Research Article

Geochemical Characteristics and Their Marine Environmental and Organic Source Implications for the Lower Cambrian Shales in Guizhou Province, South China

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In this study, we conducted systematic analysis of total organic carbon (TOC) content, lipid biomarkers, carbon isotopes of kerogen (δ13Ckerogen), and mineral composition in Niu-ti-tang (Є1n) and Pa-lang (Є1p) shales from Guizhou Province in order to provide a better understanding of the organic sources and marine environmental condition during deposition of the Lower Cambrian shales of South China. The results show that a broad variety of lipid biomarkers, such as n-alkanes, pristane, phytane, terpanes, hopanes, and steranes, are in these shales, which suggests a significant contribution of various paleobios with bacterial microorganisms and algae thriving under a low-salinity and stable anoxic environment. The negative δ13Ckerogen value (minimum −36.4‰) and occurrence of pyrite (1–7.5%) and carbonates (2.4–57.3%) indicate that bacterial sulfate reduction prevailed under anoxic conditions during deposition of the Lower Cambrian shales. Moreover, the difference in mineral and δ13Ckerogen composition between Є1n and Є1p shales might imply significant changes in primary production and paleoocean environments due to sea-level rise, as shown by the higher average TOC content in Є1p shales (2.52%) compared to that in Є1n shales (1.79%). The covariances of TOC content and mineral and δ13Ckerogen composition suggest that the Є1p shales might have been deposited under a higher sea level associated with high primary productivity, compared to Є1n shales. Thus, high primary productivity driven by sea-level rise is suggested to be the main controlling factor on organic matter enrichment in Є1p shales under stable anoxic conditions.

1. Introduction

The Early Cambrian was a critical interval in geological history and featured profound oceanic and biotic changes, i.e., “Cambrian Explosion” [1, 2]. During this critical time interval, organic-rich black shale was deposited during global sea-level rise and oceanic anoxic events [3–7]. The formation of organic-rich black shales is a complicated issue due to the interplay of various atmospheric, oceanographic, and biological factors and therefore has been an important research target for understanding life evolution and geochemical conditions of the Early Cambrian ocean.

Meanwhile, a set of organic-rich Lower Cambrian black shales in South China, e.g., Niu-ti-tang (Є1n) and Qiongzhusi Formations (Є1q), is widely distributed throughout the Yangtze Platform. They have been identified as essential source rocks for shale gas exploration and development in this region because of their considerable thicknesses, large distribution area, relatively high total organic carbon (TOC) content, and thermal maturity [8–10]. Over the past decades, organic-rich black shales in the Yangtze region have attracted interest due to their significant geological and economic importance as shale gas [11–15]. In particular, shale reservoir characteristics and gas potential, including their
TOC content, pore size distribution, and methane sorption capacity, have been extensively determined [16, 17]. However, there are still many challenges in promoting shale gas exploration and development in China. One of the primary challenges includes the poor understanding regarding the organic matter enrichment mechanisms of marine shales in South China.

Recently, studies have been conducted to reconstruct the palaeoenvironment and paleoproductivity of the Lower Cambrian marine shales in South China and to constrain the main factors controlling the formation of organic-rich black shales [3, 5, 6, 13–15, 18–27]. Of these studies, considerable advances have been made in our understanding of the organic matter enrichment mechanisms of these Lower Cambrian shales and shale gas resources, which play a critical role in delineating shale gas exploration and development targets in South China [23]. However, the organic matter enrichment mechanisms of marine shales in this area is complex, and the depositional environments during different time intervals of the Early Cambrian could have resulted in markedly different organic matter enrichment mechanisms [24]. For instance, Huang et al. [6] tried to unravel the oceanic redox condition changes within a sequence stratigraphy framework of the Є1p (~528–521 Ma) shales of the Yangtze Platform by performing high-resolution analyses of iron speciation and redox-sensitive trace elements (Mo and U). They concluded that anoxic-ferruginous and euxinic bottom waters with moderately strong restriction resulted in high production and good preservation of organic matter. On the other hand, Wang et al. [7] proposed that paleoproductivity was the main factor controlling the high organic content of the Є1q black shales in the Sichuan Basin due to the covariation among P$_{org}$, C$_{bio}$, and TOC. Liu et al. [22] also proposed that productivity was the dominant factor controlling organic matter preservation within the black shales of South China. Jin et al. [21] applied multiple paleoproductivity, paleoredox, upwelling/restriction, and terrigenous flux proxies on these shales and suggested that a combination of primary productivity, redox conditions, and terrigenous fluxes driven by sea-level change may play a key role in organic matter accumulation on the western Yangtze Platform during the Early Cambrian. As a whole, the marine redox conditions and biogeochemical cycling in the Early Cambrian ocean changed spatiotemporally due to paleogeographic, paleoclimatic, and eustatic sea-level variations [6, 15, 20]. Therefore, the organic matter enrichment mechanisms of marine shales in this area are still not fully understood. In addition, previous studies focused mainly on inorganic geochemical ratios, i.e., iron speciation and redox-sensitive trace elements, of the Lower Cambrian organic-rich black shales of the Yangtze Platform [6, 21]. The lack of studies linking bulk organic geochemical, lipid biomarkers, and mineral composition to decipher the mechanisms driving organic matter accumulation hinders our understanding of the spatiotemporal evolution of primary productivity and redox conditions of paleoceans, in particular, what factors control the enrichment of organic matter.

The north region of the Guizhou Province was located in the southeast Yangtze Platform (Figures 1(a) and 1(b)). Massive black shales were deposited with a thickness of more than 100 m under global sea-level rise and oceanic anoxic events during the Meishucunian and Qiongzhusian Ages [4, 28]. These shales exhibit significant lateral and vertical variation in both geochemical and mineral compositions (Figure 1(c)). They were formed through multiple tectonic events, which significantly influenced the productivity and environmental conditions of the paleocean [29]. In this study, we collected samples from a continuous core (ZK601 core) covering the Lower Cambrian Є1n and Pa-lang (Є1p) shales in northern Guizhou Province, which provides the opportunity to decipher the geochemical characteristics of organic-rich black shales and their marine environmental and organic source implications. This study presents geochemical evidence including lipid biomarker composition and carbon isotopes of kerogen ($\delta^{13}$C$_{kerogen}$), together with bulk geochemical parameters (i.e., TOC content) and mineral composition, to decipher the biodiversity, primary productivity, and paleoocean environment during the Early Cambrian. The particular focus of this study is to shed new light on the predominant controlling factors for organic matter accumulation in the Lower Cambrian shales from Guizhou Province, South China, which will benefit delineating shale gas exploration and development targets in the northern Guizhou area.

2. Materials and Methods

2.1. Geological Background and Sampling. During the Early Cambrian, water depths in the Guizhou area shifted from shallow to deep from west to east, forming significant stratigraphic variations [30]. The Lower Cambrian system in the Guizhou area can be divided according to its stratigraphic and biota differences into the Yangtze region, a transition region, and the Jiangnan region from west to east [31]. The ZK601 core samples of the Lower Cambrian shale were collected from a mineral exploration drill core in the Tong-ren district of northern Guizhou Province (Figures 1(a) and 1(b)), a geological transition region between the Yangtze Platform and the Cathaysia Platform with a restricted deep water marine environment which prevailed during the deposition of these Lower Cambrian shales. The Lower Cambrian strata in this region can be divided into the Є1n, Є1p, and Qing-xu-dong Formations [32]. A stratigraphic correlation of cores was conducted by the Guizhou Bureau of Geology and Mineral Exploration and Development based on the regional geology, lithology, and biostratigraphy [33–37]. The lithology of these shales has been described in detail in our previous study [28]. In brief, the Є1n is mainly composed of carbonaceous and siliceous shale, and the Є1p consists of silt shales, calcareous shales, siliceous shales, and argillaceous limestones (Figure 1(c)). The core profile covers the lower part of the Є1n and part of the overlying Є1p shales with a total depth of 397.8 m. The shale samples were measured for total organic carbon (TOC) content, pyrolysis parameters, mineral composition, biomarker signatures, and $\delta^{13}$C$_{kerogen}$ composition.
2.2. Total Organic Carbon, Pyrolysis, and Mineral Composition Analysis. The TOC contents were measured using a Leco C230 Carbon/Sulfur analyser after carbonates of each powder sample were removed with 5% HCl. The instrument was automatically programmed, and the combustion temperature was set to about 1500°C. The TOC values were calculated according to the peak area of CO₂ generated from the combustion of organic matter. The pyrolysis analyses were determined using a Rock-Eval 6 Standard analyser. Mineral composition analyses were carried out on a Bruker D8 Advance X-ray diffractometer (XRD). The relative mineral percentages were estimated semiquantitatively based on the intensity of specific reflections, the density, and the mass sorption coefficient of the identified mineral phases. Those data (Table S1 and S2) were published by our team in previous studies [28, 38].

2.3. Extraction, Separation, and Biomarker Analysis. Clean analytical procedures were followed during sample preparation and analysis [39]. The solvents, including n-hexane, dichloromethane (DCM), and methanol (MeOH), are of HPLC grade. All glassware was heated in an oven at 400°C for 4h before use. Filter paper, alumina, and silica gel were extracted by DCM before use. The surfaces of the bulk samples were cleaned in order to eliminate possible contamination and crushed to less than 100 mesh powders for further treatment.

The methods for extraction and separation followed those of [40]. Briefly, powder samples were subjected to Soxhlet extraction for 72h with a mixture of DCM and MeOH (9 : 1, v/v). Activated copper were added for removing elemental sulfur. After the removal of the solvent using an evaporator, the extractions were dissolved in n-hexane.
to remove asphaltenes. Alumina/silica gel column chromatography was used to separate the resultant maltene fraction into saturated hydrocarbons, aromatic hydrocarbons, and polar compounds, using n-hexane, a mixture of n-hexane and DCM (4:1, v/v), and a mixture of DCM and MeOH (1:1, v/v) as elution solvents, respectively.

Saturated hydrocarbons were analysed using an Agilent HP6890 gas chromatograph (GC) with a flame ionization detector and a Thermo Finnigan Gas Chromatography Mass Spectrometer (GC–MS). The analytical conditions were identical to those of [40]. In brief, a DB–5 fused silica column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used. The samples were injected in the splitless mode; N₂ was the carrier gas at a constant flow mode. The oven temperature was initially set at 80°C (held for 5 min) and programmed to increase at 3°C/min to 290°C (held for 10 min). An electron impact ion source of 70 eV was used for GC–MS, and the MS full scan range was m/z 50–600.

2.4. Stable Carbon Isotope Analysis. The δ¹³Ckerogen composition was measured by an Isotope Ratio Mass Spectrometer (Finnigan Delta Plus XL). Before analysis, each powdered sample was treated repeatedly with diluted HCl and HF for the removal of carbonate and silicate minerals, then washed with distilled water until a neutral state was attained, and finally freeze-dried. After that, approximately 2 mg of each sample was loaded into a clean tin capsule for analysis. The results were reported in the standard delta notation as δ¹³C vs. VPDB. Instrument performance was routinely checked using a standard, and the reported δ¹³C values represented the average values of two parallel measurements with an error of less than 0.5‰.

3. Results and Discussion

3.1. Bulk Organic Geochemical Parameters. The TOC content and pyrolysis data are cited from previous studies and summarized in Table S1 [28, 38]. In brief, the TOC content ranges from 0.29% to 6.52% and averages 2.52% for the 1p shales, for the 1n shales, the values vary from 0.07% to 7.34% and average 1.79%. The TOC contents > 2% are mainly within depth ranges of 290 m to 360 m, and the 1p shales display a higher average TOC content than the 1n shales. The TOC values in this study are comparable to those of the 1q shales (0.87–7.21%) in the Sichuan Basin [7].

In this study, T max values vary from 450°C to 599°C, suggesting varied maturities. Thus, it is necessary to acquire other effective maturity indices, i.e., bitumen reflectance and vitrinite equivalent reflectance. Since there is a lack of vitritinite particles in marine source rocks of the Lower Paleozoic, bitumen reflectance (R0) is widely used to calculate the vitrinite equivalent reflectance (VRequiv) of kerogen [41, 42]. The calculated VRequiv values of representative samples are ranged from 2.37 to 3.64% [38]. Meanwhile, the measured Raman reflectance (τRmcRo) values for representative shales vary from 2.92% to 3.54% [38]. These results are generally consistent and suggest that these Lower Cambrian shales show high to overmaturity [43]. The clay minerals in the studied samples consist mainly of illite further suggesting that the 1n and 1p shales have entered the late diagenetic stage with a high to overmaturity [44–48].

The TOC content is usually used to represent the relative content of organic matter in rocks, but it needs to be used with caution when it comes to highly matured rocks [44, 49]. In fact, the TOC content of the highly matured rocks represent the residual carbon or dead carbon; therefore, the original TOC (TOC o) would be underestimated. It is well documented that the measured residual TOC of these highly matured shales from the Early Cambrian is far from the TOC o [44]. Meanwhile, previous research showed that there is a simple formula to recover the TOC o, and the recovery coefficients of the Lower Cambrian shales from South China are largely between 3.0 and 3.4 [49]. Assuming a recovery coefficient of 3.0, the TOC o of these Lower Cambrian shales reach 22%. In addition, the plot of S1 versus TOC content reflects that all of the studied shales from the Lower Cambrian are characterized by autochthonous hydrocarbons (Figure 2(a)) [50, 51]. Pyrolysis parameters, such as T max versus hydrogen indices (HI), are often used to indicate kerogen types. As is shown in Figure 2(b), the kerogen type of the studied samples is type III, which contradicts geological fact that no vitrinite particles existed in the Lower Cambrian shales [41, 42]. For example, Tian et al. [44] recovered the original kerogen type in the Lower Cambrian 1n shales in the Micangshan-Hannan Uplift, SW China, and suggested a mixture of kerogen types I and II, which are more aligned with the geological fact and previous evidence [29, 42].

Overall, the bulk organic geochemical parameters suggest that these Lower Cambrian shales have a high TOC content (maximum 22%) with high to overmaturity, and contain a mixture of original kerogen types I and II, with average TOC content of the 1p shales (2.52%) being higher than that of the 1n shales (1.79%).

3.2. Mineral Composition. The mineral composition of these shales is reported in previous studies and compiled in Table S2 [28, 38]. These Lower Cambrian shales consist mainly of clay minerals, quartz,feldspars, carbonates, and pyrite. The 1n shales consist mainly of quartz (mean: 64.9%), while the 1p shales consist mainly of clay minerals (>50%) with lower quartz content (mean: 30.9%) (Figure 3). The 1n and 1p shales all show poor correlations between TOC and quartz/clay mineral content (Figure 4), indicating that quartz and clay mineral have an insignificant effect on the enrichment of TOC. The 1n and 1p shales have variable carbonate contents (of 2.4–57.3%), which are dominated by dolomite and calcite, respectively. The pyrite content of 1n and 1p shales is largely less than 5%, with the 1p shales being slightly higher. The different characteristics of mineral composition between 1n and 1p shales demonstrate that the paleomarine environment (i.e., water depth and sedimentary facies) might fluctuate. A previous study suggested that high quartz content is generally interpreted to develop in a shallow water environment, while high clay mineral content and low quartz content suggest deep water conditions [52]. Therefore, the heterogeneity of these shales...
might be controlled by changes in sea level during the Early Cambrian when an extensive marine transgression occurred in the Upper Yangtze Platform [3–7, 21, 28, 29, 52], with the Єp shales deposited under a higher sea level, compared to Єn shales.

Iron speciation, including total iron (Fe\text{Tot}) and highly reactive iron (Fe\text{HR}), carbonate iron (Fe\text{carb}), (oxyhydr)oxide iron (Fe\text{ox}), magnetite iron (Fe\text{mag}), and pyrite iron (Fe\text{pyr}), has been widely used in fine-grained siliciclastic sediments to reconstruct redox conditions [6]. For instance, a Fe\text{HR} content of >38% of the total sedimentary iron pool generally indicates anoxic water conditions, whereas a much lower proportion of Fe\text{HR} commonly suggests an oxic water setting [53]. Fe\text{pyr}/Fe\text{HR} ratios > 0.8 are considered to mark anoxic conditions [54]. As shown in Table S2, pyrite was identified in most samples, particularly in the Єp shales, with contents ranging from 1% to 7.5%. Although iron speciation data was not available in this study, the dominance of pyrite, which is the only iron mineral detected in these shales, can also reflect anoxic water conditions. In addition, framboidal pyrite has been identified in these shales [38], which is considered to be the result of rapid nucleation and crystallization under a fluid environment with high iron and high sulfur content. The presence of framboidal pyrite has been used as an indicator of redox conditions [55–57]. It is inferred that the precipitation of pyrite was commonly induced by organic sulfide reduction (OSR) (2CH\text{2}O + SO\text{4}^{2−} → 2HCO\text{3}^{−} + H\text{2}S) and sulfate-driven anaerobic oxidation of methane (SO\text{4}− → CH\text{4} + H\text{2}O + HCO\text{3}− + H\text{S}− + H\text{2}S). It is noteworthy that elemental sulfur, the intermediate product of pyrite formation, was observed in bitumens of the studied shales [40], which further confirms the occurrence of OSR and/or SO\text{4}-AOM. In addition, bacteria sulfate reduction is responsible for an increase in alkalinity that favors the precipitation of authigenic carbonates, including calcite and dolomite [63, 64]. The Єn and Єp shales contain different carbonates (dolomite and calcite, respectively), which might be the result of different depositional settings and a difference in dominated microbial communities [63, 64].

3.3. Composition and Distribution of Lipid Biomarkers. Lipid biomarkers, together with their parameters, can provide insights into changes in biodiversity, primary productivity,
Figure 4: Correlations between TOC content and (a) quartz and (b) clay mineral in the Pa-lang (ε1p) and Niu-ti-tang (ε1n) shales.
Lipid biomarkers are not only used as marks for organic source input identification but also used as indicators for environment conditions. The ratios of Pr/Ph, Pr/n-C_{17}, and Ph/n-C_{18} are often used in the analysis of sedimentary conditions. However, these parameters may be altered by source input, maturation, and biodegradation [68]. Generally, the Pr/Ph ratio < 0.8 indicates anoxic conditions. In this study, the low values of Pr/Ph (0.30-0.85) in the studied shales, combined with the cross-plot of Pr/n-C_{17} and Ph/n-C_{18} ratios, suggest a strong anoxic environment with considerable marine organic matter input (Figure 8(a)). The cross-plot of Pr/Ph versus Ga/C_{30} Hop also supports a strongly...

**Figure 5:** TIC gas chromatograms of representative samples in the extracts of the (a–c) Pa-lang and (d–f) Niu-ti-tang shales. Notes: Pr: pristane; Ph: phytane; Ė1p: Pa-lang Formation; Ė1n: Niu-ti-tang Formation.

**Figure 6:** m/z 191 gas chromatograms of representative samples in the extracts of the (a–c) Pa-lang and (d–f) Niu-ti-tang shales. Notes: TT: tricyclic terpanes; Ga: gammacerane; Ė1p: Pa-lang Formation; Ė1n: Niu-ti-tang Formation.

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reducing marine shale environment (Figure 8(b)). High abundances of gammacerane and C$_{35}$ hopane are typically observed in evaporitic or high-salinity environments [81], which were not observed in these samples. Their low Ga/C$_{30}$ Hop values (0.12–0.33) and minor abundance of C$_{35}$ hopane reflect a moderately saline environment [82]. The diasterane/regular sterane ratio is also used as an indicator of a sedimentary environment because oxic conditions are favorable for diasterane formation. At comparable levels of thermal maturity, it can be used to reflect the redox condition, with high values indicating an oxic environment [68]. However, considering the high thermal maturity of these shales, the abundance of diasteranes in this study with Dia/Reg C$_{27}$ St ratios around 0.6 likely suggests an anoxic water column.

In summary, a broad variety of lipid biomarkers including n-alkanes, pristane, phytane, tricyclic terpanes, C$_{27}$–C$_{35}$ hopanes, gammacerane, 25-norhopanes, C$_{21}$–C$_{22}$ diginanes, C$_{27}$–C$_{29}$ regular steranes and diasteranes, and C$_{30}$ 4α-methyl-24-ethyl steranes is detected in the Є$_{1n}$ and Є$_{1p}$ shales. However, the composition and distribution of these biomarkers are similar in the Є$_{1n}$ and Є$_{1p}$ shales, which likely resulted from high thermal maturity. The biomarker signatures in this study are generally consistent with those

![Figure 7: m/z 217 gas chromatograms of representative samples in the extracts of the (a–c) Pa-lang and (d–f) Niu-ti-tang shales. Notes: St: steranes; Є1n: Niu-ti-tang Formation; Є1p: Pa-lang Formation.](image)

![Figure 8: Cross-plots of (a) Pr/n-C$_{17}$ versus Ph/n-C$_{18}$ and (b) Ga/C$_{30}$ H versus Pr/Ph ratios in the studied samples to indicate the source input and sedimentary environment (after [83]).](image)
reported from Lower Cambrian shales in the Sichuan Basin, Tarim Basin, and Ordos Basin [83–86]. In addition, our previous study suggests that the biomarkers in the studied samples can provide in situ evidence [40]. Therefore, the molecular evidence reveals a significant contribution of various paleobios with bacterial microorganisms and algae prosperous in a low-salinity and anoxic environment of the €1n and €1p shales but failed to decipher variations of primary productivity between the €1n and €1p shales because of high thermal maturity.

3.4. δ13C Composition of Organic Matter. The δ13C value of organic matter is generally controlled by the organic carbon fractionation process during photosynthesis, organic matter depositional rates, and postdepositional alteration through thermal alteration and diagenesis [15, 87]. Based on the significant variation in δ13Ckerogen ratios (~36.4‰ to ~29.8‰) and similar thermal maturity of these shales, we suggest the δ13Ckerogen values undergo minimal postdepositional alteration [88–91]. Therefore, the variation of carbon isotopic composition in this study is controlled mainly by the evolution of source organisms and geochemical conditions of the paleocean [87].

Based on the rules of photosynthesis fractionation, enhancing primary productivity over a period time likely led to higher carbon isotope values by reducing the preferential selectivity of 13C during photosynthesis [89, 92]. In this study, the €1n and €1p shales show different δ13Ckerogen values. The €1n shales are depleted in 13C and have minimum δ13Ckerogen values of ~36.4‰, which gradually increase towards the €1p shales with δ13Ckerogen excursion of 6.6‰ (Table S3). The positive excursion of δ13Ckerogen values is consistent with an average TOC increasing from 1.79% (€1n shales) to 2.52% (€1p shales). This means that higher primary productivity might account for the positive isotope values and higher TOC contents in the €1p shales compared to the €1n shales.

On the other hand, previous studies suggest that the organic carbon isotopes of marine biomass and marine sedimentary organic matter are generally higher. For instance, organic matter derived from marine algae has a typical δ13C range of ~23‰ to ~16‰ with an average of ~19‰ [93]. The marine phytoplanktons in the Black Sea also have positive δ13C values (~25‰) [94]. Hayes et al. [89] reported an average δ13C value of ~28‰ for marine sedimentary organic matter over the past 800 Ma. Therefore, the increase in the contribution of 13C-depleted organisms to bulk organic matter may greatly contribute to the negative δ13Ckerogen values because of the prevailing anoxic water conditions in the €1n and €1p shales. It is generally accepted that chemosaurotrophic bacteria and prokaryotic organisms have the most negative carbon isotopic composition [68]. For example, the carbon isotopic values of organic matter derived from chemoautotrophic bacteria vary from ~45‰ to ~34‰ [72, 73], nitifying bacteria have an isotopic composition of about ~38‰ to ~36‰ [94], and sulfate-reducing bacteria and methanogenic bacteria are characterized by negative δ13C values of about ~90‰ to ~40‰ [89, 92]. Abnormal depletion of 13C in organic matter during the Early Cambrian is widely observed [15, 29, 83]. The negative δ13C values of these samples, particularly in the €1n shales, suggest a significant contribution from chemosaurotrophic bacteria and other prokaryotic organisms as revealed by biomarker evidence, especially sulfate-reducing bacteria. The widely distributed pyrite and high carbonate contents are consistent with the speculation that bacterial sulfate reduction might have prevailed under anoxic conditions during deposition of these Lower Cambrian shales, whereas the shift to higher isotopic values in the €1p shales reflects higher primary productivity, which is also consistent with the higher average TOC content in the €1p shales.

3.5. Controls on Organic Matter Enrichment. The causes of organic matter enrichment and their relationship with paleoenvironmental changes and primary productivity in the Yangtze Platform of South China are still debated [4–6, 14, 15, 18–20, 22–27]. Of these studies, several mechanisms have been proposed to control the formation of organic-rich black shales, including primary productivity, preservation conditions, sea-level change, terrigenous detrital supply, paleoclimate change, sedimentation rates, tectonic activity, and hydrothermal activity [22–27]. Among those mechanisms, higher organic carbon fluxes caused by high primary productivity, and anoxic conditions favoring organic matter preservation, have been proposed as two major factors for increasing the accumulation of organic matter in these shales.

In this section, we summarize the depth variation of TOC content, δ13Ckerogen values, mineral composition, and key biomarker parameters of the Lower Cambrian €1n and €1p shales in Figure 9. As indicated by the mineralogical evidence, the €1p shales might have been deposited under higher sea levels compared to the €1n shales. And primary productivity was higher during this period, as evidenced by the TOC content and δ13Ckerogen values. The covariance of mineralogical and organic geochemical evidence suggests that sea-level rise may be the main driver of higher primary productivity in the €1p shales. This is consistent with the viewpoint that the rise in sea level could have stimulated the material exchange and brought rich nutrients and increased the primary productivity, which would result in high TOC content, positive δ13Ckerogen values, and anoxic bottom conditions [15]. It is notable that the role of sea-level change on organic matter accumulation has only recently been taken into consideration. Recent geochemical and mineralogical studies have emphasized that sea-level change is the controlling factor on the redox conditions and primary productivity of marine shales [23, 25, 26].
There is consensus that the increase in water depth may result in an increase in water mass circulation and nutrient upwelling, which carried the nutrient-rich bottom waters to the photic zone, leading to high primary productivity and strongly reducing bottom waters [25, 26]. Meanwhile, these shales all show a poor correlation between depth variations of TOC contents and varied biomarker indicators (i.e., St/Hop, Pr/Ph, Ga/C₃₀ Hop) (Figure 9), which might be the result of alteration associated with thermal maturity during the deposition of these Lower Cambrian shales. The anoxic conditions favored organic matter preservation and resulted in high TOC contents [20, 21]. However, the stable anoxic environment within the Eln and Elp shales illustrate that anoxic conditions should not be the dominant factor controlling the enrichment of organic matter. Overall, we suggest that high primary productivity driven by sea-level rise was the main factor controlling organic matter enrichment in the Elp shales on the premise of the stable anoxic condition.

4. Conclusions

The biodiversity, primary productivity, and paleoocean environment have been deciphered based on lipid biomarker composition and δ¹³Ckerogen values, along with bulk geochemical parameters (i.e., TOC content, Tₓ max ratio) and mineral composition through the Lower Cambrian Eln and Elp shales from Guizhou Province, South China. The composition and distribution of a broad variety of lipid biomarkers in these shales, including n-alkanes, pristane, phytane, TT: tricyclic terpane; Ga: gammacerane; St: sterane; Hop: hopane.

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 conflict of interest.

Authors’ Contributions
Yan Li conceived and designed the experiments. Sibo Wang and Jia Xia conducted field observations and sampling. Yan Li performed the experiments. Yan Li wrote the paper. Yan Li handled the data processing and assessment. Zhiguang Song modified the manuscript. All authors approved the final version of this work.

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Supplementary Materials
Table S1: geochemical data of the Lower Cambrian shales in core ZK601. Table S2: mineral composition of the Lower Cambrian shales in core ZK601. Table S3: biomarker parameters of the Lower Cambrian shales in core ZK601. (Supplementary Materials)

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