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Sedimentary Environment and Organic Accumulation of the Ordovician–Silurian Black Shale in Weiyuan, Sichuan Basin, China

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Abstract: The sedimentary environment and organic matter enrichment relationship of the Upper Ordovician Wufeng Formation black shale, Guanyinqiao mudstone, and Lower Silurian Longmaxi Formation black shale in the Sichuan Basin of Weiyuan are analyzed using geochemical methods such as organic carbon, sulfur, major elements, and trace elements. The experimental results illustrate that the upper section of the Wufeng Formation and the lower section of the Longmaxi Formation are organic matter enrichment layers. The presence of P indicates a high productivity level in the Sichuan Basin from the Late Ordovician to the Early Silurian. In addition, indicators such as V/Cr, Ni/Co, and S/C suggest that the Wufeng Formation was deposited under anoxic reductive conditions, that the ice age Guanyinqiao segment was in an oxygen-rich to oxygen-poor environment, and that the Longmaxi Formation was in a sulfidic environment. Mo/TOC indicates that the Wufeng Formation shale was controlled by a restricted basin and that the Guanyinqiao segment and the Longmaxi Formation were in a medium-to-weak retention environment. The weak correlation of TOC with P/Al and Al indicates that the level of primary productivity and terrigenous detritus had a minor effect on the organic matter enrichment of the Wufeng and Longmaxi Formation black shale. Conversely, the positive correlation of TOC with V/Cr and Ni/Co illustrates that the anoxic reductive sedimentary environment is the main factor affecting the organic matter enrichment of the Wufeng and Longmaxi Formation black shale. Based on these studies, the development model of organic-rich shales of the Ordovician–Silurian in Weiyuan, Sichuan Basin is proposed. This paper may provide a reference for shale gas exploration in the Wufeng–Longmaxi Formation and a sedimentary response to the major geological events of Ordovician–Silurian.

Keywords: south Sichuan; Weiyuan area; black shale; sedimentary environment; Wufeng formation; Longmaxi formation

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1. Introduction

Black shale, characterized by its high organic content, represents a substantial reservoir for diverse resources, including hydrocarbons, such as oil and gas, and various metal deposits [1]. As such, research has focused extensively on elucidating the mechanisms underlying the organic enrichment process within black shale [2]. Two predominant models have been proposed to account for this organic enrichment in black shale [3]. The first model, the productivity model, posits that elevated productivity within the surface seawater culminates in an increased rate of organic matter burial. The second model, the preservation model, advances the idea that the anoxic or oxygen-deficient conditions prevailing in deep-water environments preserve and subsequently bury organic carbon in

sediment [4]. However, the accumulation of organic materials in black shale is typically multifactorial, with numerous elements acting in synergy. These two models significantly influence this multifaceted process [5]. The literature proposes that many environmental factors modulate the organic matter enrichment in shale. These encompass sedimentation rates, the influx of terrigenous detritus, tectonic activity, and climatic shifts. Consequently, a comprehensive reconstruction of the paleoenvironment of black shale building on diverse perspectives is imperative to derive a nuanced understanding of its organic enrichment mechanisms [6].

The black shales of the Upper Ordovician Wufeng and Lower Silurian Longmaxi Formations in the Sichuan Basin are significant source rocks for Lower Paleozoic hydrocarbons in China, and critical horizons for shale gas exploration and paleoenvironmental research [7]. As early as in the 1980s, Chinese scholars such as Rong et al. [8], Chen et al. [9], and Wang et al. [10] conducted extensive research on lithofacies paleogeography, biostratigraphy, and petrogeochemistry of black shales in the Wufeng–Longmaxi Formations in the Yangtze region. They concluded these shales were primarily formed during the Early Silurian period under plate compression and global sea-level rise. Recent studies have focused on reservoir evaluation, accumulation conditions, and resource potential of the black shale of the Wufeng–Longmaxi Formations. However, discussions regarding its sedimentary environment and organic enrichment mechanisms are scarce. When investigating the development conditions of Upper Ordovician–Lower Silurian source rocks in the Yangtze area, Yan et al. [11] and Li et al. [12] posit that high biological productivity is critical for organic carbon enrichment, while Zhou et al. [13] and Wang et al. [10] contend that the formation of high-quality source rocks results from substantial organic carbon preservation within anoxic reduction depositional environments. However, the Wufeng–Longmaxi Formation black shales were formed during the intersection of the Ordovician and Silurian periods, which witnessed frequent glaciation events, biological extinction events, and even volcanism. Any of these occurrences can influence source rock development [14,15]. Therefore, it is crucial to reconstruct the paleoenvironmental evolution to identify organic matter accumulation. Furthermore, scholars frequently treated the two sets of shales from the Wufeng and Longmaxi Formations as a single black rock series, neglecting the distinct impacts of geological events, such as sea-level fluctuations and biological extinctions, caused by glaciation during the Ordovician–Silurian transition on each set [16]. Furthermore, studies have focused on the middle and lower Yangtze regions. These are situated in the Yangtze Sea region, exhibiting a moderately open paleogeography, whereas a comparatively restricted basin has not been thoroughly investigated. Only with the recent advancement of shale gas exploration have scholars once again directed their attention toward the sedimentary environment of the black shale within this basin [17]. In conclusion, it is imperative to investigate the organic enrichment process in black shale within the Wufeng–Longmaxi Formations in the Sichuan Basin to enhance our understanding of the sedimentary environment during the Ordovician–Silurian transition and enable us to evaluate the potential for shale gas resources [18].

Geochemical methods, such as major and trace elements, are frequently used to reconstruct paleoenvironmental characteristics [18]. The contents of biological nutrient elements, such as Ba and P, directly indicate the ancient productivity level in sedimentary basins. Redox-sensitive elements, such as V, Ni, Cr, Mo, and U, are also frequently used indicators of paleo-oxygen facies in sedimentary environments. Furthermore, organic elements, including C, N, and S, constantly circulate within the biosphere, lithosphere, and hydrosphere [19]. The conversion process between inorganic and organic matter is accompanied by alterations to sedimentary environments and the accumulation of organic material. This study uses these geochemical techniques to investigate the correlation between organic enrichment and the environmental evolution of black shale within the Upper Ordovician Wufeng and Lower Silurian Longmaxi Formations in the SW Sichuan Basin [20]. The results will serve as a valuable reference for shale oil and gas exploration and evaluation.

2. Geological Setting

The Upper Ordovician Wufeng and Lower Silurian Longmaxi Formations were deposited during the extinction of the South China Basin and the formation of South China [20]. Under the influence of the Guangxi movement, convergence occurred between the Yangtze and Cathaysian landmasses, leading to successive uplifts in the southeast of the Yangtze region and the Jiangnan Basin at the end of the Cambrian period [21]. This transformation turned the Yangtze region from a passive continental margin basin into a foreland basin. The Early and Middle Ordovician witnessed the predominant development of carbonate platform deposits in the Yangtze region. In the Late Ordovician, the Yangtze region underwent clastic rock–carbonate mixed-platform sedimentation and carbonate gentle-slope deposition [22]. During the Ordovician to Silurian period, a rapid global sea-level rise occurred, accompanied by the extensive uplift of ancient land. During this period, the Upper Yangtze region underwent successive south-to-north developments, encompassing the Middle Qianzhong Uplift, Wuyi-Yunkai Uplift, Xuefeng Uplift, Leshan–Longnusi Ancient Uplift, and Hannan Ancient Land [23]. The back basin of the Middle–Upper Yangtze was between these uplifts (Figure 1), with a sedimentary environment primarily characterized by shallow- and deep-water basins. In the Early Silurian period, the south-eastward compression was intensified, resulting in the continuous uplift of the Middle and Upper Yangtze regions (Figure 1).

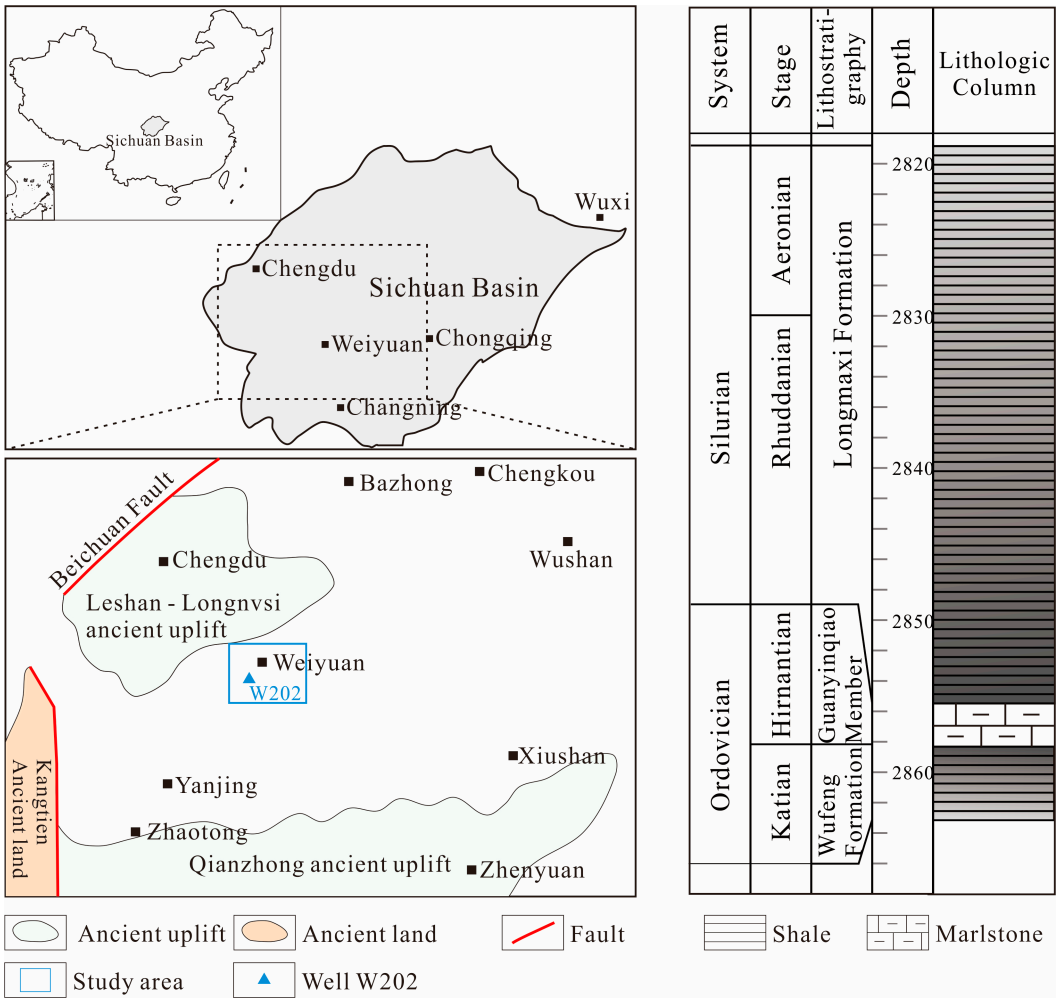

Figure 1. Study area and stratigraphic column of this study.

Researchers have investigated the current tectonics in the study area extensively. The study area has undergone multiple stages of tectonic movements in chronological

sequences, such as the Caledonian, Hercynian, Indosinian, Yanshan, and Himalayan movements [24]. During the late Caledonian movement, the northwest of the area uplifted rapidly, denudated by the Cambrian to Silurian strata to varying degrees, and the low uplift core formed the prototype of the Weiyuan anticline. The Hercynian orogeny caused continuous regional uplift and contraction, resulting in Devonian and Carboniferous deposition failure and strata loss [25]. The Permian–Middle Triassic was a stable period of the Weiyuan anticline, with weak tectonic activity and stable sedimentation. The Late Triassic to Eocene experienced a period of moderate adjustment, characterized by up–down movements in the area and discontinuity between the Jurassic and Cretaceous periods, without significant structural deformation [26]. From the Oligocene to the present, the Himalayan movement caused the rapid formation of a low-amplitude uplift and the development of some low-angle reverse and inverse faults, and finally formed the domed Weiyuan anticline structure. The fault system in the region is poorly developed, with only localized natural fractures and a complex geo-stress field [27].

The Wufeng–Longmaxi Formations, deposited during the Late Ordovician–Early Silurian period in the Sichuan Basin, comprise a series of continuous deep-water organic-rich shelf facies with siliceous or calciferous shells [28]. The Longmaxi Formation primarily comprises black siliceous and gray-black siliceous calcareous shales, which gradually transition to mixed shale with increasing clay content. Massive bedding, horizontal bedding, wavy bedding, pyrite nodules, and structural scratches are developed [29]. The strata in the Weiyuan area are 30–60 m thick, stable, and contain many graptolite fossils.

3. Materials and Methodology

All study samples were exclusively obtained from parameter well W202, which was drilled through the Wufeng and Longmaxi Formations to ensure sample continuity and mitigate the impact of weathering. W202 is located in Weiyuan, a city in the southwestern Sichuan Basin. According to the equal spacing principle, 33 fresh samples were collected for analysis and testing, including 7 black shale members in the Wufeng Formation, 3 in the Guanyinqiao Member, and 23 in the Longmaxi Formation. All samples were washed and freeze-dried, followed by manual grinding to a 200-mesh size. Subsequently, they were evaluated for organic carbon, sulfur, main contents, and trace elements.

The total organic carbon (TOC) and total sulfur (TS) content were measured with a infrared absorption carbon-sulfur analyzer, following the Chinese National Standard (GB/T 19145-2022) [30]. TOC was extracted using an acid acidification method. The sample was treated with 4 mol/L HCl for 12 h, followed by three washes with deionized water and centrifugation. After drying, the inorganic carbon-free sample was obtained. The infrared absorption carbon-sulfur analyzer was then used for testing TOC and TS. The model of the carbon and sulfur analyzer is LECO CS-600 (LECO Corporation, San Joseph, MI, USA), and its analysis accuracy is $\pm 0.5\%$.

The major elements were characterized by X-ray fluorescence spectrometry. After being subjected to a temperature of 920 °C, the 0.5 g sample was homogeneously blended with eight times its mass of $Li_2B_2O_7$ and treated with one to two drops of LiBr–NH_4I cosolvent before being poured into a platinum crucible for melting preparation at 1150 °C, and evaluated by machine. The instrument model is Rigaku 100e (Rigaku Corporation, Tokyo, Japan), and its analysis accuracy is better than 5%.

The trace elements were analyzed and evaluated using inductively coupled plasma mass spectrometry (ICP-MS). First, the sample was combusted at 700 °C to remove organic matter. Then, a 40 mg sample was weighed and 0.8 mL of HNO_3 and HF was added before the sample was dissolved in a sealed autoclave at 190 °C for 48 h, followed by drying. Subsequently, it was diluted to a ratio of 1:2000 with purified HNO_3, and then internal standard solution of Rh was added. Finally, the sample was tested by ICP-MS. The instrument model is PE Elan6000 (PerkinElmer Inc., Waltham, MA, USA), and the analysis error was less than 5%.

4. Experimental Results

4.1. Sedimentological and Petrological Characteristics

The black shale is predominantly deposited in shelf facies. Within the deep-water shelf facies, high organic content and thicknesses of up to 10–20 m characterize the black carbonaceous shales (Figure 2). These shales exhibit a gradual lightening in coloration and increased sandy content. The black shale of the Longmaxi Formation is abundant in graptolite, comprising 20%–90% of the organic volume, and is a significant hydrocarbon source rock for shale gas [31]. Furthermore, different combinations of graptolite fossils are biomarkers for indicating the paleowater depth of an environment. The larger and more symmetrical the graptolite monomer is, the deeper the water; conversely, smaller individual graptolites indicate shallower water.

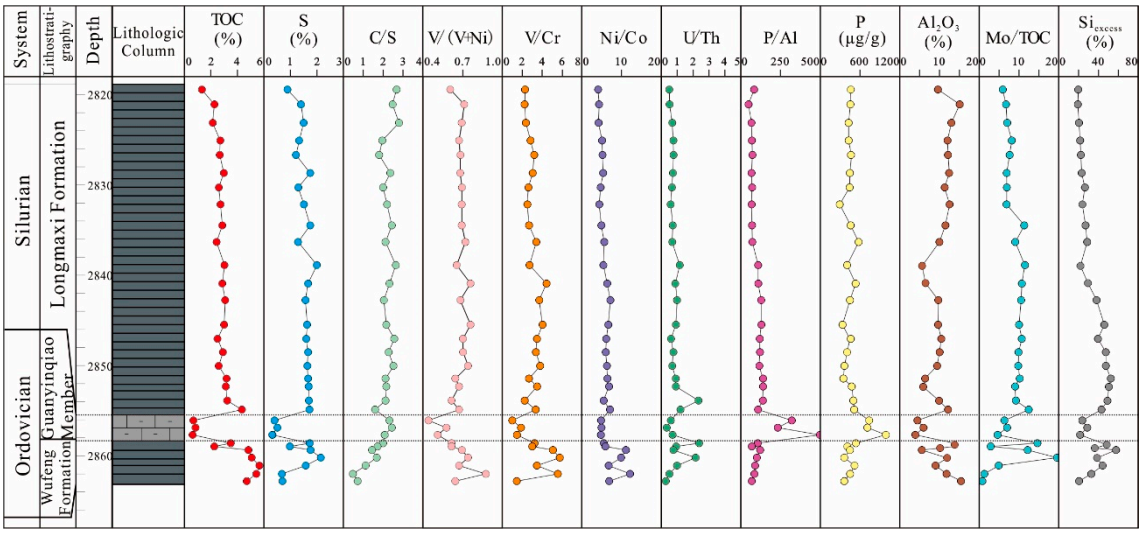

Figure 2. Histogram of paleo-environmental indexes in Wufeng–Longmaxi Formation.

4.2. Total Organic Carbon and Sulfur Content

At present, the lower limit of total organic carbon (TOC) for black shale to be considered an effective source rock is generally set at 2%. However, some scholars suggest that for shale with high thermal evolution maturity, this limit can be reduced to 1.5% [32]. The Wufeng Formation exhibits a high organic carbon content, with total organic carbon (TOC) ranging from 2.01% to 5.54%, and with an average of 4.18%. The TOC of the Guanyinqiao Member samples range from 0.72% to 0.94%, with an average of 0.79%. The middle and lower parts of Longmaxi Formation show TOC between 2.60% and 4.66%, averaging at 4.07%. TOC in the upper part of the Longmaxi Formation decreased relatively, ranging from 1.61% to 2.54% with an average of 1.79%. Generally, the TOC of the Wufeng–Longmaxi Formation black shale is relatively high and exhibits a gradual decrease from bottom to top. The sulfur content trend was in line with that of the TOC. The sulfur content of the Wufeng Formation ranges from 0.61% to 2.54%, with an average of 1.59%. The sulfur content of the Longmaxi Formation ranges from 0.64% to 2.43%, with an average of 1.52%. The sulfur content of the Guanyinqiao Member is relatively lowest, ranging from 0.45% to 0.53%.

4.3. Major Element

The major constituents of shale are Si, Ca, Al, Fe, K, and Ti—the six principal lithogenic elements in the Earth's crust [33]. SiO_2 is the major element with the highest occurrence in shale. The SiO_2 content of the Wufeng Formation is 9.54%–90.24%, with an average of 52.18%, and the silica content at 2859.18–2859.74 m is the highest, amounting to more than 74%. The SiO_2 content of the Longmaxi Formation is 10.31%–89.91%, with an average of 50.35%. The silica content at 2850.94–2853.62 m is the highest, with an average of 78.38%. The silica content of other intervals is relatively stable, with more than 90% of the data

within the range of 30%–60%. Next to SiO_2 are CaO and Al_2O_3, with average contents of 11.10% and 10.85%, respectively. The CaO content is higher in the lower bottom of the Wufeng Formation and Longmaxi Formation, while remaining relatively stable in other sections. Al_2O_3 exhibits a consistently low value within the bottom 5 m of the Longmaxi Formation. In addition to the aforementioned major elements, Fe_2O_3 exhibits the highest concentration, while the Wufeng Formation ranges from 0.88% to 5.47%, with an average of 3.45%. The Longmaxi Formation displays an Fe_2O_3 content range of 1.03% to 37.19%, averaging at 4.96%. The K_2O content in the Wufeng Formation ranged from 0.54% to 8.09%, with an average of 2.92%. In contrast, the K_2O content in the Longmaxi Formation varied between 0.02% and 7.79%. The TiO_2 content in the Wufeng Formation remained relatively stable, ranging from 0.03% to 1.30%, with an average of 0.45%. Meanwhile, the TiO_2 content in the Longmaxi Formation was found to be between 0.01% and 1.83%, with an average of approximately 0.52%. TiO_2/Al_2O_3 values were low and relatively stable, ranging from 0.01% to 0.18% with an average of 0.05%. The stable low TiO_2/Al_2O_3 value may indicate the slow deposition rate and relatively stable water environment during the development of the Wufeng–Longmaxi Formation black shale.

Biological silicon (Si_{bio}) can be used as a reliable indicator of changes in productivity. Si_{bio} refers to Si involved in biological processes [34]. Excess silicon (Si_{excess}) is generally used to describe biological silicon in shale. Si_{excess} is obtained by subtracting the terrigenous Si content from the total Si content. The formula for calculating biological Ba is:

$$Si_{excess} = Si_{total} - Al_{total} \times (Si/Al)_{PAAS} \quad (1)$$

Equation (1) assumes all Excess silicon in sediments, except for terrigenous clastic Si, is of biogenic origin. The $(Si/Al)_{PAAS}$ ratio represents the average value of terrigenous aluminosilicates and is calculated using Post-Archean Australia shale (PAAS) as the standard. The value of $(Si/Al)_{PAAS}$ is 3.11 [35]. The results indicate significant variations in the Si_{excess} of black shales from the Wufeng and Longmaxi Formations. The Si_{excess} of Wufeng Formation black shale exhibits 10.14%–61.37% (average of 33.71%), while the Guanyinqiao Member displays 19.12%–22.29% (average of 21.45%). And the Si_{excess} of Longmaxi Formation black shale exhibits 11.23%–46.11% (average of 29.08%). The Si_{excess} in black shales at the bottom of the Longmaxi Formation is significantly higher than in silty shales at the top (Figure 2).

4.4. Trace Element

Compared to other sedimentary rocks, shale exhibits a higher concentration of trace elements, particularly those sensitive to redox and closely linked with biological activities, such as V, Ni, Mo, U, Co, Ba, and Cu. The enrichment factor (EF) is frequently used in shale analysis to assess the enrichment degree for various elements [36]. The formula for calculating EF is:

$$X_{EF} = (X/Al)_{Sample}/(X/Al)_{Average} \quad (2)$$

where X represents a trace element, and $X_{EF} > 1$ indicates that X is more enriched than average shales. The average value of the X element content takes the average of Post-Archean Australian crustal shales (PAAS) of Australia as the reference in this paper [37]. The calculation results indicate that the black shale of the Wufeng–Longmaxi Formations is enriched in redox-sensitive elements, including V, Ni, Mo, U, and Co. The variation range of X_{EF} within the Wufeng Formation was substantial and slightly higher than in the Longmaxi Formation (Table 1). In addition to elements with strong redox sensitivity, such as Mo, U, and V, biotrophic elements like P_{EF} (0.7–7.3, average of 1.7) were moderately enriched throughout the well (Figure 3).

Table 1. Statistics of trace element enrichment factor.

X_{EF}	V_{EF}		Ni_{EF}		Mo_{EF}		U_{EF}		Co_{EF}	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Wufeng Formation	1.5–7.2	4.7	1.5–7.9	4.6	3.2–188.5	78.2	3.08–23.8	12.7	0.5–2.1	1.1
Longmaxi Formation	0.7–3.9	2.7	1.5–3.6	2.6	15.3–69.4	39.5	4.3–20.8	8.5	0.8–1.3	1.0

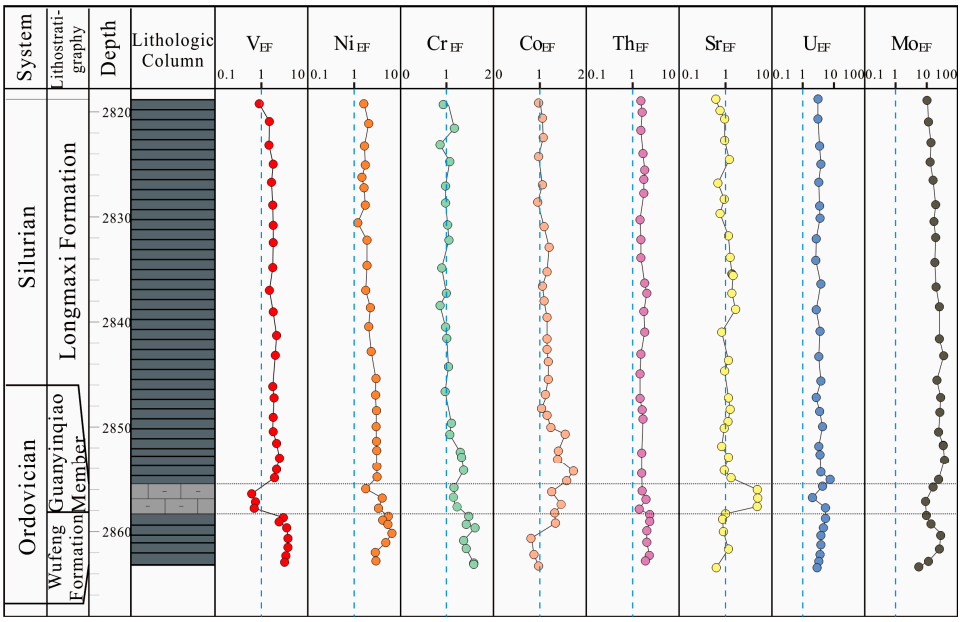

Figure 3. Histogram of trace elements in the formations of this study.

Enrichment trends of redox sensitive elements generally parallel those of the TOC, and the ratios V/(V + Ni), V/Cr, Ni/Co, and U/Th also increase with increasing TOC (Figure 2). The V/(V + Ni) (0.61–0.87), V/Cr (1.45–5.78), Ni/Co (5.5–11.1), and U/Th (0.3–2.4) of the black shale in Wufeng Formation have the highest values in the middle part, gradually decrease upward, and decrease to the lowest values in the Guanyinqiao Member, with an average value of 0.49, 1.44, 4.87, and 0.55. During the transition to the Longmaxi Formation, there was a rapid increase in V/(V + Ni) (0.59–0.75), V/Cr (2.23–4.45), Ni/Co (4.11–7.17), and U/Th (0.51–2.34).

The Wufeng–Longmaxi black shale exhibits generally high levels of P. Within the Wufeng Formation, P displays significant variability, ranging from 358.5 to 565.1 μg/g with an average value of 499.4 μg/g; the P content of the Longmaxi Formation exhibited relative stability, ranging from 410.1 to 555.1 μg/g with an average value of 491.4 μg/g, while that of the Guanyinqiao Formation was notably higher at an average value of 842.9 μg/g.

5. Discussion and Implications

5.1. Redox Condition

The geochemical indices of the water's paleo-oxygen phase can be evaluated based on the content and proportion of redox-sensitive elements, such as V, Ni, Mo, U, and Co [38]. These transition elements typically exist in polyvalent states within marine water, and their properties under various redox conditions can be used to determine the oxygen levels of the water. Under oxidation conditions, elements such as V, Mo, and U are in high valence states, while (V(V), Mo(VI), and U(VI)) are prone to dissolution and migration. Conversely, (V(V), Mo(VI), and U(VI)) in low valence states tend to precipitate and accumulate under reduction conditions. For instance, V and Ni are preferentially deposited in sediments as organic complexes under anoxic conditions. Ni and Mo accumulate significantly in

the presence of H_2S. These elements transform into dissolved ions in seawater in oxygen-rich environments; however, some elements, such as Th, remain insoluble regardless of redox conditions. Although some scholars argue that the V/Ni-equivalent value might be biased by diagenesis, typical indicators, such as V/(V + Ni), V/Cr, Ni/Co, and U/Th, consistently exhibit a positive correlation with the increasing hypoxic reduction degree of the bottom water.

In a sulfidic environment, element V preferentially precipitates with element Ni. Therefore, when element V and element Ni are enriched at the same time, it means that they are in a sulfide surplus environment [39]. Based on the study of Pennsylvania shale in the United States, Hatch and Leventhal (1992) found that there is an obvious correlation between the degree of pyritization (DOP) and the ratio of V/(V + Ni). By comparing the value of V/(V + Ni) with other geochemical redox indicators, the thresholds of redox conditions were proposed (Table 2) [40].

Table 2. Geochemical indicators of redox conditions.

Sedimentary Environment Discrimination Indicators	Anoxic Environment		Oxidizing Environment
	Anaerobic	Hypoxic	
V/(V + Ni)	>0.6	0.45–0.6	<0.45
V/Cr	>4.25	2–4.25	<2
Ni/Co	>7	5–7	<5
U/Th	>1.25	0.75–1.25	<0.75
S/C	high, >0.36		low, <0.36

When the seawater is in an oxidizing environment, element Cr exists stably in the form of ions (CrO_4^{2-}), and element V mainly exists in the form of $H_2VO_4^-$. When the seawater gradually changes from an oxidizing environment to an anoxic environment, V is reduced to VO_2^{2+}, which is complexed with organic matter and enriched in the sediment, and Cr is reduced to $Cr(OH)_2^+$, which forms a complex with humic acid/fulvic acid and is enriched in the sediment. When the environment continues to change into a sulfidic environment, V is further reduced to insoluble V_2O_3 and $V(OH)_3$, which further increases the enrichment degree in the sediment, while Cr is not sensitive to the sulfidic environment [41]. Therefore, the V/Cr ratio can be used to classify the sedimentary environment (Table 2).

In oxidizing water, element Ni exists in the form of dissolved ions (Ni^{2+}) or is adsorbed by organic matter in the form of carbonate ($NiCO_3$). In an anoxic environment (in the presence of H_2S), Ni forms an insoluble sulfide (NiS) that is slowly absorbed by authigenic pyrite. Element Co is preferentially activated over Ni in a reducing environment, resulting in the increase in the Ni/Co ratio in sediments. Jones et al. found that the Ni/Co ratio can judge whether a water body is oxygen-rich or anoxic, and proposed the comparative relationship between them for the first time, as well as the threshold of the Ni/Co ratio (Table 2) [42].

Element U combines with fluoride in anoxic water to form insoluble complexes and easily forms organometallic ligand in humic acid. Element U forms dissoluble $[UO_2(CO_3)_3]^{4-}$ with carbonate ions in an oxidizing environment, which results in a decline of U content in the sediment in an oxidizing environment [4]. Element Th is less sensitive to redox conditions and exists in the dissolved form of Th^{4+} in water. Due to the difference in the chemical quality of U and Th, its ratio can be used to indicate a redox condition of seawater. A lower U/Th ratio indicates a more oxygen-rich environment. The thresholds of redox conditions are proposed in Table 2.

The thresholds proposed in Table 2 were obtained by scholars based on their own research projects. The threshold values are highly variable depending on the depositional environments and affected by a lot of local factors. Therefore, these thresholds cannot be used directly to judge the redox environment. At present, there is no reliable research on the redox thresholds in the study area, but the thresholds and trends suggested in Table 2 can provide a provisional reference for judging the sedimentary environment.

The average V/(V + Ni), V/Cr, and Ni/Co values in the black shale segment of the Wufeng Formation are 0.71, 3.76, and 8.10, respectively, indicating a relatively anaerobic environment (Figure 2). However, at the bottom, one sample has noticeably lower ratios than the upper section, with the lowest V/Cr and U/Th values being 1.38 and 0.25, respectively (Figure 2). This result indicates a relatively oxygen-rich environment, indicating unstable redox conditions in the lower section of the Wufeng Formation, with intermittent oxidation environments appearing at the base. The bottom of the Longmaxi Formation black shale has a Ni/Co value greater than 5 and a U/Th value greater than 0.75, and peaking at 7.3 and 2.4, respectively, which indicates a relatively anaerobic environment. The middle–upper part is similar to the bottom, implying hypoxic to anaerobic conditions. However, the top of the formation has Ni/Co and U/Th values of 4.3 and 0.6, respectively, proposing an oxygen-rich environment. This result shows a decrease in anoxic conditions in the middle–upper part of the Longmaxi Formation compared to the anaerobic state at the bottom. The Guanyinqiao mudstone segment exhibits relatively oxygen-rich conditions between the two shale formations. Thus, during the development of the Wufeng–Longmaxi Formation black shale in the study area, the bottom water environment was primarily characterized by long-term hypoxic conditions accompanied by multiple brief periods of oxidation (Figure 2).

Under seafloor anoxic conditions, bacterial sulfate reduction (BSR) can consume organic matter and generate H_2S, which reacts with active iron in seawater to produce pyrite which then enters the sediment. Therefore, based on the principle of the co-burial of organic carbon and pyrite, the correlation between organic carbon and sulfur (C–S) in shale can be effectively used to assess the oxygen level of the bottom water [43]. A S/C ratio of 0.36 is usually used as a reference value for judging the sedimentary environment of normal marine shale in the Phanerozoic [44]. Under anoxic conditions, due to pyrite generation and organic carbon consumption, the S/C value in shale increases, and on the S–C convergence graph, it exhibits a positive y-intercept for S (for instance, in the Black Sea, it could be 1%–2%).

In oxidizing conditions, its trend line passes through the origin [45]. The S/C values of the Wufeng Formation shale vary significantly, with the lowest S/C value at the bottom being only 0.15 (Figure 2). However, the S/C values of samples from the middle–upper section are mostly greater than 0.36 (Figure 4), indicating that occasional oxidation occurred at the bottom of the Wufeng Formation shale, but that the conditions were still primarily anoxic, which is consistent with the results of redox indicators such as V and Ni. Although the S/C value of the Guanyinqiao mudstone is moderately high (with a peak of 0.72), the S and C contents are very low (averaging 0.45% and 0.80%, respectively). Moreover, the y-intercept on the S–C convergence graph tends toward the origin, or even less than 0, indicating oxygen-rich conditions. Due to the oxygen-rich water body, organic carbon cannot be preserved and is low in content, increasing the S/C value of the Guanyinqiao Member.

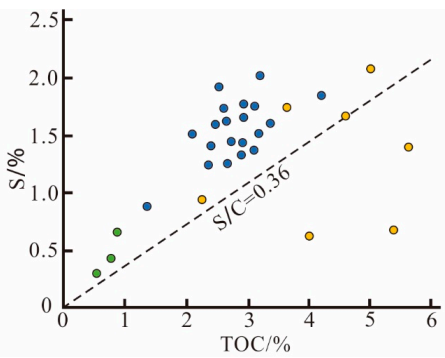

Figure 4. C–S cross-plot of the Wufeng–Longtan Formation in the Weiyuan area.

Although the S/C values of the Longmaxi Formation black shale vary considerably, they are all greater than 0.36 and exhibit a positive y-intercept on the S-axis, indicating

an anoxic environment (Figure 4). Additionally, in the bottom section of the Longmaxi Formation, the S content in the black shale remains stable regardless of the changes in S/C values (Figure 2). This result is because the H_2S produced by BSR consumes a large amount of active iron in seawater under confined, stagnant, anoxic conditions. Since the bottom water is stagnant and limited, the active iron cannot be replenished, the production of pyrite ceases, and the S content entering the sediment remains stable. If the H_2S generated by BSR cannot be consumed, it will form a sulfidic sedimentary environment in the bottom water.

Researchers have used various geochemical indicators to study the redox conditions of seawater in the Yangtze region during the Late Ordovician to Early Silurian. Yan et al. [11] analyzed the C–S–Fe correlations in the Wangjiawan section in Hubei and the Nanbaizi section in Guizhou. They concluded that during the Late Ordovician Katian and Early Silurian Rhuddanian stages, corresponding to the depositional period of the Wufeng and Longmaxi Formations, the bottom waters were sulfidic. However, during the Hirnantian and Guanyinqiao stages, the conditions were oxic. This conclusion aligns with the results revealed by the S/C values in our study. Furthermore, Zhou et al. [13], based on Mo isotope results, proposed that the degree of anoxic reduction was greater due to deeper waters outside the basin. Furthermore, they found that the reducing conditions in the Wufeng Formation shale were stronger than in the Longmaxi Formation shale. However, the anoxic conditions in the Longmaxi Formation persisted for longer, even possibly continuing into the Early–Middle Silurian. Consequently, the thickness of the Longmaxi Formation shale exceeds that of the Wufeng Formation shale.

5.2. Paleo-Productivity

The accumulation of organic material in shale necessitates the provision of sufficient organic carbon sources from the environment, which requires the seawater to maintain a high level of primary productivity and nutrient elements essential for sustained and efficient metabolism and biochemical degradation [46]. P is a crucial nutrient in biological metabolism and a constituent of the skeletal structures of numerous marine organisms. Following death, organisms can become incorporated into sediments and, thus, they indicate paleo-productivity levels. When P is used as an indicator of paleo-productivity, it is also affected by the redox conditions of seawater. The reducing environment will cause the Fe oxides in the sediment to dissolve, so that the P adsorbed on the surface of the Fe oxides is released into the water. Therefore, the content of P in sediments under a reducing environment is not necessarily high, while in oxidizing environments, mineralized organic P can be adsorbed to the surface of Fe oxides and retained in sediments [47]. According to the results on redox conditions in this paper, both the Wufeng Formation and the Longmaxi Formation in the study area were deposited in an anoxic environment, while the Guanyinqiao Member was deposited in an oxidizing environment. Therefore, due to the similar redox conditions, the variation in P content can to a certain extent represent the change in paleo-productivity within the Wufeng Formation and the Longmaxi Formation. However, due to the different redox conditions, the P content of the Guanyinqiao Member should not be compared with that of the Wufeng or Longmaxi Formations.

The P content in the Wufeng–Longmaxi Formation black shale is generally high, indicating high productivity. However, the presence of sandy debris in the upper part of the Longmaxi Formation might lead to errors when identifying paleo-productivity levels based on P content in terrigenous and autologenetic minerals. The P/Al or P/Ti ratios can better represent paleo-ocean primary productivity to eliminate the influence of terrigenous debris than absolute P content can.

The variation in P/Al throughout the well indicates a gradual increase in productivity levels within the Wufeng Formation black shale, as evidenced by an increasing P/Al ($\times 10^{-4}$) value from low to high. The highest level is reached in the middle and upper strata. In the Longmaxi shale, the P/Al ($\times 10^{-4}$) value of the lower member remains stable within 85.5–134.3, indicating a consistently high level of productivity over an extended period. Conversely, the upper member exhibits a reduced P/Al ($\times 10^{-4}$) value, with a minimum of

52.8, indicating a slight weakening trend in primary productivity toward the higher strata in the Longmaxi Formation shale (Figure 2). The P/Al value of the Guanyinqiao Member is significantly higher than that of black shale due to it being deposited in an oxidizing environment, leading to P being adsorbed in Fe oxides and thus enriched.

Si in sediments is mainly preserved in clastic quartz or biological quartz [48]. In most cases, quartz in sediments is mainly from clastic sources, which means Si is often used to determine the input of terrigenous clastic material. However, studies have shown that marine shales are usually abundant in biological siliceous. In the Paleozoic, the main sources of biological silicon were sponge spicule, radiolarian, diatoms, and other plankton, which were the main providers of marine primary productivity. Biological silicon content is often closely related to the surface productivity of the ocean. Therefore, biological silicon can be used as a reliable indicator of changes in productivity. Si_{excess} is generally used to describe biological silicon in shale.

The variation in Si_{excess} throughout the well also indicates a similar trend with the P/Al ratio in the Wufeng Formation and the Longmaxi Formation. The value of Si_{excess} increases gradually from the bottom to the top in the Wufeng Formation. This phenomenon indicates that the paleo-productivity of the Wufeng Formation increased gradually from bottom to top. In contrast, the value of Si_{excess} decreased significantly from the bottom to the top in the Longmaxi Formation, which indicates that the paleo-productivity of the Longmaxi Formation decreased from bottom to top. The Si_{excess} value of the Guanyinqiao Member is relatively low, which is different to the P content. This phenomenon is presumably due to the changes in biological community, which were caused by the variation in the water environment.

Based on the value of P/Al and Si_{excess}, the Wufeng–Longmaxi Formation black shale in the Weiyuan area, southern Sichuan Basin, has a high level of primary productivity, and disparities exist in shale productivity before and after the glacial epoch. Before and after the glacial period, a sample from the top of the Wufeng Formation and one from the bottom of the Longmaxi Formation exhibited decreased P/Al and Si_{excess}, respectively. The TOC of the sample from the Wufeng Formation decreased with reduced productivity, however, the TOC of the sample in the Longmaxi Formation increased, indicating that varying productivity levels significantly influenced the organic enrichment between these two shales. These two declines in productivity could be linked to the two episodic extinctions at the end of the Ordovician; however, the overall productivity levels remain high. Yan et al. [11] posited that the paleo-productivity of the Yangtze region was higher during glacial periods than interglacial periods due to the water from the melting glaciers enhancing the connectivity of the water inside the basin to the outside, bringing abundant nutrients, and increasing biological productivity.

5.3. Degree of Water Restriction in Basin

Enclosed and confined ancient sea basins frequently result in the differential accumulation of trace elements in the sedimentary environment due to the hindered circulation of the bottom water. Algeo et al. [4] proposed using the Mo–TOC model to determine the water's degree of restriction in a basin (Figure 5). As an element sensitive to redox conditions, Mo generally accumulates under anoxic conditions but is also easily affected by organic matter in sediments. Furthermore, a coupled relationship occurs between Mo/TOC values and the concentration of Mo in seawater.

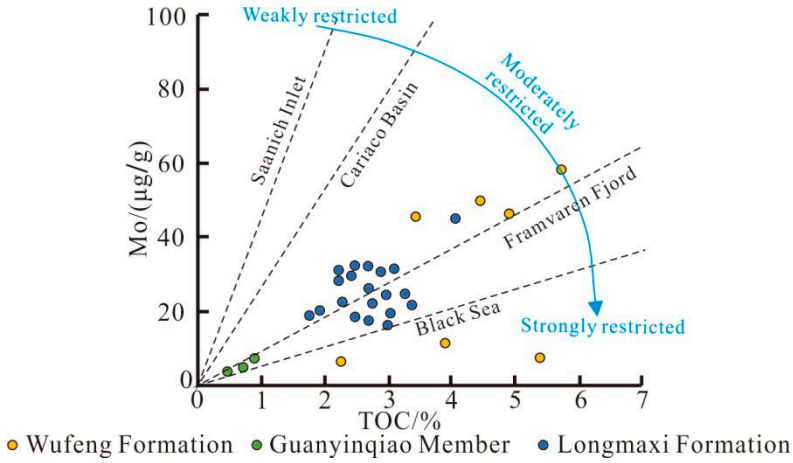

Figure 5. Relationship between Mo and TOC of the Wufeng–Longtan Formation in Weiyuan area.

In an open circulating water body environment, there is ample Mo in the seawater, and correspondingly, the Mo/TOC values in sediments are also high. However, in a restricted and enclosed environment, the replenishment of Mo is slow or even stops, leading to a decrease in the Mo concentration in the bottom water. Particularly under anoxic conditions, the rate of absorption and accumulation of Mo by sediments exceeds the rate of replenishment. The low Mo concentration in the bottom water, due to insufficient supply, results in the sediments' absorption of Mo being in a "starvation state". Consequently, Mo/TOC values are also low.

The Mo/TOC values in the Wufeng Formation shales of the study area vary considerably, with an average of 8.1 and a lowest of only 0.8. Aside from one sample that might have an overly high Mo accumulation due to an anoxic sulfide-reducing environment, two samples fall within the moderately restricted area. The remaining samples belong to a strongly stagnant and confined environment similar to the current Black Sea environment. This result indicates that the uplift of the seabed elevation in the Yangtze area during the Late Ordovician restricted water circulation, leading to a strong stagnation of the water body during the Wufeng period. The fluctuations between strong and moderate degrees of basin restriction could be because of periodic sea-level rises and falls, which lead to different water connections and a different basin restriction.

Although the Guanyinqiao Member has lower Mo/TOC values (average of 6), redox conditions primarily control the Mo accumulation. Hypoxic-to-oxic environments are inconducive to organic matter preservation and Mo enrichment, which explains the lower Mo/TOC values. However, they still fall within the moderately to strongly restricted stagnant environment. The lower section of the Longmaxi Formation shales has higher Mo/TOC values (average of 10.1), indicating a moderate to strong degree of basin restriction, similar to the modern stratified anoxic basin of the Framvaren Fjord in Norway. However, the upper section, influenced by redox conditions, has lower Mo/TOC values but still belongs to a moderately stagnant environment.

This result shows that the two sets of shales developed under markedly different environments. The Wufeng Formation shales were formed in a strongly confined stagnant environment where water circulation was obstructed, whereas the degrees of basin restriction in the Longmaxi Formation shales were reduced. Li et al. [12] also concluded that the degrees of basin restriction were stronger during the Wufeng period when using the U–Mo covariant model to study the intensity of water body stagnation in the Sichuan Basin. However, this study found no apparent correlation between organic matter accumulation and the water stagnation degree, especially in the Wufeng Formation. The TOC content fluctuated significantly under strong stagnation conditions, with the lowest being 2.8 wt.%, whereas that of the samples under moderate stagnation conditions could reach as high as 5.1 wt.%.

5.4. Tectonic Environment Analysis

Previous studies have shown that the tectonic background of the Wufeng–Longmaxi Formation shale in Weiyuan area is a passive continental margin, which is a stable continental margin from late Ordovician to early Silurian, and that the sediments are mainly terrigenous detrites [49]. In addition, many volcanic eruptions occurred in the Yangtze area during the late Ordovician and early Silurian, which resulted in the development of multi-layer tuff deposits in the periphery of the Yangtze platform [50]. These periodic volcanic eruptions also brought abundant nutrients to the Yangtze Sea area and enhanced the productivity of the sea surface. In the late Ordovician, due to the convergence of the Cathaysia plate and the Yangtze plate, the ancient land around the plate was uplifted, and the southeast margin of the Yangtze block began to transform from a passive continental margin to a foreland basin. At the same time, many underwater paleo-uplifting and depressing processes developed locally. At this time, the Weiyuan area became one of the sedimentary centers within the plate. The deep-water sedimentary environment provides an ideal setting for the development of Wufeng–Longmaxi Formation shale; on the other hand, it also drives changes in paleo-productivity, redox conditions, water closure and sea level, creating a sedimentary environment that is conducive to organic matter enrichment.

5.5. Detritus Input

The input of terrestrial detritus can have multiple impacts on the enrichment of organic matter in shale. On the one hand, it can act as a diluent, directly reducing the content of organic matter [51]. On the other hand, it can also carry terrestrial organic matter onto the seafloor, increasing the abundance of organic matter in sediments, and may disrupt the preservation of organic matter in seabed sediments by affecting the burial rate.

Al and Ti are the primary components of the continental crust and can be used to evaluate the level of terrestrial detritus injected into the seafloor. Al mainly enters seafloor sediments as aluminosilicates, such as feldspar and clay minerals, whereas Ti is a major component of various heavy minerals, such as ilmenite. Therefore, Ti and Al values can effectively assess the impact of terrestrial detritus on organic matter enrichment. And there is a good correlation between the content of Al_2O_3 and TiO_2 in the black shale of Wufeng–Longmaxi Formation in well W202 (R^2 = 0.79, p value = 2.57×10^{-30}) (Figure 6d). This indicates that the main terrigenous input source of black shale may be relatively simple in this area, and that content of Al_2O_3 can be used as an effective parameter to characterize the input of terrigenous material.

The content of Al_2O_3 frequently fluctuates, especially in the Wufeng Formation. Due to the influence of sea-level changes or ancient land uplift, the initial injection of terrestrial detritus was large, but with the deepening of the water, the detritus content gradually decreased. The content of Al_2O_3 in a sample increased significantly before entering the Ice Age, which could be related to a rapid drop in sea level or intensified land weathering. The terrestrial detritus remained stable after entering the Guanyinqiao Member, continuing until the early Longmaxi Formation without an increase in detritus. Two prominent decreases occurred mid-term, until the top content of Al_2O_3 increased, and the TOC content decreased.

The low content of Al_2O_3 indicates that despite frequent paleo-land uplift and sea-level changes in the study area, the impact of terrestrial detritus on seafloor sediments could be small, concentrated in the early Wufeng and late Longmaxi periods. The diagram of the content of Al_2O_3 and TOC intersection shows no significant correlation (R^2 = 0.05) (Figure 6e) between detritus and organic matter enrichment, indicating that in the Late Ordovician–Early Silurian, the study area was likely in a distal shelf region with a greater distance from the shore and weaker terrestrial input. However, in the Upper Longmaxi Formation, the content of Al_2O_3 shows an increasing trend related to the increased content of siltstone at the top. This result indicates that the increase in terrestrial detritus in the upper part of the Longmaxi Formation could decrease organic matter concentrations due to the dilution effect.

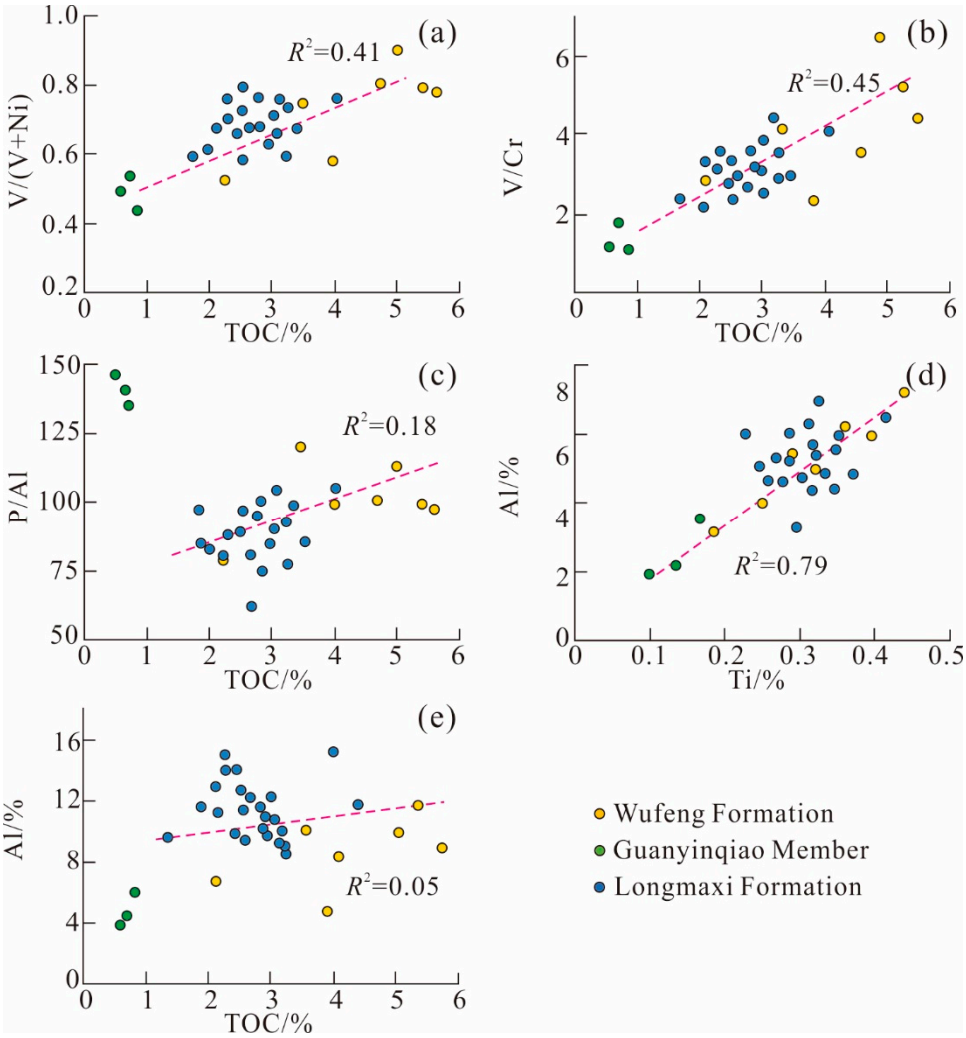

Figure 6. Relationship between TOC and redox condition, productivity, and clastics. (**a**) V/(V+Ni) versus TOC; (**b**) V/Cr versus TOC; (**c**) P/Al versus TOC; (**d**) Al versus Ti; (**e**) Al versus TOC.

5.6. Organic Enrichment Characteristics and Controlling Factors

The productivity and preservation condition models emphasize their dominant roles in organic matter enrichment. However, organic matter enrichment is a complex physicochemical process where any variable, such as paleo-productivity, redox conditions, or detrital input, could have an impact. Figure 6 shows that the organic matter content in the Wufeng–Longmaxi Formation black shale in the study area positively correlates with paleo-productivity levels and anoxic environments. However, the correlation between TOC and redox indicators, such as V/(V + Ni) (R^2 = 0.41, *p* value = 3.90×10^{-16})and V/Cr (R^2 = 0.45, *p* value = 4.72×10^{-11}), is significantly higher than paleo-productivity level indicators like P/Al (R^2 = 0.18, *p* value = 7.04×10^{-10}). This result indicates that redox conditions are critical in organic matter enrichment.

The Guanyinqiao Member also shows that despite having a high level of paleo-productivity, the TOC content is lower, even showing a negative correlation. The weak correlation between content of Al_2O_3 and TOC eliminates the influence of terrestrial detritus during low sea-level periods (Figure 6e). Organic matter cannot be preserved because of the oxidizing water environment. Furthermore, the TOC content fluctuates in the intermittent oxygen-rich samples at the bottom of the Wufeng shale, indicating that the anoxic preservation conditions are crucial in organic matter enrichment in the Wufeng–Longmaxi black shale in the study area.

Despite the high productivity levels and anoxic conditions of the Wufeng and Longmaxi Formations, their formation mechanisms differ. In recent years, researchers have noticed the differences in their environmental origins. During the Late Ordovician, the tectonic squeezing from the Cathaysia Plate affected the Yangtze Plate [7], causing uplifts of the peripheral ancient lands and submarine ridges. The sedimentary environment transitioned from an open platform in the early stage to a restricted basin.

In the early Wufeng period, the water body of the basin gradually deepened due to tectonic uplift. The Mo–TOC plot indicates that the intensely restricted environment led to gradual anoxia and reduction in bottom water. The fluctuations in the ancient sea level resulted in different degrees of water connection and different basin restrictions, leading to intermittent oxidative features in the lower part of the Wufeng Formation. This result can be confirmed through redox indicators like V/Cr and Ni/Co.

Additionally, multiple thin tuff layers in the black shale indicate active tectonic movements triggering volcanic eruptions, supplying abundant nutrients to the seawater surface. Indicators such as P and the prosperity of planktonic organisms like graptolites confirm high productivity levels in seawater. Under the conditions of anoxic conditions, reduced bottom water, and high productivity surface water, the environment was conducive to organic matter enrichment.

The above indicates that tectonic activity is a major factor influencing changes in water depth, paleo-productivity, and redox conditions during the early sedimentation period of the Wufeng–Longmaxi shale formations. Following the onset of the Ice Age, the formation of polar glaciers led to a global sea-level decline and a large-scale marine regression in the Yangtze region. The environment of deep-water stagnation transitioned to shallow continental shelf sedimentation with more frequent sedimentary environment changes. Even though benthic organisms like brachiopods and gastropods thrived, the organic matter could not be preserved due to the disruption of anoxic conditions. This result is consistent with the correlation results of indicators like TOC, V/Cr, and Ni/Co in the Guanyinqiao Member.

Following the onset of the Longmaxi epoch, as the climate warmed and the glaciers melted, the Yangtze area was again extensively transgressed. The rapid deepening of the water resulted in stratified anoxia in the bottom water. The water from the melting glaciers enhances the connectivity of water inside the basin to the outside and brings abundant nutrients. Additionally, the influx of nutrients like SiO_2 and P from terrestrial debris increased the nutrient content of the water, causing a bloom of surface plankton, and productivity peaked. The resurgence of planktonic organisms like graptolites and the continuous settling of organic matter depleted the dissolved oxygen in the bottom water, creating an anoxic environment. The sulfate reduction in seawater produced H_2S, eventually creating an anoxic sulfur environment, leading to abundant organic matter enrichment in the lower part of the Longmaxi shale formation. This event continued until the late Longmaxi period, when the increasing terrestrial debris disrupted the preservation of organic matter, decreasing the organic carbon content in the upper section of the shale. In conclusion, organic matter enrichment in the Wufeng–Longmaxi black shale is a complex result of the Ordovician–Silurian sedimentary environmental evolution. Tectonic conditions, paleo-productivity, redox conditions, sea-level changes, and sedimentation rates jointly control the organic matter enrichment in the Wufeng–Longmaxi Formation black shale.

5.7. Organic-Rich Black Shale Development Model

An analysis of the correlation between TOC, ancient redox conditions, paleo-productivity, and terrigenous detritus input in the Wufeng–Longmaxi black shales reveals that redox conditions primarily control the formation of organic-rich shales in the Weiyuan area. The paleo-productivity level affects the organic matter enrichment, and the influence of terrestrial debris input is minor. Therefore, the preservation conditions of organic matter primarily influence the organic-rich shale development in the Weiyuan area, which follows

a preservation mode. The following models were established based on the characteristics of different sedimentary stages of the Wufeng–Longmaxi Formations in the Weiyuan area (Figure 7).

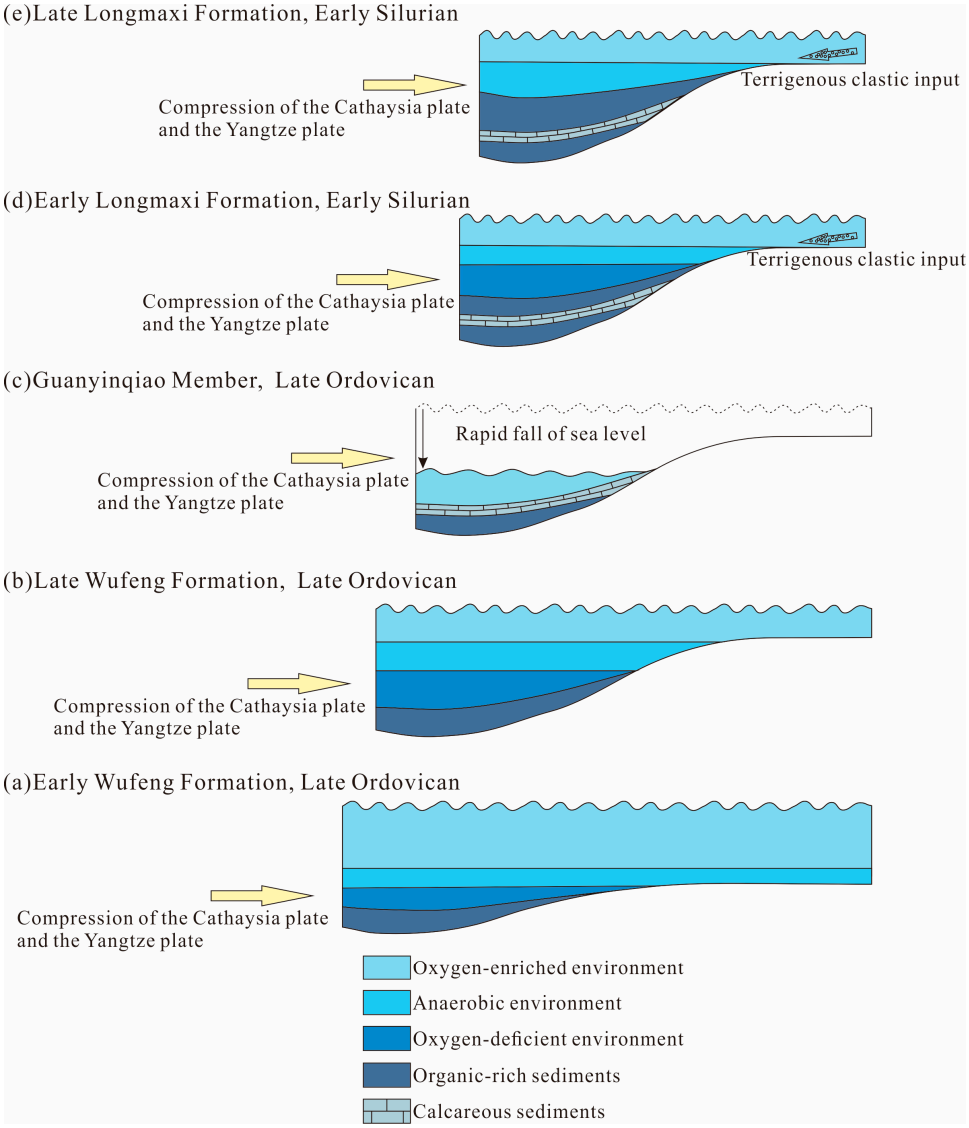

Figure 7. Organic matter enrichment model. (**a**) Early Wufeng Formation: oxygen-rich basin, low productivity; (**b**) Late Wufeng Formation: basin with medium productivity and strong retention; (**c**) Guanyinqiao Member: high productivity, oxygen-rich water basin; (**d**) Early Longmaxi Formation: high productivity, strong reducing water basin; (**e**) Late Longmaxi Formation: low productivity, oxidized water basin.

1. During the early sedimentation of the Wufeng Formation, the Cathaysia and Yangtze plates had not fully amalgamated. A vast ocean exited at the southeastern edge of the Yangtze Plate, connecting the Yangtze continental shelf and the open ocean. Therefore, the reducing conditions were weak, and the abundance of organic matter was low.
2. As the plate amalgamation movement intensified in the later stages of the Wufeng Formation sedimentation, the water body had poorer connectivity with the open ocean. The sediments were predominantly muddy and devoid of biological disturbances, forming an anoxic sedimentary environment. Furthermore, several volcanic activities provided abundant nutrients for plankton, elevating the paleo-productivity level.

Consequently, the mudstone of the later Wufeng Formation sedimentation had a higher organic matter abundance.

3. During the Guanyinqiao period, global sea levels fell, leading to the proliferation of cold-water animal groups like bivalves and brachiopods, which resulted in an oxidizing water environment. Although the paleo-productivity level was high during this period, the oxidizing environment was inconducive to organic matter preservation.
4. After the end of the Hirnantian glaciation, sea levels rapidly rose again. The tectonic pattern of the Yangtze Plate was still similar to that of the late Wufeng Formation, an enclosed and restricted sea basin. The high sea level and the restricted tectonic background of the sea basin provided abundant organic matter sources, creating large-scale anoxic environments on the seafloor, which provided favorable conditions for effective organic matter preservation. Intense tectonic activities increased the terrigenous detritus input, bringing terrestrial organic matter into the seabed and increasing the organic matter abundance in the sediments. In the early stage of the Longmaxi Formation sedimentation, high paleo-productivity and strong reducing conditions promoted organic matter enrichment.
5. In the later stages of Longmaxi Formation sedimentation, as terrigenous detritus input continued to increase, the sedimentary water continuously shallowed. The depositional environment of the study area gradually transitioned from deep-water shelf deposition to shallow-water shelf deposition, forming more siltstone and claystone shales. The hypoxic/anoxic environment of the sediments was disrupted. The low level of paleo-productivity also affected organic matter accumulation, resulting in a low abundance of organic matter.

6. Conclusions

1. The value of P/Al indicators reveal that the black shales of the Wufeng–Longmaxi formations were deposited under high paleo-productivity levels. High organic carbon fluxes provided the material basis for organic matter development and enrichment in the shales.
2. The values of V/(V + Ni), V/Cr, and Ni/Co indicated that the shales of the Wufeng–Longmaxi Formations were primarily formed in an anoxic sedimentary environment. The anoxic conditions correlate well with the organic carbon content, making it crucial for controlling organic matter enrichment.
3. The content of Al and Ti indicated that terrigenous detritus has some impact on organic matter enrichment. Detritus noticeably increased in the late Longmaxi period, reducing organic matter concentration.
4. Tectonic activity and glaciers melting due to global warming are crucial for black shale development. Tectonic activity played a dominant role in controlling the initial paleo-productivity and redox conditions of shale formations. The Longmaxi Formation was also influenced by widespread marine transgression after the glaciation, which lasted longer and had a greater sediment thickness.

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