

Article

Effect of Paleoenvironmental Conditions on the Distribution of Lower Carboniferous Shale in Yaziluo Rift Trough, South China: Insights from Major/Trace Elements and Shale Composition

Xianglin Chen ^{1,2}, Qiuchen Xu ^{1,2,*}, Yinglun Qin ^{3,*}, Rong Chen ^{1,2}, Yufang Wang ^{1,2}, Dishi Shi ^{1,2}, Jing Bai ^{1,2}, Kun Yuan ^{1,2}, Wenpan Cen ⁴, Fei Li ^{1,2} and Tuo Lin ^{1,2}

¹ Oil and Gas Survey, China Geological Survey, Beijing 100083, China; chenxianglin@mail.cgs.gov.cn (X.C.); chenrong@mail.cgs.gov.cn (R.C.); wangyufang@mail.cgs.gov.cn (Y.W.); shidishi@mail.cgs.gov.cn (D.S.); baijing@mail.cgs.gov.cn (J.B.); yuankun@mail.cgs.gov.cn (K.Y.); lifeicgs@mail.cgs.gov.cn (F.L.); lintuo@mail.cgs.gov.cn (T.L.)

² State Key Laboratory of Continental Shale Oil, Beijing 100083, China

³ Guangxi Energy Group Co., Ltd., Nanning 530201, China

⁴ Geological Survey Institute of Guangxi Zhuang Autonomous Region, Nanning 530023, China; cenwp23@163.com

* Correspondence: xuqiuchen@mail.cgs.gov.cn (Q.X.); qinyinglun1990@163.com (Y.Q.)

Abstract: Paleoenvironmental conditions significantly influence the distribution patterns and organic matter enrichment of shale. This study investigated the vertical variations of major elements, trace elements, and total organic carbon (TOC) in the Lower Carboniferous marine shale from the Yaziluo Rift Trough, South China, to understand the paleoenvironmental conditions, including redox conditions, terrigenous detrital input, paleoproductivity, and paleo-seawater depth. The Lower Carboniferous formation consists of three sedimentary facies: basin facies, lower slope facies, and upper slope facies. From the basin to the lower slope and then to the upper slope facies, TOC, quartz, and pyrite contents gradually decrease, whereas the carbonate mineral content shows an increasing trend. A continuous decline in paleo-seawater depth transformed a deep-water anoxic environment with high paleoproductivity and low detrital input in the basin facies into a semi-deep-water environment with dysoxic-oxic conditions and moderate detrital influx in the lower slope facies, evolving further into a suboxic environment with high detrital flux in the upper slope facies. The geochemistry results suggest that anoxic conditions and high paleoproductivity were the primary controls on organic matter enrichment in the siliceous shale of the basin facies. In contrast, redox conditions significantly influenced organic matter accumulation in the mixed shale of the lower slope facies, attributed to relatively low paleoproductivity in a more restricted marine setting. Additionally, the adsorption of carbon components by clay minerals facilitated the preservation of organic matter in the calcareous shale of the upper slope facies.

Keywords: Lower Carboniferous shales; paleoenvironment; shale distribution; major/trace elements; Yaziluo Rift Trough



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1. Introduction

Recently, the Lower Carboniferous marine shales of the Yaziluo Rift Trough have become a primary target for shale gas exploration and exploitation in southern China, which are characterized by medium total organic carbon (TOC) content, considerable thickness, and high levels of carbonate minerals [1–3]. The trough, shaped like a “V” in the cross-section, is a narrow, long trench formed in the continental crust under tectonic tension, bounded by high-angle syngenetic faults [4]. It features a “slope-basin” sedimentary structure that results in an environment with frequent changes in seawater energy and varied material sources during the deposition process [5]. The Yaziluo Rift Trough spans

the southwestern Guizhou, southern Guizhou, and northern Guangxi areas in South China, recording the evolution of paleoclimate, paleoenvironment, and paleobios during a global marine transgression in the early Carboniferous period [6–8].

Much geological research has been conducted on the Lower Carboniferous shales, encompassing geological conditions, geochemical characteristics, and paleoenvironments. Yi et al. (2022) [9] suggest that the sedimentary facies and paleoenvironmental conditions of Lower Carboniferous shale on the northwest margin of the rift trough are platform facies and low-oxygen environments, respectively, based on the analysis of core samples. Su et al. (2017) [10] describe the paleoenvironment of Lower Carboniferous shale in the center of the Yaziluo Rift Trough as an oxygen-deficient environment, based on geochemical studies. Chen et al. (2017) [11] identify the paleoenvironment on the eastern side of the Yaziluo Rift Trough as a neritic environment with shallow marine shelf facies. Tao et al. (2022) [12] report that the sedimentary facies in the eastern part of the Yaziluo Rift Trough include basin facies and platform facies. Evidently, there is significant variation in the paleoenvironment, sedimentary facies types, and spatial distribution of lithofacies within the Lower Carboniferous formation of the Yaziluo Rift Trough. Understanding the impact of the paleoenvironment on shale lithofacies distribution patterns and organic matter enrichment is crucial for evaluating reservoir properties and identifying ‘sweet spots’ for exploration.

Compared to other regions in southern China, such as the Sichuan Basin, western Hubei, and eastern Chongqing, the Yaziluo Rift Trough has received relatively less attention in the early stages of shale gas exploration and exploitation. With increasing exploration and development, several exploratory wells in the Yaziluo Rift Trough have revealed shale gas with content greater than $1.0 \text{ m}^3/\text{t}$. The thickness, TOC content, and thermal maturity (R_o value) of the rich organic shale range from 100 to 400 m, 0.5 to 4.5%, and 2.6 to 3.2%, respectively. Despite being regarded as one of the most promising shale gas reservoirs, the depositional distribution patterns and enrichment mechanisms of organic matter in the Lower Carboniferous shales of the Yaziluo Rift Trough have not been systematically studied. Addressing these questions will provide a theoretical basis for the next stage of shale gas exploration, exploitation, and resource evaluation in the Yaziluo Rift Trough.

In this study, we present a suite of geochemical proxy data and sedimentological data from three wells located in the Yaziluo Rift Trough. The primary objectives of this research are as follows:

- (i) To analyze the paleoenvironmental conditions of Lower Carboniferous shales in the Yaziluo Rift Trough by examining variations in geochemical proxy data.
- (ii) To discuss the various controlling factors on organic matter accumulation in the Lower Carboniferous shale during the deposition process.
- (iii) To reconstruct the lithofacies distribution pattern of Lower Carboniferous shale and propose a relevant model for the Yaziluo Rift Trough.

2. Geological Setting

The formation of the Yaziluo Rift Trough was initiated in the early Devonian period due to the expansion of the Paleo-Tethys Ocean and the stretching action along a NE-SW axis [13,14]. It reached its maximum extent during the middle Devonian, with sedimentary successions of shale extending as far as the Zhaotong region in Yunnan Province. In the early Carboniferous period, although the overall range of shale distribution contracted, the sedimentary characteristics largely retained the patterns established during the Devonian period [15,16]. The farthest extension of these formations along the northwestern direction of the Yaziluo Rift Trough reached the Weining area in Guizhou. Subsequent tectonic ruptures and extensional processes further stretched and subsided the crust, creating a pronounced contrast between deep-water and shallow-water depositional environments within the rift trough [13,15]. During the late Carboniferous period, the paleo-seawater depth gradually decreased from both sides of the rift trough along the line from Liupanshui

to Hechi, resulting in the division of the Yaziluo Rift Trough into three distinct zones: a depocenter zone, a transition zone, and a margin zone (Figure 1A).

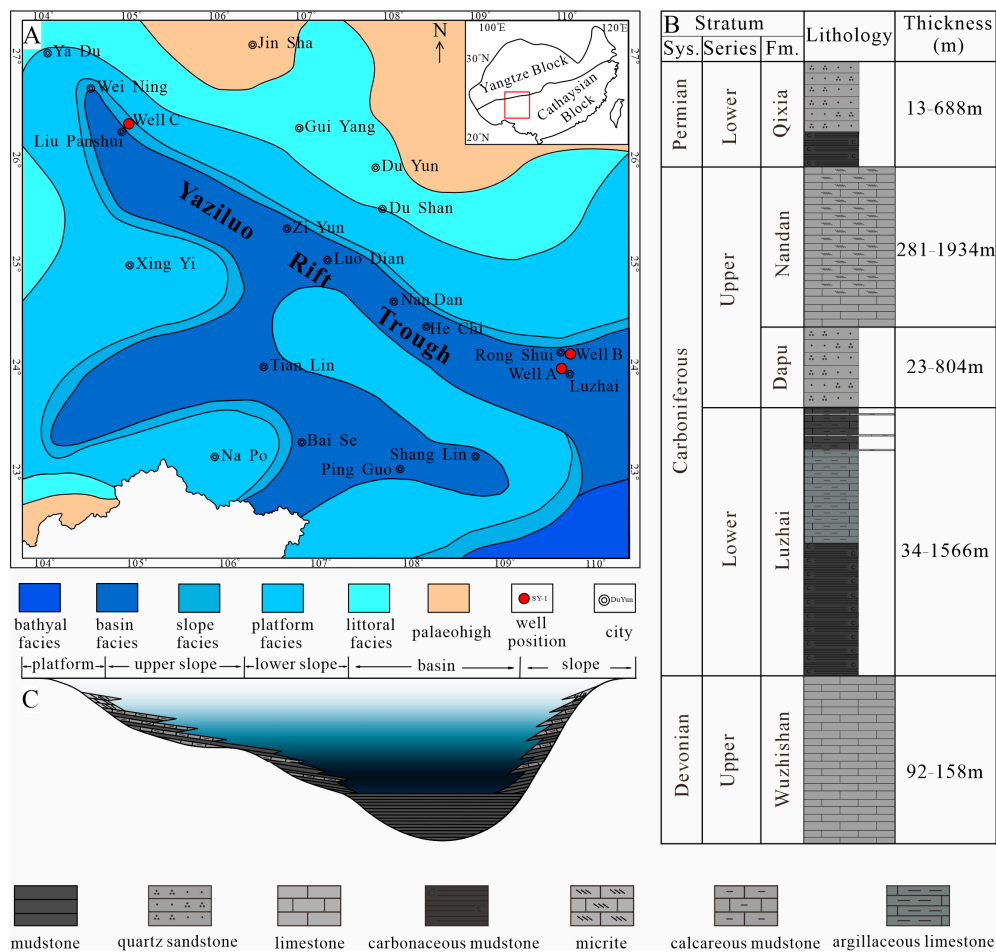


Figure 1. (A) Distribution of the Yaziluo Rift Trough during the late Carboniferous period, showing the sampling wells (Well A, Well B and Well C); (B) sequence stratigraphic framework according to Geology and Mineral Resources Bureau of Guangxi Zhuang Autonomous Region, 1985 [17].

Specifically, the depocenter zone extends from the Luzhai–Yishan area in the southeast to the Liupanshui–Weining area in the northwest of the Yaziluo Rift Trough, where the sediments are predominantly calcareous mudstone, argillaceous limestone, and carbonaceous mudstone (Figure 1B). In the transition zone between the depocenter and the margin of the Yaziluo Rift Trough, the sediments primarily consist of calcareous mudstone and argillaceous limestone. However, the lithology of the margin zone is composed mainly of micrite and bioclastic limestone. The paleo-seawater depth exhibits a general shallowing trend from southeast to northwest along the Yaziluo Rift Trough, aligning with the direction of paleo-seawater influx during the marine inundation process. Three exploratory wells (Well A, Well B, and Well C) for shale gas development are strategically located in the Luzhai area (depocenter zone), the Rongshui area (margin zone), and the Liupanshui area (margin zone), respectively (Figure 1A).

3. Materials and Methods

3.1. Samples

A total of 107 shale samples were collected from the Lower Carboniferous strata within the Yaziluo Rift Trough in South China, distributed among three wells: 28 samples from Well A, 41 samples from Well B, and 38 samples from Well C. These samples were prepared for the analyses of total organic carbon (TOC), major and trace element concentrations,

kerogen types, and mineralogy using X-ray diffraction (XRD) in the China University of Petroleum (East China), Qingdao, China.

3.2. Analytical Methods

Total Organic Carbon (TOC): The TOC contents were measured using the Leco-CS230 Carbon and Sulfur Analyzer, with an accuracy of $\pm 5\%$, adhering to the Chinese National Standard GB/T 19145-2003 [18] for the determination of TOC in sedimentary rocks. Shale samples were first pulverized to a particle size below 200 mesh (75–90 μm). The powdered samples were then treated with hydrochloric acid at 60 $^{\circ}\text{C}$ to eliminate inorganic carbons. After acid treatment, the samples were rinsed with distilled water and dried in an oven at temperatures between 60 and 80 $^{\circ}\text{C}$.

Mineralogy: Mineralogical analyses were performed using X-ray diffraction (XRD) on a Rigaku Smart Lab-9, following the Oil and Gas Industry Standard SY/T 5163-2010. All powdered shale samples (finer than 40 μm) were oven-dried at 40 $^{\circ}\text{C}$ for 48 h. The mineral composition was reported as semi-quantitative, based on parameters and formulas detailed by Yang et al. (2018) [19].

Major and Trace Elements: Major elements were analyzed using a Rigaku 100E X-ray Fluorescence Spectrometer (XRF) in the China University of Petroleum (East China), Qingdao, China. Approximately 1 g of powdered shale samples were calcined at 700 $^{\circ}\text{C}$ for over 2 h to remove organic matter and carbonates. Trace elements were quantified using an Agilent 7500A Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). For these analyses, powdered samples were dissolved in a mixture of hydrofluoric acid (HF) and nitric acid (HNO_3), with detailed procedural descriptions provided by Lu et al. (2019) [20].

4. Results

4.1. Major and Trace Elements

Aluminum (Al) and Titanium (Ti) are used as proxies for terrigenous detrital input [21]. In the Lower Carboniferous shales, Al content ranges from 1.55% to 10.59%, with average values of 5.62% in Well A, 5.95% in Well B, and 6.40% in Well C, respectively (Table 1). Ti content varies from 0.02% to 0.60%, with average values of 0.22% in Well A, 0.29% in Well B, and 0.34% in Well C, respectively (Table 1). Phosphorus (P), an indicator of organic matter productivity, ranges from 0.01% to 0.23% (Table 1). Trace elements are also employed to assess paleoenvironmental conditions. For example, trace element ratios in Well A, such as V/Cr (1.49–7.57, avg. 3.54), U/Th (0.17–3.65, avg. 1.72), Co/Ti (34.46–237.17, avg. 100.49), and Sr/Ba (0.16–5.57, avg. 1.60) are generally higher than in the other wells. Furthermore, the ratio of V/Cr (avg. 2.18) in Well B is higher than that in Well C (avg. 0.89), and the ratio of U/Th (avg. 0.60) in Well B is higher than that in Well C (avg. 0.21). However, the average trace element ratio of Sr/Ba in Well A (1.60) is lower than that in Well B (3.15) and Well C (2.45).

Table 1. Sedimentary facies and their average geochemical indexes in the Lower Carboniferous shale.

Well	Geochemical Proxies							
	Redox Conditions		Paleo-Seawater Depth		Detrital Influx		Paleoproductivity	
	V/Cr	U/Th	Co/Ti	Sr/Ba	Al (wt.%)	Ti (wt.%)	P/Ti	Ba/Al (10 ^{−4})
Well A	3.54	1.72	100.49	1.60	5.62	0.22	0.27	67.99
Well B	2.18	0.60	37.60	3.15	5.95	0.29	0.14	65.13
Well C	0.89	0.21	38.87	2.45	6.40	0.34	0.11	178.77

4.2. Characteristics of Organic Geochemistry

The organic carbon content (TOC) varies significantly across the wells. In Well A, 14 samples exhibited TOC ranging from 1.46% to 5.70%, with an average of 3.63% (Table 2). In Well B, 26 samples showed TOC ranging from 0.86% to 3.51%, with a median of 1.85%

(Table 2). Well C had the lowest TOC, with 20 samples ranging from 0.71% to 1.63% and an average of 1.02% (Table 2). The kerogen types identified in samples from Wells A, B, and C are predominantly Type I, Type II₁, and Type II₂, respectively, reflecting differences in sedimentation influences (Table 2).

Table 2. Lithofacies, kerogen types, and their average mineral compositions in the Lower Carboniferous shale.

Lithofacies	Kerogen Types	TOC (wt.%)	Average Mineral Content (wt.%)					
			Quartz	Feldspar	Calcite	Dolomite	Pyrite	Clay
Siliceous lithofacies	I	3.63	57.56	7.20	8.18	5.15	5.77	19.14
Mixed lithofacies	II ₁	1.85	41.85	0.15	26.21	4.20	2.65	24.62
Calcareous lithofacies	II ₂	1.02	13.60	0.30	40.20	21.20	2.30	22.40

4.3. Mineralogical Characteristics and Lithofacies

Based on the mineral compositions, four types of lithofacies can be divided in the Lower Carboniferous shale. The clay minerals contain illite, kaolinite, chlorite, and illite/smectite (I/S). The carbonate minerals comprise calcite and dolomite. The siliceous minerals refer to quartz and feldspar. The Lower Carboniferous shale exhibits significant heterogeneity across various lithofacies, reflecting dynamic paleoenvironmental changes (Figure 2). For instance, Well A shows the highest average contents of quartz and pyrite at 57.56 wt.% and 5.77 wt.%, respectively (Table 2). These components significantly decrease in Well C, where the averages are 13.60 wt.% for quartz and 2.30 wt.% for pyrite (Table 2). Conversely, the carbonate content in Well A is the lowest at 13.33 wt.%, but it increases significantly in Well C to an average of 61.40 wt.%, which is approximately four times higher than in Well A (Table 2). The values in Well B are intermediate, with quartz, carbonate, and pyrite contents at 41.83 wt.%, 30.41 wt.%, and 2.65 wt.%, respectively (Table 2). This distribution indicates that the Well A samples are typically siliceous shale lithofacies, characterized by high quartz and pyrite content and low carbonate content (Figure 2). Well C samples are carbonate shale lithofacies with high carbonate and low quartz content (Figure 2), while samples from Well B are classified as mixed shale lithofacies, characterized by medium levels of carbonate, quartz, and pyrite.

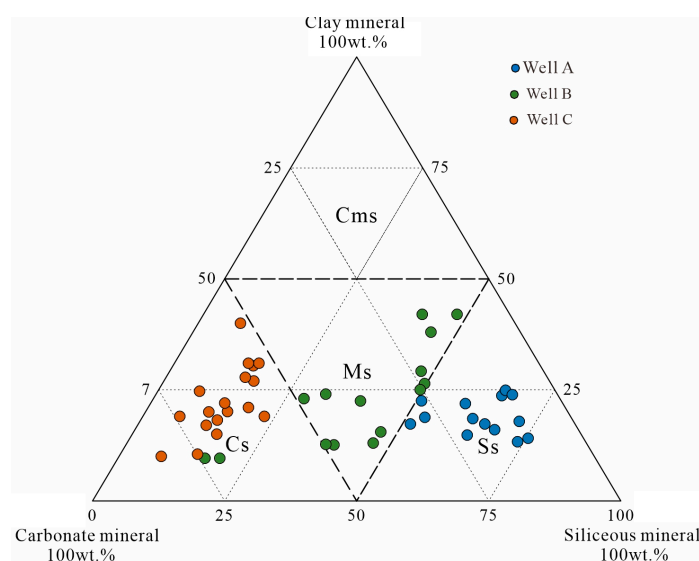


Figure 2. Ternary diagram showing the mineralogy of the three major lithofacies of Lower Carboniferous shale in the Yaziluo Rift Trough (modified from Ma et al. [2], the Cms, Ms, Cs, and Ss represent argillaceous shale lithofacies, mixed shale lithofacies, carboniferous shale lithofacies, and siliceous shale lithofacies, respectively).

5. Discussion

5.1. Reconstruction of Paleoenvironmental Conditions

5.1.1. Redox Proxies

In sedimentary environments, molybdenum (Mo) and uranium (U) are often derived from autogenous enrichment. Under oxidizing conditions, Mo and U exist as molybdate ions (MoSO_4^{2-}) and uranyl carbonate complexes, respectively, with limited aggregation. In hypoxic-sulfidic conditions, molybdate can transform into thiomolybdate, which enriches in conjunction with sulfide organic matter and iron sulfide deposits. The limited Mo concentration in the oxic environment represents redox conditions instead of water-mass restriction levels [21,22]. Furthermore, the amount of Mo absorbed by sediments is determined by both the Mo concentrations in seawater and organic matter concentrations [22]. Meanwhile, U precipitates as insoluble uranyl ion (UO_2^{2+}) or as a weakly soluble uranium fluoride complex. Since the reductibility of U is not affected by the H_2S concentrations, U is mainly enriched in sediments compared with Mo enriched in the seawater [21,22]. According to Algeo and Tribouillard (2009) [21], the co-variation of $\text{Mo}_{\text{EF}}\text{-U}_{\text{EF}}$ ratios serves as an indicator for assessing redox conditions and seawater residence status, classifying marine environments into non-restricted, weakly restricted, and strongly restricted categories.

In non-restricted marine environments under dysoxic conditions, U enrichment generally precedes that of Mo, with the Mo/U ratio in sediments typically being about 0.3 times that of modern seawater (Mo/U in modern seawater is about 7.5 [22]). As the seawater reduction increases, the Mo enrichment rates surpass U, causing the Mo/U ratio to double compared to modern seawater. In strongly sulfidic and anoxic environments, sediments accumulate higher concentrations of both Mo and U, with free H_2S in the seawater enhancing Mo's accumulation rate, significantly increasing the Mo/U ratio up to three times or more compared to modern seawater [23,24]. In weakly restricted water-mass environments, metal hydride particles such as manganese and iron facilitate rapid Mo enrichment, resulting in a Mo/U ratio generally 3–10 times that of modern seawater. Conversely, in water-mass-restricted environments, the Mo/U ratio is typically lower than in modern seawater, impeding Mo and U replenishment, with U enrichment exceeding that of Mo.

In the depocenter zone, the Mo/U ratio of shale samples is higher than in modern seawater (Figure 3), showing a positive correlation with increasing Mo and U enrichment coefficients. However, the trend does not strictly conform to non-restricted marine environments, as it deviates due to metal hydride adsorption, which usually causes a 3 to 10 times higher ratio than observed in modern seawater. The results indicate that the depocenter zone shale does not align strictly with either weakly or strongly restricted marine environments but suggests a semi-restricted, marine setting with limited connectivity to open seawater. The shale in the transition zone, particularly from Wells B and C, shows low Mo and U enrichment coefficients, with a Mo/U ratio generally 0.3 times that of modern seawater (Figure 3), indicating that the shale originated from a dysoxic to anoxic environment.

Vanadium (V) and Chromium (Cr), sensitive to redox conditions, also play a critical role in identifying environmental oxygen levels. Under oxidizing conditions, V exists as vanadates like HVO_4^{2-} and H_2VO_4^- and is not readily enriched in sediments. Conversely, under anoxic conditions, V^{5+} reduces to V^{4+} , forming compounds like $\text{VO}(\text{OH})_2$ and organo-metal ligands, enriching in sediments [25,26]. Similarly, Cr transitions from soluble chromate (CrO_4^{2-}) in oxidizing conditions to less soluble forms like Cr_2O_3 and $\text{Cr}(\text{OH})_3$ under anoxic conditions, enriching at different points of the denitrification interface [27–29]. A V/Cr ratio greater than 4.25 indicates anoxic conditions, a range of 2.0 to 4.25 suggests dysoxic conditions, and less than 2.0 indicates oxic conditions [30].

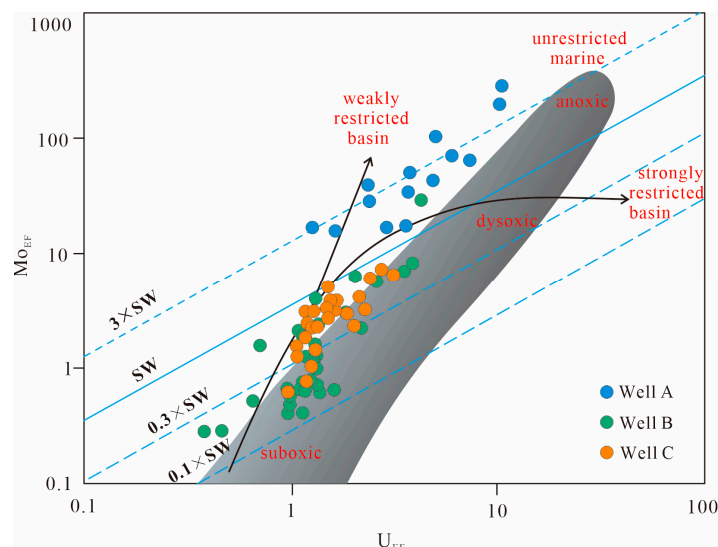


Figure 3. Covariation of Mo_{EF} and U_{EF} from the Lower Carboniferous shale (modified from Algeo and Tribovillard (2009) [21]), exhibiting water-mass restriction and redox conditions.

Implications for Lithofacies Distribution:

In Well A, primarily composed of siliceous lithofacies shale, the progressive reduction in V/Cr and U/Th values from the bottom to top layers suggests a transition from anoxic to dysoxic conditions. The average values indicate an anoxic marine environment at the lower levels, transitioning to a dysoxic state higher up.

In Well B, situated in the transition zone with mixed shale lithofacies, there is a consistent decrease in redox proxy values from bottom to top, indicating a shift from an anoxic-dysoxic to a dysoxic-oxic environment. The lower values in Well B compared to Well A suggest a closer proximity to the edge of the Yaziluo Rift Trough, reflecting different environmental impacts on sedimentation and organic matter preservation.

The carbonate lithofacies shale in Well C, primarily found in the upper slope facies, shows the lowest redox values, indicating higher oxygen content in the paleo-seawater and a partial oxidation environment. This shift is attributed to the southeastern to northwestern paleo-oceanic invasion along the Yaziluo Rift Trough, leading to a shallowing paleo-seawater depth and influencing the overall oxidation state and sedimentary dynamics. The results indicate a higher degree of oxidation and less favorable conditions for organic matter preservation in the upper slope facies, correlating with a lower TOC content in these shales.

The paleoenvironment during the early Carboniferous sedimentary period in the Yaziluo Rift Trough was influenced by seawater intrusion and the development of synsedimentary faults [12,13]. This environment is typified by a long-term, partially oxidized sedimentary environment in the upper slope facies shale [5,10,12]. In contrast, the basin facies and lower slope facies shale in the Yaziluo Rift Trough are characterized by deeper seawater depths and lower oxygen content, resulting in significantly higher redox proxies compared to the upper slope facies. The results indicate that the upper slope facies exhibit a higher degree of oxidation and suboptimal preservation conditions for organic matter, leading to lower total organic carbon (TOC) content in the shale of these facies.

5.1.2. Paleoproductivity Proxies

Barium (Ba), primarily existing in seawater as barite, is characterized by its extended residence time, high preservation rate (exceeding 30%), and exceptional stability [31–33]. Goldberg and Arrhenius (1958) [34] demonstrated a strong correlation between Ba concentrations and paleoproductivity, establishing biogenic Ba as a reliable proxy for assessing productivity levels. To accurately gauge paleoproductivity, it is crucial to eliminate the influence of terrigenous Ba. The Al element serves as an effective indicator of terrigenous input; thus, the Ba/Al ratio is employed in this study to assess paleoproductivity.

Phosphorus (P) plays a vital role as an essential nutrient for marine organisms and significantly influences the paleoproductivity of marine ecosystems [29,32]. Approximately 80% of the P in marine sediments originates from organic matter [31], with a smaller fraction deriving from terrigenous detrital sources [22,35]. Given its critical role in metabolic activities and its enrichment being primarily biologically controlled, P is one of the most reliable indicators for paleoproductivity. Additionally, the Ti element serves as an effective marker of terrigenous input, and the P/Ti ratio is selected to mitigate the influence of terrigenous clastic input on P content.

In Well A, the Ba/Al and P/Ti values of Carboniferous shale show a gradual decrease from the bottom to the top (Figure 4), suggesting relatively stable paleoproductivity. Specifically, the basin facies shale in the lower interval exhibits values ranging from 32.77×10^{-4} to 104.19×10^{-4} for Ba/Al and 0.10 to 0.68 for P/Ti, with averages of 69.67×10^{-4} and 0.30, respectively, indicating relatively high paleoproductivity. The lower slope facies in the upper interval show further declines in paleoproductivity, with values ranging from 51.73×10^{-4} to 85.80×10^{-4} for Ba/Al and 0.08 to 0.24 for P/Ti, and averages of 63.79×10^{-4} and 0.17, respectively.

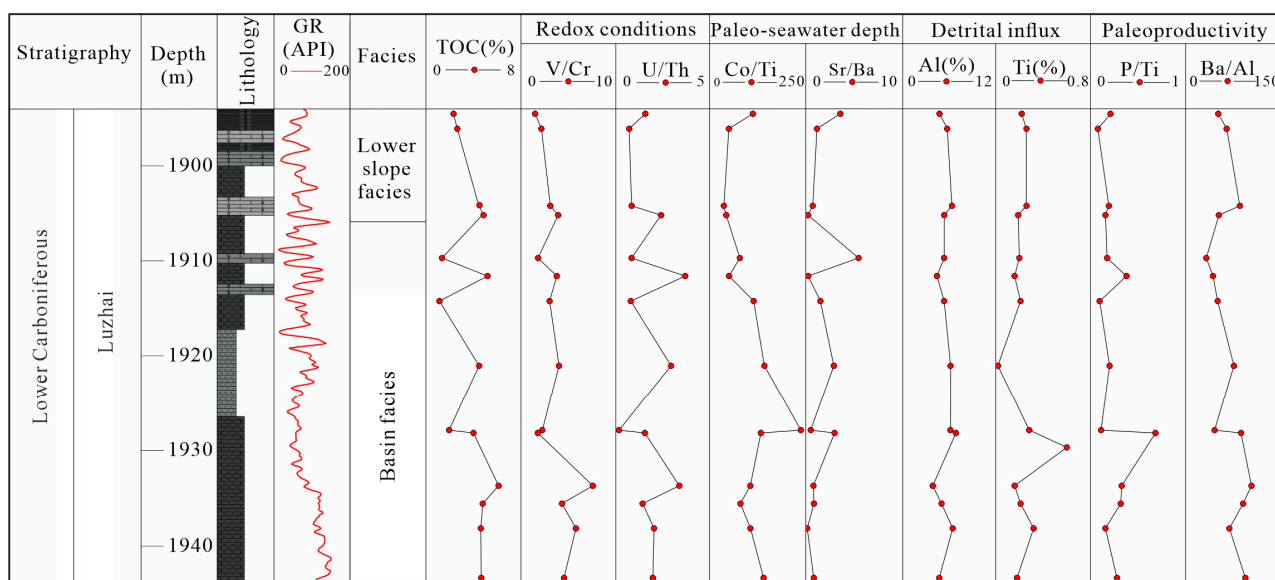


Figure 4. Stratigraphic distributions of redox (V/Cr and U/Th), paleo-seawater depth (Co/Ti and Sr/Ba), detrital influx (Al and Ti), and paleoproductivity (P/Ti and Ba/Al) proxies in Well A, respectively.

Well B displays a slight downward trend in Ba/Al and P/Ti values from bottom to top (Figure 5), maintaining general stability in paleoproductivity. The basin facies shale in the lower interval ranges from 42.84×10^{-4} to 228.04×10^{-4} for Ba/Al and 0.10 to 0.72 for P/Ti, with average values of 77.64 and 0.18, respectively, suggesting relatively high paleoproductivity. The lower slope facies values range from 27.88×10^{-4} to 141.11×10^{-4} for Ba/Al and 0.06 to 0.17 for P/Ti, with averages of 52.63 and 0.10, respectively, indicating a slight decline in paleoproductivity compared to Well A.

In Well C, the ratios of Ba/Al and P/Ti show little fluctuation from bottom to top (Figure 6). The lower slope facies shale exhibits high concentrations, with values ranging from 34.74×10^{-4} to 237.64×10^{-4} for Ba/Al and 0.03 to 0.24 for P/Ti, and average values of 180.36×10^{-4} and 0.12, respectively, indicating elevated paleoproductivity. These results also suggest that terrigenous plant debris entering the lower slope may enhance the seafloor sediment organic content, thereby promoting increased paleoproductivity. Conversely, the upper slope facies exhibit significantly reduced paleoproductivity, with Ba/Al and P/Ti values ranging from 19.41×10^{-4} to 487.16×10^{-4} and 0.04 to 0.21, respectively, with averages of 177.70×10^{-4} and 0.11.

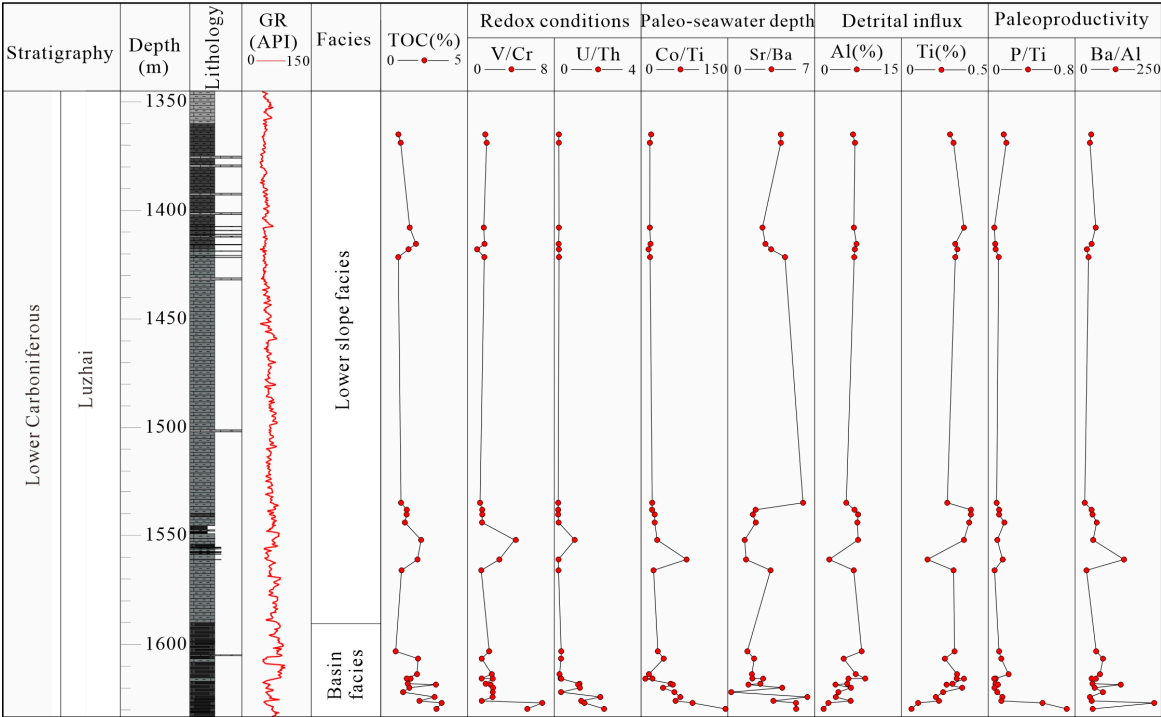


Figure 5. Stratigraphic distributions of redox (V/Cr and U/Th), paleo-seawater depth (Co/Ti and Sr/Ba), detrital influx (Al and Ti), and paleoproductivity (P/Ti and Ba/Al) proxies in Well B, respectively.

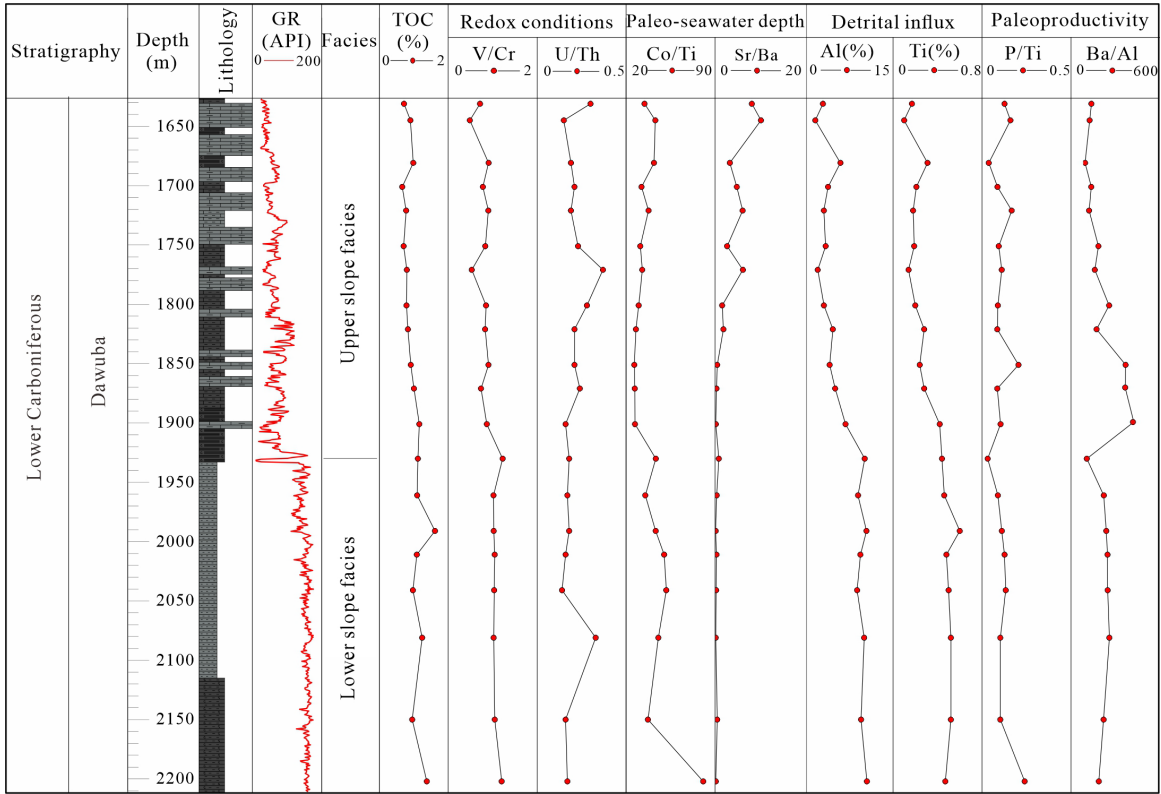


Figure 6. Stratigraphic distributions of redox (V/Cr and U/Th), paleo-seawater depth (Co/Ti and Sr/Ba), detrital influx (Al and Ti), and paleoproductivity (P/Ti and Ba/Al) proxies in Well C, respectively.

5.1.3. Terrigenous Detrital Influx Proxies

Al and Ti are primary components of the continental crust, mainly found in aluminosilicate clay minerals and heavy minerals such as rutile and ilmenite. These elements are notably stable throughout the diagenetic process and are frequently used as indicators of terrigenous detrital influx [26,36]. In Well A, the Al and Ti contents in the Carboniferous shale exhibit a remarkable similarity (Figure 4), suggesting a consistent influx of terrigenous detritus. Specifically, the Al and Ti contents in the basin facies shale of the lower interval range from 4.06 to 6.98 and 0.02 to 0.34, respectively, with average values of 5.58 and 0.21, indicating a relatively low terrigenous detrital influx. In the lower slope facies shale of the upper interval, the contents range from 4.91 to 6.98 for Al and from 0.19 to 0.26 for Ti, with averages of 5.70 and 0.23, suggesting a stable terrigenous detrital influx.

Similarly, in Well B, the variation in Al and Ti contents of the Carboniferous shale is minor, indicating a stable terrigenous detrital influx. Specifically, in the basin facies shale of the lower interval, the contents range from 1.55 to 8.74 for Al and from 0.06 to 0.36 for Ti, with average values of 5.32 and 0.25 (Figure 5). The lower slope facies shale in the upper interval shows Al and Ti contents ranging from 2.53 to 7.50 and from 0.15 to 0.40, respectively, with average values of 6.57 and 0.32 (Figure 5).

However, the Al and Ti contents in the Carboniferous shale of Well C are comparatively high, indicating its proximity to the terrigenous detrital influx source and a heightened susceptibility to further terrigenous detrital deposition. Both elements show a downward trend vertically from bottom to top (Figure 6), signaling a progressive reduction in the influx of terrigenous detritus. Specifically, in the lower slope facies shale of the lower interval, the contents range from 9.10 to 10.59 for Al and from 0.46 to 0.60 for Ti, with averages of 9.77 and 0.51, respectively, denoting a relatively high terrigenous detrital influx. Conversely, in the upper slope facies shale of the upper interval, the Al and Ti contents range from 1.90 to 10.22 and from 0.10 to 0.44, respectively, with averages of 4.58 and 0.24, indicating less terrigenous detrital influx compared to the lower slope facies.

5.1.4. Paleo-Seawater Depth

The geochemical behaviors of strontium (Sr) and barium (Ba), both lithophile elements, differ significantly during the deposition process. Sr tends to precipitate directly in seawater and shows limited affinity for adsorption onto clay material surfaces. In contrast, Ba readily adsorbs onto fine-grained sediments and clay minerals. Thus, the Sr/Ba ratio serves as a commonly used indicator of paleo-seawater depth in marine environments. A low Sr/Ba ratio suggests a relatively deep paleo-seawater depth, characterized by weak hydrodynamic influence and increased adsorption of Ba ions by clay minerals, indicative of a deep- or semi-deep-water environment. Conversely, a high Sr/Ba ratio points to shallow paleo-seawater depth and strong hydrodynamic conditions, typical of shallow marine environments [37,38].

Additionally, paleoenvironmental conditions such as paleoproductivity, redox condition, and terrigenous detrital influx are significantly influenced by sea level fluctuations [39,40]. Rising sea levels can stratify seawater, fostering anoxic conditions at the seabed that hinder benthic organism development and reduce oxidation rates, thus enhancing organic matter preservation [41]. In such anoxic environments, lipid components undergo preferential enrichment and preservation by anaerobic bacteria, increasing organic matter abundance [42,43]. Elements like cobalt (Co) and titanium (Ti) are indicative of aquatic and terrestrial environments, respectively, making the Co/Ti ratio a useful proxy for monitoring sea level changes.

In Well A, the Sr/Ba ratio in Carboniferous shale ranges from 0.16 to 5.57, with an average of 1.60, indicating significant paleo-seawater depth and limited hydrodynamic influence. The Co/Ti values range from 34.46 to 237.17, averaging 100.49 (Figure 4), and exhibit a gradual decline from bottom to top, reflecting a continuous sea level decrease.

In Well B, the Sr/Ba values range from 0.27 to 6.41, with an average of 3.15, suggesting a shallower paleo-seawater depth than in Well A. The Co/Ti values range from 7.42 to

145.83, with an average of 37.60, and also show a downward trend from bottom to top (Figure 5). This indicates that the Rongshui area, closer to the edge of the rift during the early Carboniferous period, likely fostered an anoxic benthic environment conducive to organic matter enrichment. Sea level fluctuations played a significant role in controlling organic matter enrichment.

In Well C, the Sr/Ba values range from 0.14 to 10.31, with an average of 2.45 (Figure 6). Despite the potential for increased Ba content due to clay mineral adsorption, the overall Sr/Ba values remain relatively high, indicating shallower paleo-seawater conditions. The Co/Ti values range from 26.45 to 80.66, with an average of 38.87, showing a gradual vertical decline with intermittent upward fluctuations on a secondary scale. This variability further underscores the complex interactions between sea level changes and terrigenous input in shaping paleo-marine environments.

5.2. Influencing Factors of Organic Matter Enrichment

In the Yaziluo Rift Trough, benthic redox conditions show significant regional variations, primarily influenced by the direction and magnitude of seawater intrusion and the development of syndimentary faults. Analysis and comparison reveal a positive correlation between both V/Cr and U/Th ratios and TOC content in Well A and Well B, indicating that organic matter enrichment is significantly influenced by redox conditions (Figure 7). The results suggest that anoxic conditions provide a conducive environment for the preservation of organic matter, and an increase in the degree of oxygen depletion enhances this preservation. Conversely, the V/Cr and U/Th ratios in Well C do not show a significant correlation with the TOC content, indicating limited organic matter preservation in environments with relatively high oxidation levels (Figure 7). Clearly, in transition zones with oxic and shallow-water conditions, redox conditions have little influence on organic matter enrichment [44,45].

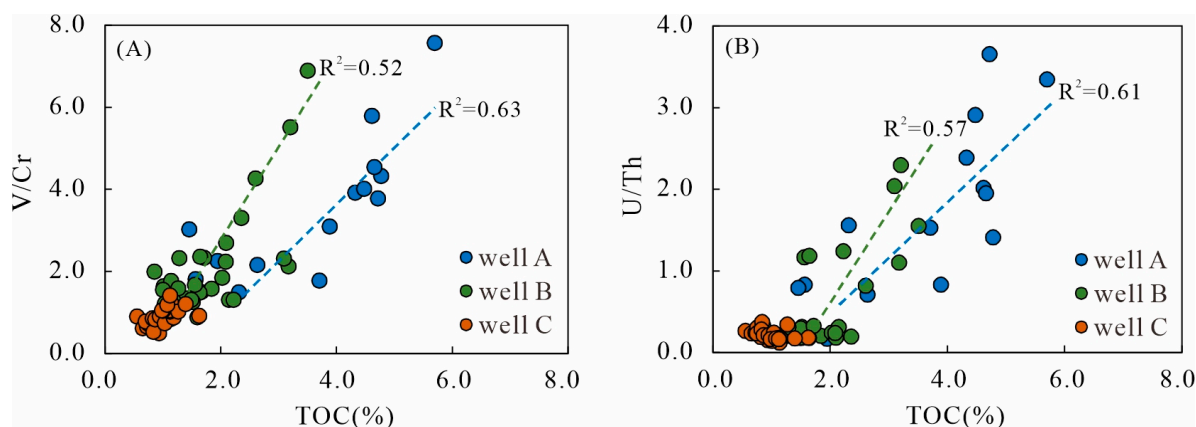


Figure 7. Correlation between redox proxies and TOC in the Lower Carboniferous formation. (A) V/Cr and TOC; (B) U/Th and TOC.

Regarding paleoproductivity proxies, there is no significant correlation between the Ba/Al ratio and TOC content in Wells A and B. However, a weak positive correlation exists between the P/Ti ratio and TOC content in Well A, suggesting that anoxic-dysoxic conditions may moderately enhance the input of organic matter by marine planktonic organisms; however, the impact is not substantial (Figure 8). Collectively, redox conditions and paleoproductivity synergistically contribute to the enrichment of organic matter. In Well C, correlations between the TOC and both Ba/Al and P/Ti are not statistically significant, indicating that paleoproductivity has limited control over organic matter enrichment in low oxygen benthic conditions (Figure 8). Thus, deep anoxic environments play a fundamental role in preserving organic matter and can partially facilitate paleoproductivity enhancement in the Lower Carboniferous shales of the Yaziluo Rift Trough. Furthermore,

paleoproductivity exerts more significant control over organic matter enrichment in anoxic environments.

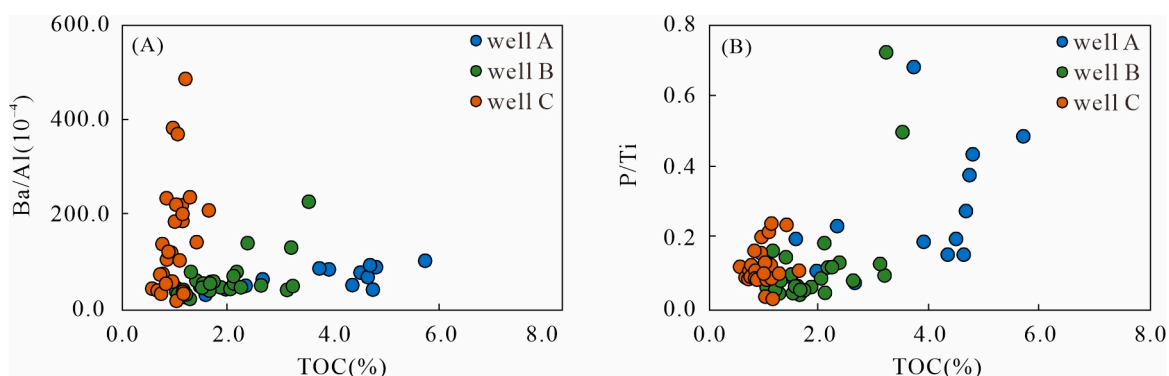


Figure 8. Correlation between paleoproductivity proxies and TOC in the Lower Carboniferous formation. (A) Ba/Al and TOC; (B) P/Ti and TOC.

When considering terrigenous detrital influx proxies, the concentrations of Al and Ti elements are negatively correlated with the TOC content in Wells A and B, respectively (Figure 9). This indicates that terrigenous detrital input can disrupt water stratification, impair the anoxic environment, and dilute marine primary productivity in anoxic-dysoxic environments, thereby hindering organic matter enrichment. Conversely, in Well C, the concentrations of Al and Ti elements show a positive correlation with the TOC content (Figure 9). This suggests that as paleo-seawater depth becomes shallower, a limited number of higher terrestrial plants provide material sources for the enrichment and supplement of organic matter, facilitating the transition of organic matter from type II₁ to type II₂. Additionally, an appropriate amount of terrigenous detrital input helps form clay-organic complexes through the amalgamation of clay minerals and organic matter. The organic matter adsorbed by clay minerals can rapidly reach the seafloor from surface water, reducing oxidation decomposition and destruction of organic matter, and effectively preserving it in relatively low oxic environments [22,46]. In the transition zone, where shallow seawater depth prevails during the deposition process, conditions are not favorable for the mass propagation of microorganisms, such as algae, which contribute to productivity and organic matter preservation.

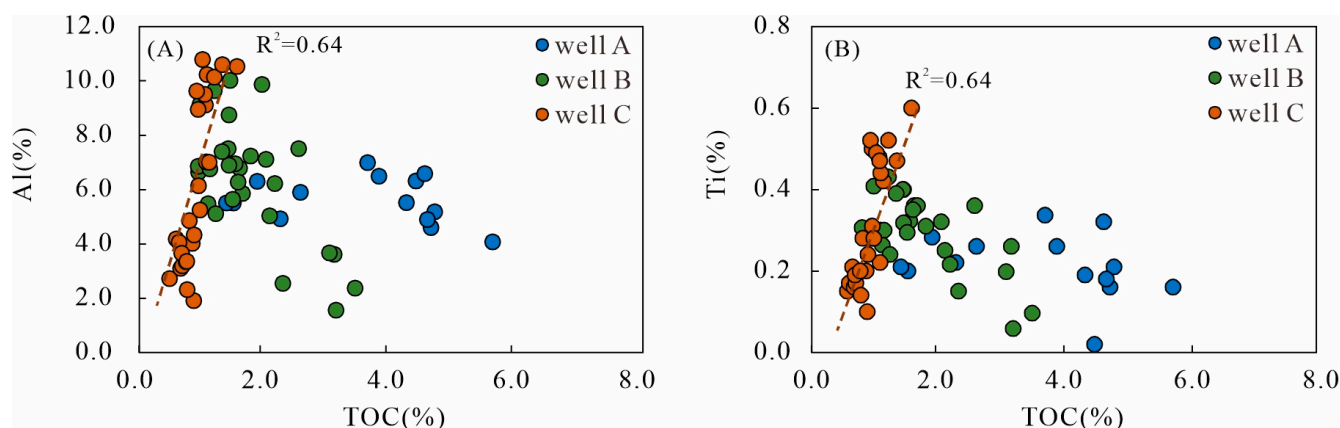


Figure 9. Correlation between detrital proxies and TOC in the Lower Carboniferous formation. (A) Al and TOC; (B) Ti and TOC.

5.3. Shale Distribution Patterns

The Late Devonian period in the Yaziluo Rift Trough was marked by a significant marine transgression from the southeast to northwest, which facilitated the invasion of the

Paleo-Tethys Ocean. This transgression expanded the distribution area of the rift trough, extending the northwestern terminus as far as Zhaotong, Yunnan Province. Since the early Carboniferous period, the distribution of the rift trough has gradually diminished as the seawater retreated southeastward, continuing the sedimentary pattern established in the Late Devonian [15]. Analysis indicates that the Lower Carboniferous shale has a widespread distribution, suggesting a sedimentary profile characterized by basin facies–slope facies. The sedimentary facies types exhibit a strong correlation with the primary quality of shale, such as mineral composition, TOC content, and kerogen types. In the Yaziluo Rift Trough, carbonate lithofacies shale is predominantly found in the upper slope facies, developed within a paleo-seawater environment characterized by relatively shallow depths, low oxygen levels, and strong water-mass restrictions. This lithofacies is marked by high carbonate mineral content, low pyrite abundance, and low TOC content. The dominant kerogen type in the carbonate lithofacies shale is primarily II₂, indicating a limited organic carbon preservation capacity. The deposition process results in the rapid oxidation and decomposition of organic matter, while a limited number of higher terrestrial plants provide additional sources for enriching organic matter content. Concurrently, paleoproductivity increases with the input of organic matter into seafloor sediments (Figure 10).

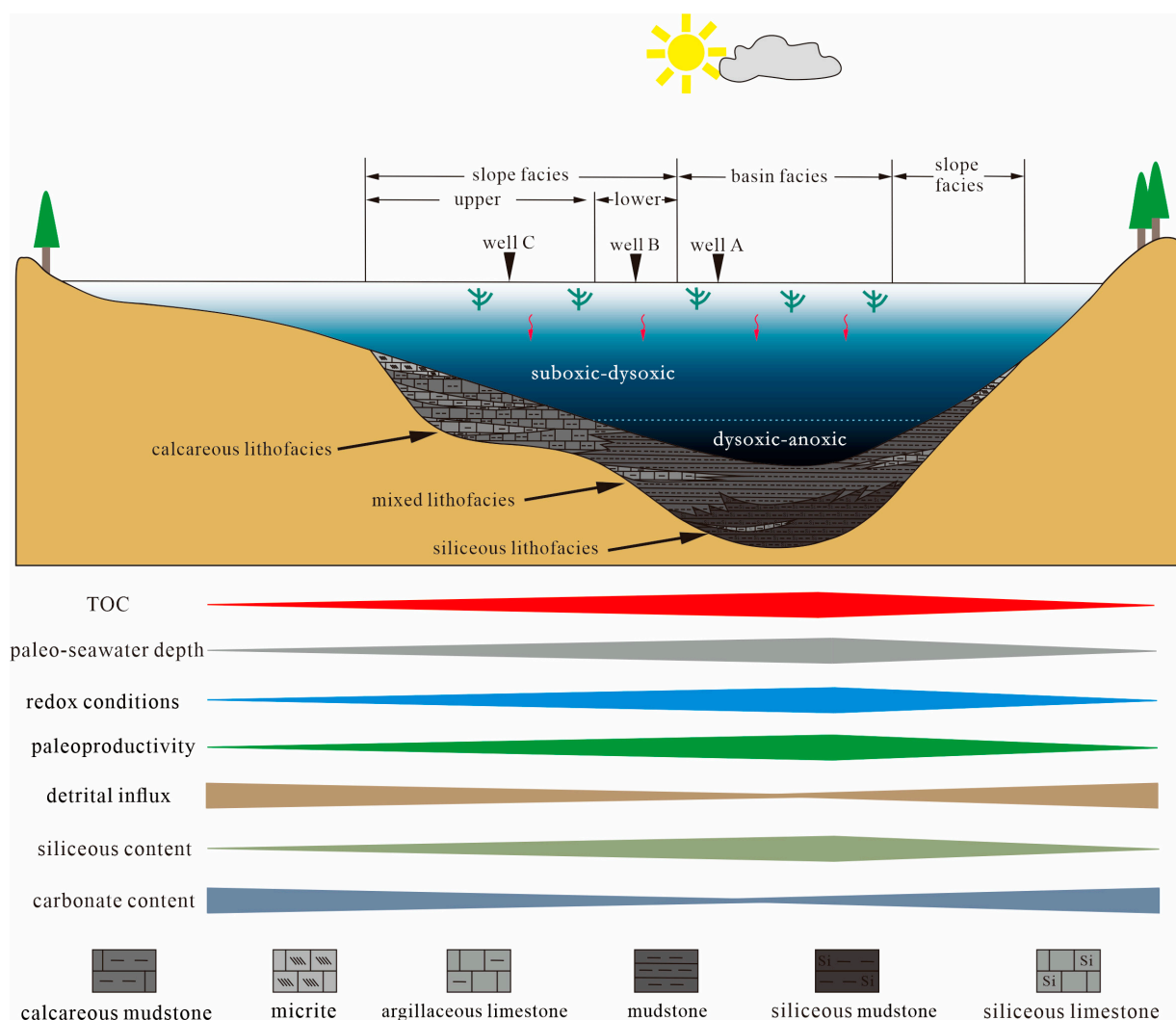


Figure 10. Sedimentary model of the Lower Carboniferous formation. The location of well and variations in paleoenvironment proxies and shale components are schematic.

As the scale of marine transgression and paleo-seawater depth within the rifting trough gradually expanded and deepened from the margin to the depocenter, oxygen

deficiency in the paleoenvironment increased. The development of basin facies shale is less influenced by terrigenous input, reducing the dilution effects on organic matter by terrestrial clastics. Consequently, aquatic phytoplankton becomes the main source of organic matter, leading to increased shale organic richness and silica content. This transition facilitates a shift in kerogen type from II₂ to I and II₁. Therefore, siliceous lithofacies shale is predominantly found in the basin facies, developed under anoxic conditions with significant paleo-seawater depths. The TOC and silica mineral content of the siliceous lithofacies shale are relatively high, with enriched pyrite content and developed spicule fossils. The benthic anoxic conditions not only provide a foundation for organic matter preservation but also create a conducive environment for enhancing paleoproductivity. Overall, the degree of organic matter enrichment is primarily regulated by redox conditions and paleoproductivity, with the influx of terrigenous debris disrupting benthic anoxic conditions and diluting the paleoproductivity of seawater, thereby impeding organic matter enrichment (Figure 10).

In contrast, the Yaziluo Rift Trough experienced gradual crustal stretching during the Devonian period, resulting in the formation of depressions and the deposition of slope facies shale along the trough margins. Due to the influence of syndepositional faulting with a NW to SE direction, the deposition of slope facies on both sides of the rift trough became more pronounced since the early Carboniferous period. The Rongshui area, representing lower slope facies, and the Luzhai area, characterized by basin facies, show discernible disparities in redox conditions, terrigenous detrital supply, and paleoproductivity of seawater. In the Rongshui area, the decrease in paleo-seawater depth has led to increased dissolved oxygen content, disrupting benthic anoxic environments and transforming the paleoenvironment into a dysoxic environment unfavorable for organic matter preservation. Additionally, due to its proximity to terrigenous source regions, there has been an increase in terrigenous detrital influx, evidenced by increased concentrations of Al and Ti elements and a heightened abundance of clay minerals, further diluting the organic matter content within shale. Therefore, mixed shale is predominantly found in the lower slope facies, characterized by a dysoxic environment and a relatively shallow paleo-seawater depth. The abundance of organic matter and siliceous minerals in the mixed shale exhibits a decrease, with kerogen type primarily classified as II₁. The enrichment of organic matter is mainly controlled by anoxic preservation conditions (Figure 10).

The Lower Carboniferous shales in the Yaziluo Rift Trough are developed in a paleoenvironment characterized by frequent water changes and diverse material sources. Due to complex control by extensional faulting, the shale exhibits a complex lithological composition with frequent interlayers of limestone, resulting in variations in the depositional position, seawater depth changes, and distance from the terrigenous source area. These factors contribute to differences in the origin and distribution of shales, ultimately controlling their development scale and thickness. This also determines the degree of organic matter enrichment, types of lithology combinations, and mineral composition. Therefore, the establishment of a correlation between sedimentary facies, lithofacies, and paleoenvironments has been achieved. The paleo-seawater depth is relatively shallow for the upper slope facies, exhibiting a suboxic and shallow-water environment. The lithofacies predominantly comprise carbonate lithofacies shale with low organic matter abundance and high carbonate mineral content. Additionally, the preservation of organic matter is influenced by clay derived from terrigenous detrital material, which exerts an impact on its enrichment. The basin facies exhibit a deep paleo-seawater depth with an anoxic environment, low terrigenous detrital influx, high silica mineral content, high organic matter abundance, and predominantly siliceous lithofacies shale type. The enrichment of organic matter is jointly controlled by redox conditions and paleoproductivity. Compared to the basin facies located in the depocenter of the Yaziluo Rift Trough, the lower slope facies exhibit a semi-deep paleo-seawater depth with a dysoxic environment and moderate terrigenous detrital influx. The lower slope facies shale predominantly consists of mixed

shale, exhibiting a slight decrease in silica content and organic matter abundance. The enrichment of organic matter is also influenced by the benthic redox conditions.

6. Conclusions

(1) This study investigated the Lower Carboniferous shale in the Yaziluo Rift Trough to understand the impact of paleoenvironmental factors on lithofacies characteristics, shale distribution patterns, and organic matter enrichment. Three primary lithofacies were identified: siliceous lithofacies, mixed lithofacies, and calcareous lithofacies. The siliceous lithofacies shale, predominantly composed of siliceous mudstone and siliceous limestone, was deposited in an anoxic environment characterized by high paleoproductivity and minimal terrigenous detrital input. In contrast, both the mixed and calcareous lithofacies were formed in transition zones. However, the calcareous lithofacies, composed mainly of calcareous mudstone, argillaceous limestone, and interlayers of both, was deposited in relatively shallow waters with suboxic conditions, differing from the deeper paleo-seawater conditions of the mixed lithofacies shale, which is dominated by mudstone and calcareous mudstone with argillaceous limestone layers.

(2) In the basin facies, the accumulation of organic matter was primarily governed by anoxic benthic conditions and high paleoproductivity. However, in suboxic-dysoxic benthic conditions, paleoproductivity had limited influence on organic matter enrichment. Terrigenous detrital input disrupted water stratification and diluted marine primary productivity in anoxic-dysoxic environments. Nevertheless, the adsorption of organic components by clay minerals played a crucial role in promoting the enrichment and preservation of organic matter in environments with suboxic benthic conditions.

(3) The sedimentary profile of the Lower Carboniferous shale in the Yaziluo Rift Trough comprises basin facies, lower slope facies, and upper slope facies. These facies indicate the primary shale quality and are closely associated with specific sedimentary facies types. The lithofacies succession transitions from siliceous lithofacies in the anoxic deep-water basin facies, to mixed lithofacies in the dysoxic semi-deep water lower slope facies, and finally to calcareous lithofacies in the suboxic shallow-water upper slope facies. This sequence reflects a paleoenvironmental transition that coincides with a sea level transition within the rift trough, progressing from deep basin facies to shallower upper slope facies.

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References

1. Wang, G.C.; Ju, Y.W.; Huang, C.; Long, S.X.; Peng, Y.M. Longmaxi-Wufeng shale lithofacies identification and 3-D modelling in the northern Fuling gas field, Sichuan basin. *J. Nat. Gas Sci. Eng.* **2017**, *47*, 59–72. [[CrossRef](#)]
2. Ma, Y.Q.; Lu, Y.C.; Liu, X.F.; Zhai, G.Y.; Wang, Y.F.; Zhang, C. Depositional environment and organic matter enrichment of the lower Cambrian Niutitang shale in western Hubei Province, South China. *Mar. Petrol. Geol.* **2019**, *109*, 381–393. [[CrossRef](#)]
3. Wang, N.; Li, M.; Tian, X.; Hong, H.T.; Wen, L.; Wang, W.Z. Climate-ocean control on the depositional watermass conditions and organic matter enrichment in lower Cambrian black shale in the upper Yangtze Platform. *Mar. Pet. Geol.* **2020**, *120*, 104570. [[CrossRef](#)]
4. Ma, Y.S.; Mou, C.L.; Tan, Q.; Yu, Q. A discussion on Kaijiang-Liangping ocean trough. *Oil Gas Geol.* **2006**, *27*, 326–331. (In Chinese)

5. Ding, J.H.; Zhang, J.C.; Li, X.Q.; Lang, Y.; Zheng, Y.Y.; Xu, L.F. Characteristics and controlling factors of organic matter enrichment of Lower Carboniferous black rock series deposited in inter-platform region, Southern Guizhou Depression. *Lithol. Reserv.* **2019**, *31*, 83–95. (In Chinese)
6. Awan, R.S.; Liu, C.L.; Gong, H.W.; Chao, D.; Chao, T.; Lawali, G.C. Paleo-sedimentary environment in relation to enrichment of organic matter of Early Cambrian black rocks of Niutitang Formation from Xiangxi area China. *Mar. Pet. Geol.* **2020**, *112*, 104057. [\[CrossRef\]](#)
7. Wu, C.J.; Zhang, L.F.; Zhang, T.W.; Tuo, J.C.; Song, D.J.; Liu, Y.; Zhang, M.F.; Xing, L.T. Reconstruction of paleoceanic redox conditions of the lower Cambrian Niutitang shales in northern Guizhou, Upper Yangtze region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2020**, *538*, 109457. [\[CrossRef\]](#)
8. Zhou, L.; Kang, Z.; Wang, Z.; Peng, Y.Y.; Xiao, H.F. Sedimentary geochemical investigation for paleoenvironment of the Lower Cambrian Niutitang Formation shales in the Yangtze Platform. *J. Petrol. Sci. Eng.* **2017**, *159*, 376–386. [\[CrossRef\]](#)
9. Yi, T.; Chen, J. Occurrence characteristics and exploration potential of Carboniferous shale gas in western Guizhou. *Pet. Reserv. Eval. Dev.* **2022**, *12*, 82–94. (In Chinese)
10. Su, H.M.; Yang, R.D.; Gao, J.B.; Xu, S.L.; Zhang, Z. REE Geochemical Signatures and Sedimentary Environments of the Early Carboniferous Dawuba Formation Black Rock Series in Huishui, Guizhou. *J. Chin. Soc. Rare Earths* **2017**, *35*, 620–631. (In Chinese)
11. Chen, Y.; Huang, W.F.; Liang, Y.P.; Deng, B. Analysis on black shale feature and depositional environment of first member of Luzhai Formation, Luzhai area of Guangxi. *Miner. Resour. Geol.* **2017**, *31*, 605–612. (In Chinese)
12. Tao, J.Y.; Hu, Z.Q.; Shen, B.J.; Pan, A.Y.; Li, C.X.; Wang, R.H.; Zhang, M.L. Sedimentary characteristics and model of platform-trough shale in the Lower Carboniferous, Guizhong Depression, Dianqiangui Basin. *Oil Gas Geol.* **2022**, *43*, 365–377. (In Chinese)
13. Wang, X.W.; Guo, T.L.; Wo, Y.J.; Zhou, Y.; Wu, L.Z.; Zhang, R.Q.; Li, S.J. Characteristics of deep structure segmentation and transformation of Yaziluo fault zone. *Oil Gas Geol.* **2013**, *34*, 220–228. (In Chinese)
14. Han, S.; Zhang, Y.; Huang, J.; Rui, Y.; Tang, Z. Elemental Geochemical Characterization of Sedimentary Conditions and Organic Matter Enrichment for Lower Cambrian Shale Formations in Northern Guizhou, South China. *Minerals* **2020**, *10*, 793. [\[CrossRef\]](#)
15. Wang, S.Y.; Zhang, H.; Wang, T.H.; Wang, C.H.; Peng, C.L.; Hu, R.F.; Chen, M.H.; Shi, L. Filling and evolution the Late Paleozoic Shuicheng-Ziyun aulacogen in western Guizhou, China. *Geol. Bull. China* **2006**, *25*, 402–407. (In Chinese)
16. Tian, S.F.; Yang, R.D. Lithofacies and paleogeography evolution and characteristics of shale gas accumulation in Lower Carboniferous, Guizhou, China. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* **2016**, *43*, 291–299. (In Chinese)
17. Geology and Mineral Resources Bureau of Guangxi Zhuang Autonomous Region. *Regional Geology of Guangxi Zhuang Autonomous Region*; Geological Publishing House: Beijing, China, 1985; pp. 853–854. (In Chinese)
18. GB/T 19145-2003[S]; General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Determination of Total Organic Carbon in Sedimentary Rock. Standards Press of China: Beijing, China, 2003.
19. Yang, W.; Zuo, R.S.; Jiang, Z.X. Effect of lithofacies on pore structure and new insights into pore-preserving mechanisms of the over-mature Qiongzhusi marine shales in Lower Cambrian of the southern Sichuan Basin, China. *Mar. Orig. Pet. Geol.* **2018**, *98*, 746–762. (In Chinese) [\[CrossRef\]](#)
20. Lu, B.; Jiang, S.; Lu, Y.C.; Xu, S.; Shu, Y.; Wang, Y.X. Productivity or preservation? The factors controlling the organic matter accumulation in the late Katian through Hirnantian Wufeng organic-rich shale, South China. *Mar. Petrol. Geol.* **2019**, *109*, 22–35. [\[CrossRef\]](#)
21. Algeo, T.J.; Tribovillard, N. Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation. *Chem. Geol.* **2009**, *268*, 211–225. [\[CrossRef\]](#)
22. Zhang, L.C.; Xiao, D.S.; Lu, S.F.; Jiang, S.; Lu, S.D. Effect of sedimentary environment on the formation of organic-rich marine shale: Insights from major/trace elements and shale composition. *Int. J. Coal Geol.* **2019**, *204*, 34–50. [\[CrossRef\]](#)
23. Tribovillard, N.; Algeo, T.J.; Baudin, F.; Riboulleau, A. Analysis of marine environmental conditions based on molybdenum-uranium covariation-Applications to Mesozoic paleoceanography. *Chem. Geol.* **2012**, *324*, 46–58. [\[CrossRef\]](#)
24. Qiu, Z.; Wei, H.Y.; Liu, H.; Shao, N.; Wang, Y.M.; Zhang, L.F.; Zhang, Q. Accumulation of sediments with extraordinary high organic matter content: Insight gained through geochemical characterization of indicative elements. *Oil Gas Geol.* **2021**, *42*, 931–948. (In Chinese)
25. Jones, B.; Manning, D.A. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. *Chem. Geol.* **1994**, *111*, 111–129. [\[CrossRef\]](#)
26. Tribovillard, N.; Algeo, T.J.; Lyons, T.; Riboulleau, A. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* **2006**, *232*, 12–32. [\[CrossRef\]](#)
27. Sadiq, M. Thermodynamic solubility relationships of inorganic vanadium in the marine environment. *Mar. Chem.* **1988**, *23*, 87–96. [\[CrossRef\]](#)
28. Cranston, R.E.; Murray, J.W. The determination of chromium species in natural waters. *Anal. Chim. Acta* **1978**, *99*, 275–282. [\[CrossRef\]](#)
29. Rimmer, S.M. Geochemical paleoredox indicators in Devonian-Mississippian black shales, central Appalachian Basin (USA). *Chem. Geol.* **2004**, *206*, 373–391. [\[CrossRef\]](#)

30. Wang, S.F.; Dong, D.Z.; Wang, Y.M.; Huang, J.L.; Pu, B.L. Geochemistry Evaluation Index of Redox-sensitive Elements for Depositional Environments of Silurian Longmaxi Organic-rich Shale in the South of Sichuan Basin. *Mar. Orig. Pet. Geol.* **2014**, *19*, 27–34. (In Chinese)
31. Ingall, E.D.; Bustin, R.M.; Van, C.P. Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales. *Geochem. Cosmochim. Acta* **1993**, *57*, 303–316. [[CrossRef](#)]
32. Schoepfer, S.D.; Shen, J.; Wei, H.Y.; Tyson, R.V.; Ingall, E.; Algeo, T. Total organic carbon, organic phosphorus, and biogenic barium fluxes as proxies for paleomarine productivity. *Earth Sci. Rev.* **2015**, *149*, 23–52. [[CrossRef](#)]
33. Zhang, J.G.; Lv, D.Y.; Chen, H.Y.; Yu, C.; Zhao, K.H.; Liu, X.X.; Liu, Y.M.; Zhang, H.; Liu, B.; Qiang, X.K.; et al. Evolution of sedimentary environment in the Eastern Henan Basin since the Late Pliocene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2024**, *633*, 111896. [[CrossRef](#)]
34. Goldberg, E.D.; Arrhenius, G.O.S. Chemistry of Pacific pelagic sediments. *Geo-Chim. Cosmochim. Acta* **1958**, *13*, 153–212. [[CrossRef](#)]
35. Liu, K.; Cheng, P.; Fan, C.W.; Song, P.; Huang, Q.T. Evolutions of sedimentary facies and palaeoenvironment and their controls on the development of source rocks in continental margin basins: A case study from the Qiongdongnan Basin, South China Sea. *Petrol. Sci.* **2023**, *20*, 2648–2663. [[CrossRef](#)]
36. Xu, Q.L.; Liu, B.; Song, X.M.; Wang, Q.P.; Chen, X.D.; Li, Y.; Zhang, Y. Hydrocarbon generation and organic matter enrichment of limestone in a lacustrine mixed sedimentary environment: A case study of the Jurassic Da'anzhai member in the central Sichuan Basin, SW China. *Petrol. Sci.* **2023**, *20*, 670–688. [[CrossRef](#)]
37. Fan, D.; Zhang, T.; Ye, J. Anoxic environment and formation of superlarge ore deposits. *Sci. China Ser. D Earth Sci.* **1998**, *41* (Suppl. S1), 37–46. [[CrossRef](#)]
38. Sun, Z.Q.; Chen, Z.H.; Liu, L.L.; Li, Y.; Zhang, J.L.; Shen, W.L. How to distinguish between marine and lacustrine sedimentary environments?—A case study of Lishui Sag, East China Sea Shelf Basin. *Geoenergy Sci. Eng.* **2023**, *228*, 212032. [[CrossRef](#)]
39. Middelburg, J.J. Organic carbon, sulphur, and iron in recent semi-euxinic sediments of Kau Bay, Indonesia. *Geochim. Cosmochim. Acta* **1991**, *55*, 815–828. [[CrossRef](#)]
40. Gou, M.X.; Lu, G.; Deng, B.; Wang, C.C.; Li, Z.W.; Yu, Y.; Yang, R.J.; Jin, X. Tectonic–paleogeographic evolution of the Late Triassic in the Sichuan basin, SW China: Constraints from sedimentary facies and provenance analysis of the Xujiache Formation. *Mar. Pet. Geol.* **2024**, *160*, 106649. [[CrossRef](#)]
41. Feng, Y.; Xiao, X.M.; Gao, P.; Wang, E.Z.; Hu, D.F.; Liu, R.B.; Li, G.; Lu, C.G. Restoration of sedimentary environment and geochemical features of deep marine Longmaxi shale and its significance for shale gas: A case study of the Dingshan area in the Sichuan Basin, South China. *Mar. Pet. Geol.* **2023**, *151*, 106186. [[CrossRef](#)]
42. Li, T.; He, S.; Yang, Z. The Marine Source Rock Formation Conditions and Control Factors. *Geol. Sci. Technol. Inf.* **2008**, *27*, 63–70. (In Chinese)
43. He, D.S.; Fang, H.; Zhang, P.H.; Pei, F.G.; Ming, C.D.; He, M.X.; Zhang, X.B. Geochemical characteristics of the Middle–Late Permian sedimentary rocks in the southern Great Xing'an Range, NE China, and their constraints on the closure time of the Paleo Asian Ocean (Eastern Segment). *Sediment. Geol.* **2023**, *450*, 106375. [[CrossRef](#)]
44. Kontakiotis, G.; Karakitsios, V.; Maravelis, A.G.; Zarkogiannis, S.D.; Agiadi, K.; Antonarakou, A.; Pasadakis, N.; Zelilidis, A. Integrated isotopic and organic geochemical constraints on the depositional controls and source rock quality of the Neogene Kalamaki sedimentary successions (Zakynthos Island, Ionian Sea). *Med. Geosci. Rev.* **2021**, *3*, 193–217. [[CrossRef](#)]
45. Kontakiotis, G.; Karakitsios, V.; Cornée, J.; Moissette, P.; Zarkogiannis, S.D.; Pasadakis, N.; Koskeridou, E.; Manoutsoglou, E.; Drinia, H.; Antonarakou, A. Preliminary results based on geochemical sedimentary constraints on the hydrocarbon potential and depositional environment of a Messinian sub-salt mixed siliciclastic-carbonate succession onshore Crete (Plouti section, eastern Mediterranean). *Med. Geosci. Rev.* **2020**, *2*, 247–265. [[CrossRef](#)]
46. Yu, W.; Tian, J.C.; Wang, F.; Liang, Q.S.; Yang, T.; Kneller, B.; Liang, X.W. Sedimentary environment and organic matter enrichment of black mudstones from the upper Triassic Chang-7 member in the Ordos Basin, Northern China. *J. Asian Earth Sci.* **2022**, *224*, 105009. [[CrossRef](#)]

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