possibly due to a slowdown in ocean circulation.<sup>76,77</sup> In addition, due to the high concentration of CO<sub>2</sub> in the water and atmosphere, the photosynthesis and carbon fixation of marine phytoplankton are promoted, resulting in a lower δ¹³C<sub>org</sub> value. High CO<sub>2</sub> levels can be achieved through a warm greenhouse climate. Higher atmospheric temperature increases saturated vapor pressure, fresh water flux, and ocean surface temperature, promotes global sea level rise, and weakens the ocean thermohaline cycle.<sup>78,79</sup> All these factors can increase phytoplankton paleo-productivity. High productivity, in turn, will produce more anoxic conditions on the seabed, which will promote the formation of an organic enrichment layer and enhance the negative drift of δ¹³C<sub>org</sub>.

During deposition and diagenesis, the Pr/Ph ratio is used as a broad indicator of redox conditions such as oxygen and hypoxia.<sup>80−82</sup> A Pr/Ph >3 indicates the oxidation conditions are dominated by terrestrial plants, while a low Pr/Ph ratio less than 1 indicates anoxic conditions, and a Pr/Ph ratio between 1 and 3 indicates an intermediate state (suboxic conditions).<sup>55</sup> In this regard, organic matter in the Late Ordovician–Early Silurian sample sediments was preserved under reduced conditions with a low Pr/Ph ratio (between 0.39 and 0.79). In addition, the combination of isoprenoids with n-alkanes (pristane/n<sub>C17</sub> and phytane/n<sub>C18</sub>) indicates that the Late Ordovician–Early Silurian samples were deposited in the marine environment under reduced conditions (Figure 5).

The trace elements vanadium (V) and nickel (Ni) and their ratios were also used as indicators of paleoredox conditions during deposition. The relative proportions of V and Ni trace elements were controlled by sedimentary environmental conditions.<sup>86</sup> Reduction conditions during the deposition of the Late Ordovician–Early Silurian sediments were determined by V concentrations higher than Ni concentrations (Table 2) because V is usually enriched over Ni under anoxic (reduction) marine conditions.<sup>83,85</sup> All these factors can increase phytoplankton paleo-productivity. High productivity, in turn, will produce more anoxic conditions on the seabed, which will promote the formation of an organic enrichment layer and enhance the negative drift of δ¹³C<sub>org</sub>.

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under dysoxic to oxic conditions. In the XK-1 well, the V/Ni ratio fluctuates significantly on the Ordovician–Silurian boundary (Figure 2). More specifically, the V/Ni ratio of the Wufeng Formation usually varied from 4.27 to 5.77 (Figure 2 and Table 2). Furthermore, the ratio of V/Ni in the Guanyinqiao Formation decreased significantly to 1.40 (Figure 3 and Table 2). The V/Ni ratio then returned to a higher value and varied between 2.06 and 3.69 in the Longmaxi Formation (Figure 2 and Table 2). In addition, the V/(V + Ni) ratio is considered an indicator of paleoredox conditions. A high V/(V + Ni) ratio (>0.5) indicates an anoxic state, 0.1–0.5 indicates a suboxic state, and a value lower than 0.1 indicates an oxic state. The V/(V + Ni) ratio of the Late Ordovician–Early Silurian samples was between 0.58 and 0.85, which also fluctuates significantly on the Ordovician–Silurian boundary (Figure 2).

These geochemical results generally describe the fluctuation pattern from anoxic to oxic (or dysoxic) and then to recurrent anoxic states during the Ordovician–Silurian transition, which is consistent with the research in the Yangzi area and other areas. The change in the redox environment in the Yangtze Sea may be the result of the interaction of climate, sea level change, and other factors. During the deposition of the Guanyinqiao Formation, climate cooling during the Hernan glacial period may lead to sea level decline and bottom water oxidation, which may destroy the previously stable anoxic bottom water body. With the increase in temperature after the Ice Age, the water column returned to a stagnant anoxic environment due to slow ocean circulation.

4.4. Depositional Model and Controlling Factors. As noted earlier, the global climate–ocean system underwent major changes during the Ordovician–Silurian transition. According to the Ordovician climate curve, the Ordovician was in a warm climate for most of the time, state, and there was a short interval of icehouse interval in the Late Ordovician. The variations of Sr/Cu ratio and δ13Corg at the XK-1 well also indicate the short-term Herniant glacial event in the long-term greenhouse climate environment. At the beginning of the Longmaxi Formation, the melting of ice may lead to large-scale transgression (or sea level rise) after the Herniant glacial in the Late Ordovician. The sea level rise of the low-latitude continental shelf can promote the formation of hypoxic bottom water and the overturning of the ocean, forcing deep hypoxic water to rise along the continental shelf profile. The TOC content in the Wufeng Formation was the highest, which may reflect the influence of climate warming on organic matter accumulation. In addition, as mentioned above, low oxygen (reduction) conditions were recognized during the Late Ordovician–Early Silurian deposition. This result is supported by the low Pr/Ph, Pr/nC17, and Ph/nC19 ratios and the relatively high V/Ni and V/(V + Ni) element ratios (Tables 1 and 2). The reduction conditions are conducive to the preservation and enrichment of organic matter. In addition, the content of TOC in the anoxic interval was usually higher when the Wufeng and Longmaxi formations were deposited, while the TOC content in the oxygen-bearing interval or dyoxia was decreased when the Guanyinqiao Formation was deposited. Therefore, the warm climate and the preservation of organic matter were important control factors for the accumulation of organic matter in the Late Ordovician–Early Silurian sediments.

High biological productivity is another important controlling factor of organic matter accumulation during sedimentation. The results show that climate conditions control the increase in biological productivity in the process of sediment deposition. Hakimi et al. (2016) reported that a warm climate helps to improve the productivity and decomposition capacity of phytoplankton, while the growth and decomposition capacity of phytoplankton is weakened under cold water (arid) conditions. In this study, the Late Ordovician–Early Silurian sediments were mainly deposited under warm and humid climatic conditions, during which the biological productivity within the water-column light zone was enhanced. In addition, in the early stages of formation of the Longmaxi Formation, marine productivity may be stimulated by the supply of additional nutrients, either through land weathering or through upwelling. The upward deeper waters can bring relatively eutrophic water to the surface light belt, coupled with the increased weathering input of nutrients from the land, stimulating the mass reproduction of photosynthetic phytoplankton and improving the surface water biological productivity of the shallow water shelf. However, an increasing organic flux can increase oxygen consumption and promote the formation of anoxic water conditions to facilitate the accumulation and preservation of organic matter.

Therefore, warm climate, high productivity, and preservation of organic matter are the basic factors affecting the accumulation of sedimentary organic matter in these Late Ordovician–Early Silurian deposits.

5. CONCLUSIONS

The Late Ordovician–Early Silurian shales drilled in northern Guizhou (SW China) were studied by combining organic geochemistry with inorganic geochemistry. The results of the study provide constraints for the paleoclimate and paleo-ocean environment and the deposition of organic-rich shale in the Upper Yangtze Platform across the Ordovician–Silurian transition. This study draws the following conclusions:

1. The distribution of biomarkers indicates that the Late Ordovician–Early Silurian shale was deposited in the marine environment, and its organic matter was mainly derived from marine plankton/algae and microorganisms.

2. The low Pr/Ph ratio and high element V/Ni and V/(V + Ni) ratios indicate that the Late Ordovician–Early Silurian samples were deposited in the marine environment under reduced conditions. This reduction condition contributed to the preservation of organic matter during the deposition of the Late Ordovician–Early Silurian sediments.

3. During the deposition process, the sediments that formed the Late Ordovician–Early Silurian sediments experienced a process from a warm-humid climate to a brief period of cold-arid climate and then back to a warm-humid climate. Therefore, the biological productivity within the photic zone of the water column must have been improved during the deposition process.

4. Warm climate, high biological productivity, and good preservation of organic matter were the main controlling factors of organic matter enrichment in the Late Ordovician–Early Silurian sediments.

6. MATERIALS AND METHODS

6.1. Samples. The sample was taken from the XK-1 coring well drilled in 2017 in northern Guizhou, South China (Figure 1c). The lithology of the core sample includes silty mudstone, calcareous mudstone, black shale, and limestone (Figure 1d). In a relatively fixed time interval, 32 samples were selected. To minimize the potential impact of surface weathering and
contamination during sample collection and storage, all survey samples used for analysis were freshly cut after removing the weathered surface of the core and then crushed into powder. Each shale sample was divided into two smaller portions. The first part of the shale sample was crushed to 80 mesh (<0.25 mm), and then the organic geochemistry was analyzed by the total organic carbon (TOC), total sulfur (TS), δ13Corg and GC–MS analysis for organic geochemical characteristics. The second sample was crushed to 200 mesh (<0.075 mm), and then trace and rare earth element analyses of inorganic geochemical characteristics were performed.

6.2. Organic Geochemical Analysis. The TOC and TS of the samples were determined using a LECO CS-344 instrument after the carbonate was removed with 10% hydrochloric acid. The analysis precision was ±0.1%. The organic carbon isotopes were measured on a Thermo Fisher Mat-235-Flash 2000 instrument and expressed as mil (%) and compared with the Pee Dee Belemnite (PDB) standard. An analytical precision of ±0.3‰ was obtained using IAEA-600 as a certified laboratory standard.91

The sample was prepared into powder (80–100 mesh) and extracted in a Soxhlet apparatus with chloroform for 72 h, and the solvent was removed by distillation. The extract was concentrated and weighed. Asphalitic fractions were extracted by petroleum ether, and aliphatic, aromatic, and resin fractions were eluted by silica gel column chromatography with n-hexane, benzene, and ethanol, respectively. GC–MS analysis was performed using an HP 5973 MSD (Agilent Technologies, Wilmington, De, USA) connected to an HP 6890 gas chromatograph equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with 5% phenyl-methyl-DB-5 film (0.25 μm). For conventional GC analysis, the oven temperature was increased from 80 to 300 °C at a rate of 3 °C/min, and the final holding time was 20 min. Helium was used as the carrier gas at a linear velocity of 32 cm/s, and the syringe was operated at a holding time of 0.9 mL/min. The MS was operated at an ionization energy of 70 eV, a source temperature of 230 °C, and an electron multiplier voltage of 1900 V over the range of 35–550 Da.

6.3. Inorganic Geochemical Analysis. The concentrations of trace and rare earth elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Approximately 50 mg of each milled sample greater than 200 mesh was digested in an open-top Teflon beaker on a hotplate at approximately 140 °C with 1.5 mL of HNO3, 1.5 mL of HF, and 0.01 mL of HClO4. After evaporation to wet salt conditions, a mixture of 3 mL of HNO3 and HF (v/v, 1:1) was added to the residue and heated again for more than 48 h at approximately 195 °C. After the acid was completely evaporated, the residue was dissolved in 3 mL of nitric acid and heated to wet salt conditions. Then, 3 mL of nitric acid was added, and the residue was heated at 150 °C for 24 h to ensure complete evaporation of the acid addition. After cooling, 2 mL of HCl was added to the synthetic dry residue, and the sample was leached at 60 °C for 1 h. Finally, the material was cooled again, and 8 mL of H2O was added. The solution was placed in an eddy current mixer, poured into a new test tube, and diluted with 2% HNO3 for analysis. To test the accuracy and precision of trace element analysis, GWR07105 (GSR-3) was taken as the standard sample. Three mean analyses were performed on each sample. The analytical uncertainty was estimated at 5%. The accuracy and precision of the analysis were monitored using standard rock reference materials GSR4 and GSD12.

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Notes
The authors declare no competing financial interest.

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