

Article

Multi-Proxies Analysis of Organic Matter Accumulation of the Late Ordovician–Early Silurian Black Shale in the Lower Yangtze Region, South China

Chengcheng Zhang ^{1,2}, Chaogang Fang ^{1,3,4,*}, Qing Zhao ^{5,*}, Guixi Meng ⁶, Daorong Zhou ¹, Jianqing Li ¹ and Wei Shao ¹

¹ Nanjing Center, China Geological Survey, Nanjing 210016, China

² Exploration Research Institute, Anhui Provincial Bureau of Coal Geology, Hefei 230088, China

³ Institute of International Rivers and Eco-Security, Yunnan University, Kunming 650500, China

⁴ Hubei Key Laboratory of Paleontology and Geological Environment Evolution, Wuhan 430205, China

⁵ School of Earth and Space Sciences, Peking University, Beijing 100871, China

⁶ China United Coalbed Methane Corporation Ltd., Beijing 100015, China

* Correspondence: fangchaogang206@163.com (C.F.); qzhao@stu.pku.edu.cn (Q.Z.)

Abstract: The evolutionary process of palaeoceanic environment and its effect on the accumulation of organic matter during the Ordovician–Silurian transition in Lower Yangtze region has been overlooked compared to that in Upper Yangtze region of South China, although their paleogeographic settings were expected to be discrepant. This paper documents the marine depositional environment, paleoclimate, and sediment supply changes, and discusses their roles in controlling the organic matter enrichment in sedimentary rocks within the Ordovician–Silurian transition of the Lower Yangtze region, using the latest geochemical data of the continuous drilling core. The stratigraphic framework of the Ordovician–Silurian transition in the Lower Yangtze region is composed of two third-order sequences, each of which can be subdivided into a lower TST (transgressive systems tract) and an upper RST (regressive systems tract). TST1 represented an evident depositional transition stage which was marked by the ending of the underlying carbonate sediments and the initiation of the terrigenous clastic-dominated sediments. Geochemical proxies indicate that the relatively low productivity, dysoxic water column condition, and high sediment supply flux collectively resulted in inadequate organic matter hosted in deposits of the TST1. During the depositional period of RST1, the global sea level declined due to the Hirnantian glaciation age. The icehouse also caused the decrease in overall river flux and, thus, the terrigenous clastic sediment supply. The icehouse also strengthened the upwelling that occurred in the Lower Yangtze sea. The upwelling boosted the marine algae explosion through the delivery of abundant nutrients, which not only enhanced paleoproductivity but also led to an anoxic environment by oxygen consumption. Such high paleoproductivity, anoxic water column environment, and low sediment supply flux caused the deposition of organic-rich shale. The sea level rose during the TST2 due to the ending of an ice age. The relatively large water depth and high paleoproductivity associated with volcanic eruptions are the main factors that caused the enrichment of organic matter during this stage. During the deposition of RTS2, the increase of sediment supply flux resulted in a decrease in accommodation space and water depth and the dilution of organic matter in deposits, which was the primary constraint of organic matter accumulation.

Keywords: Ordovician–Silurian transition; sequence; organic matter accumulation; upwelling; lower Yangtze region



Citation: Zhang, C.; Fang, C.; Zhao, Q.; Meng, G.; Zhou, D.; Li, J.; Shao, W. Multi-Proxies Analysis of Organic Matter Accumulation of the Late Ordovician–Early Silurian Black Shale in the Lower Yangtze Region, South China. *Minerals* **2023**, *13*, 400. <https://doi.org/10.3390/min13030400>

Academic Editors: Egberto Pereira and Lucas Pinto Heckert Bastos

Received: 5 February 2023

Revised: 10 March 2023

Accepted: 12 March 2023

Published: 14 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The Late Ordovician to Early Silurian (O/S) transition was a crucial interval in Earth's history marked by dramatic climatic, oceanic, and biological turnovers [1–4]. Many important geological events occurred during this stage, such as the Hirnantian glaciation [5], the

first mass extinction [6,7], high-amplitude sea level fluctuations [8], volcanic activities [9], varied oceanic redox [10], and widespread deposition of organic-rich black shales [11,12]. Consequently, sedimentary records of the O/S transition are of significant academic and economic interest.

The Yangtze region of South China is a global hot spot to explore the O/S black shale and associated geological events that operated during deposition [10,13,14]. Many studies have documented the O/S organic-rich shale and its enrichment mechanism of organic matter in the upper Yangtze region and several important models have been developed (e.g., productivity model and preservation model) [3,15,16]. These models provide valuable insights into the genesis and depositional process of organic-rich shale. However, less attention has been paid to the black shale deposited in the lower Yangtze region where the paleogeographic setting is expected to be different compared to the upper Yangtze region. In contrast to the hemi-closed marine environment in the upper Yangtze region which was surrounded by many old lands and submerged highs [17–20], the lower Yangtze Sea tended to be opened and was fully connected with the broad ocean [18]. Therefore, it is unclear whether the model of organic-rich shale in the upper Yangtze region is appropriate for the black shale in the lower Yangtze region.

In recent years, the black shale that occurred in the lower Yangtze region has become an important target of shale gas exploration, after the successive breakthroughs of a number of giant shale gas fields in the Upper Yangtze region [16]. Growing geological data from O/S shale gas exploration efforts in the Lower Yangtze region, especially the continuous drill cores, provides a good opportunity for a detailed analysis of organic matter accumulation in the black shale. In the present study, the subsurface core data obtained from the latest shale gas geological survey well (SY1) in the Lower Yangtze region was selected to: (1) reveal the characteristics of total organic carbon (TOC), major and trace elements of the shale, (2) utilize multiple geochemical proxies to discuss the depositional environment, and (3) develop evolutionary models to explain the depositional process and mechanism of organic matter accumulation in the shale.

2. Geological Setting

The Lower Yangtze region is one of the potentially important shale gas provinces in Eastern China. Located in the northeastern part of the Yangtze Block, the Lower Yangtze region shows a trumpet-shaped zone and covers an area of around 230,000 km² [21] (Figure 1). Since the Neo-proterozoic era, this region has experienced an early marine basin evolution stage and a later terrestrial basin evolution stage after its collision with North China plate in the late Triassic (Indosinian movement) [22,23]. The tectonic history of the Lower Yangtze marine basin can be further divided into an early passive continental margin basin phase from the Neo-proterozoic era to middle Ordovician, a middle foreland basin phase from the late Ordovician to early Silurian, and a late craton basin phase from the late Devonian to middle Triassic [23,24]. During the late Ordovician, in response to the intracontinental orogeny of South China caused by the collision of Yangtze and Cathaysian sub-blocks, the lower Yangtze region evolved into a foreland basin and showed an overall different paleogeographic framework with the Upper Yangtze region [24].

During the stage of O/S transition, basin fills of this region mainly consisted of black shale deposits, besides the deposition of terrigenous coarse clastic rock in the proximal margin (Figure 1b). The O/S shale stratigraphic succession is composed of the Wufeng Formation (O_3w) and the first member of Gaojiabian Formation (S_{1g1}) in ascending order (Figure 1c). The O_3w is relatively thin, with a thickness of approximately 5–15 m. It consists mostly of carbonaceous and siliceous shale with abundant graptolites, which contrasts with the underlying nodular limestone of Tangtou Formation (O_3t) developed in the previously passive continental margin basin phase. Deposits of the overlying S_{1g1} are mainly composed of the lower carbonaceous shale and the upper mudstone intercalated with siltstone, with thickness ranging from 20 to 40 m. Many thin volcanic ash layers were

observed, particularly in the lower parts of both O_3w and S_{1g1} , indicating strong volcanic activities during deposition.

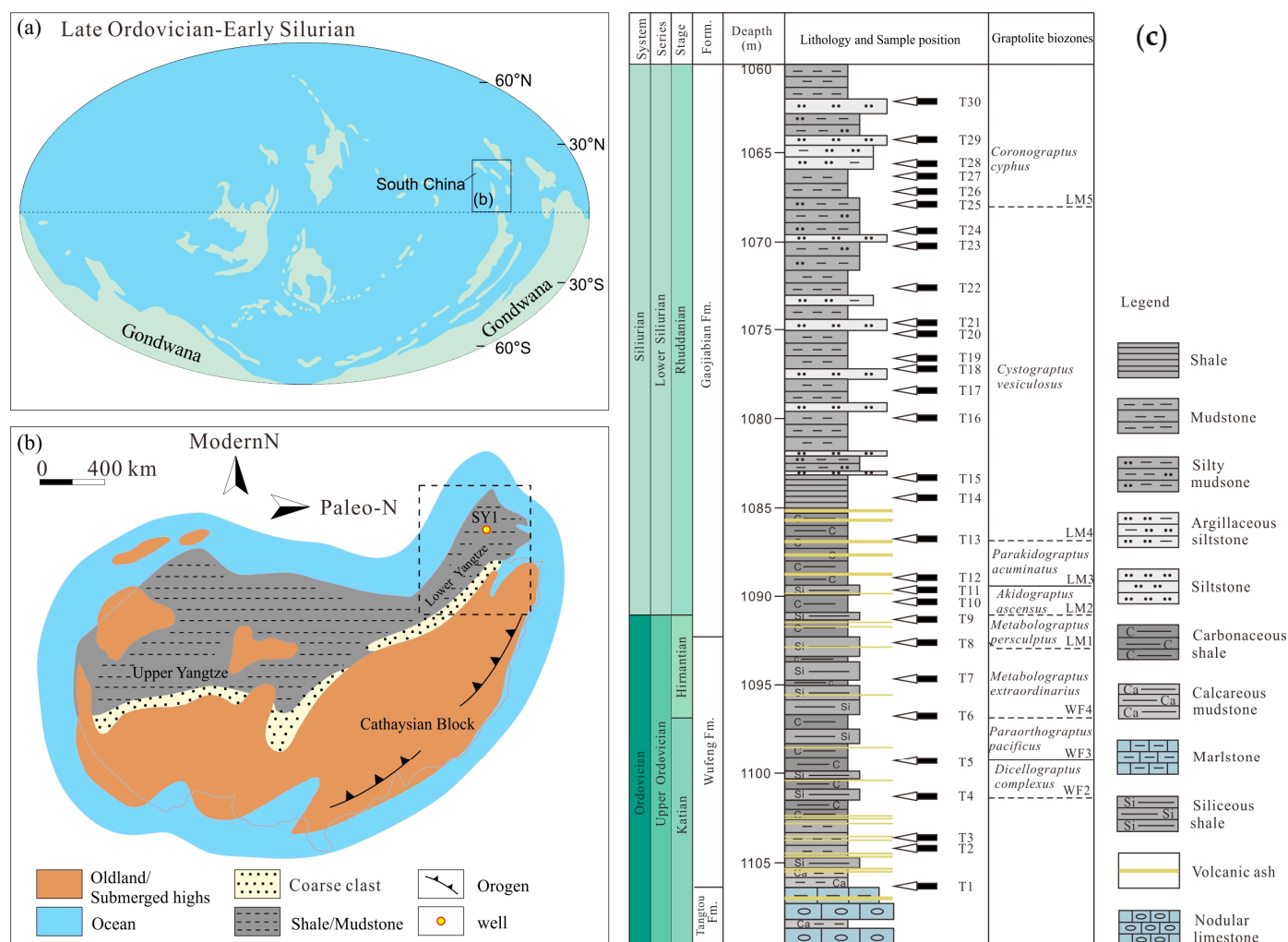


Figure 1. (a) Global paleogeography of the O/S transition (modified from [25]); (b) Paleogeography of the Yangtze region in Katian stage (modified from [18]). The dotted box shows the location of Lower Yangtze region; (c) Lithology and graptolite biozones of the O/S transition in the Well SY1 core from the Lower Yangtze region (modified from [26,27]). See yellow circle in Figure 1b for the location of Well SY1.

A drillcore section from facies deposited within the Lower Yangtze region (Well SY1) was selected for detailed geochemical research in this study (Figure 1c). The Well SY1 section in the Jiangsu Province was located in an outer shelf depositional environment. Complete drill cores of the subsurface black shale of the study interval were obtained and graptolite biozones of this section were built, which provides a high-resolution framework for correlation of relevant strata.

3. Samples and Methods

3.1. Analytical Methods

A total of 30 core samples of black shale from Well SY1 were selected for geochemical analysis, including major and trace elements and TOC content. All samples were fresh without weathered and oxidized materials and were analyzed in the East China Mineral Resources Testing Center of the Ministry of Natural Resources of China.

Prior to the analyses, samples were crushed and ground to 200 mesh for major and trace element analyses in a clean environment. The major element analysis was carried out via an X-ray fluorescence spectrometer (Axios mAX) and the analytical precision of our data was estimated to be less than 5%. Test methods used followed the Chinese National Standards GB/T 14506.14-2010 and GB/T 14506.28-2010. Trace element analysis was performed using an iCAP Q inductively coupled plasma mass spectrometer (ICP-MS) with the relative errors of the data < 5%. For the ICP-MS analysis, the powdered sample was treated with combination of acid digestion and oven heating. The test method and procedure referred to the Chinese National Standard GT/T 14506.30-2010.

The TOC content of all samples was measured using the LECO CS230 infrared carbon-sulfur analyzer. Samples were crushed and ground to powders smaller than 0.2 mm. Rock powders were treated with 2 N HCL to remove inorganic carbon at a temperature of 60 to 80 °C for 12 h for the final analysis. Precision of the TOC analysis reached 0.5%.

3.2. Data Presentation

Because the measured TOC of thermally mature samples are less than the original ones at the time of deposition, it may cause misunderstanding by using present-day TOC instead of original TOC to analyze and interpret the paleoenvironment [28]. Due to the lack of original Hydrogen Index (HI), which must be known to calculate original TOC, we assumed that the original TOC was double that of what was measured in this study, considering the high maturity of O/S transition source rocks in this region. Such a crude estimation is reasonable for marine oil-prone organic matter that is overmature. Accordingly, the TOC values presented in this study are original TOC values, which were restored twice as much as the measured TOC values.

The excess element (denoting authigenic component) was achieved by deducting the terrigenous contribution from the bulk concentrations. The calculation formula is as follows:

$$X_{xs} = X_{\text{sample}} - [Al_{\text{sample}} \times (X/Al)_{\text{PAAS}}] \quad (1)$$

where X_{ex} represents the content of excess element X, X_{sample} and Al_{sample} represent the concentration of X and Al in samples, respectively, and $(X/Al)_{\text{PAAS}}$ represents the ratio of element X to Al in Post-Archean Australian shale (PAAS) [29]. Due to the possibility of the loss of authigenic component after deposition, there are negative X_{xs} values in some of samples. We uniformly set these negative values to 0.01 ppm in this study to facilitate plotting [30].

The enrichment factor (EF) of elements is commonly used to estimate the degree of element enrichment in sediments, which provides important clues for paleoceanic environment [31]. The EF was calculated using the following formula:

$$X_{\text{EF}} = (X/Al)_{\text{sample}} / (X/Al)_{\text{PAAS}} \quad (2)$$

where X_{EF} represents the content of element X, which is normalized using the PAAS [29]. Generally, values of $X_{\text{EF}} > 1$ or < 1 suggest element X enrichment or depletion, respectively.

4. Results

4.1. Sequence Stratigraphy

Identification of the sequence borders and lithological cycles is the basis for construction of sequence stratigraphic framework [32]. The identification relies on the following two criteria: (1) large pattern and amplitude contrasts in wireline logs; (2) large lithological variations in continuous drill cores. Three sequence boundaries (SBs) were identified in the succession of O_3w and S_{1g1} in the study area (Figure 2). SB1 is the boundary between the strata of O_3t and O_3w (Figures 2 and 3a). During a regional transgression at the end of deposition of O_3t , a suite of black shale was deposited in O_3w , which shows a huge lithological difference with the underlying thick-bedded limestone of O_3t (Figure 3b,c). SB2 is the boundary between the late Ordovician O_3w and the early Silurian S_{1g1} (Figure 3d).

It is a regional scale stratigraphic boundary which shows obvious variations with the underlying argillaceous limestone and the overlying black shale in the Upper Yangtze [2,18] and the underlying siliceous rock and the overlying carbonaceous shale in the study area (Figure 3e,f). SB3 is the boundary located at the top of the early Silurian S_{1g1} (Figure 3g). The lithofacies show notable variation with the underlying gray siltstone and the overlying dark mudstone and a striking difference in well logs (Figure 3h,i).

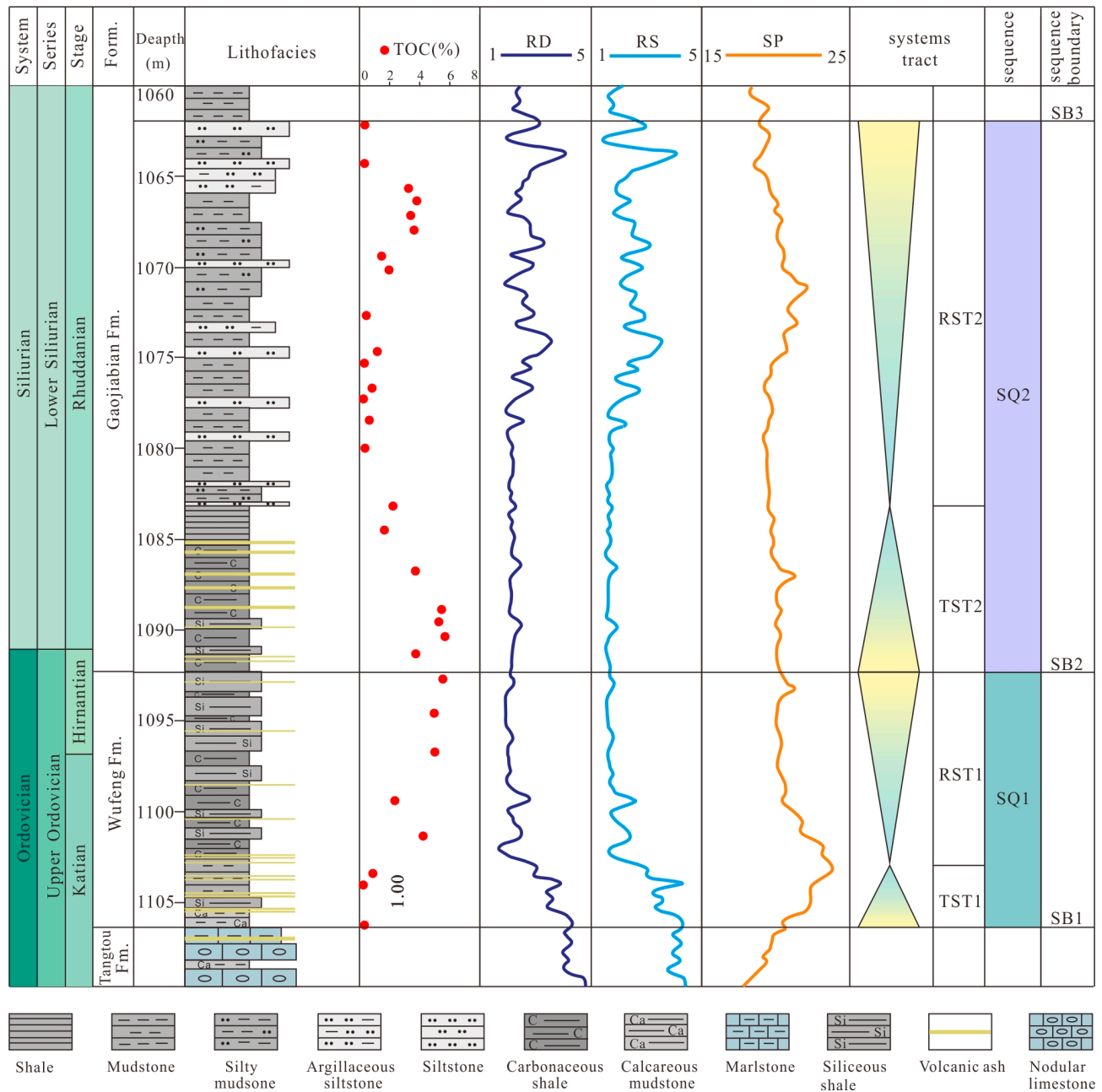


Figure 2. Sequence stratigraphic framework of the Lower Yangtze region during O/S transition based on lithology and well logs from Well SY1.

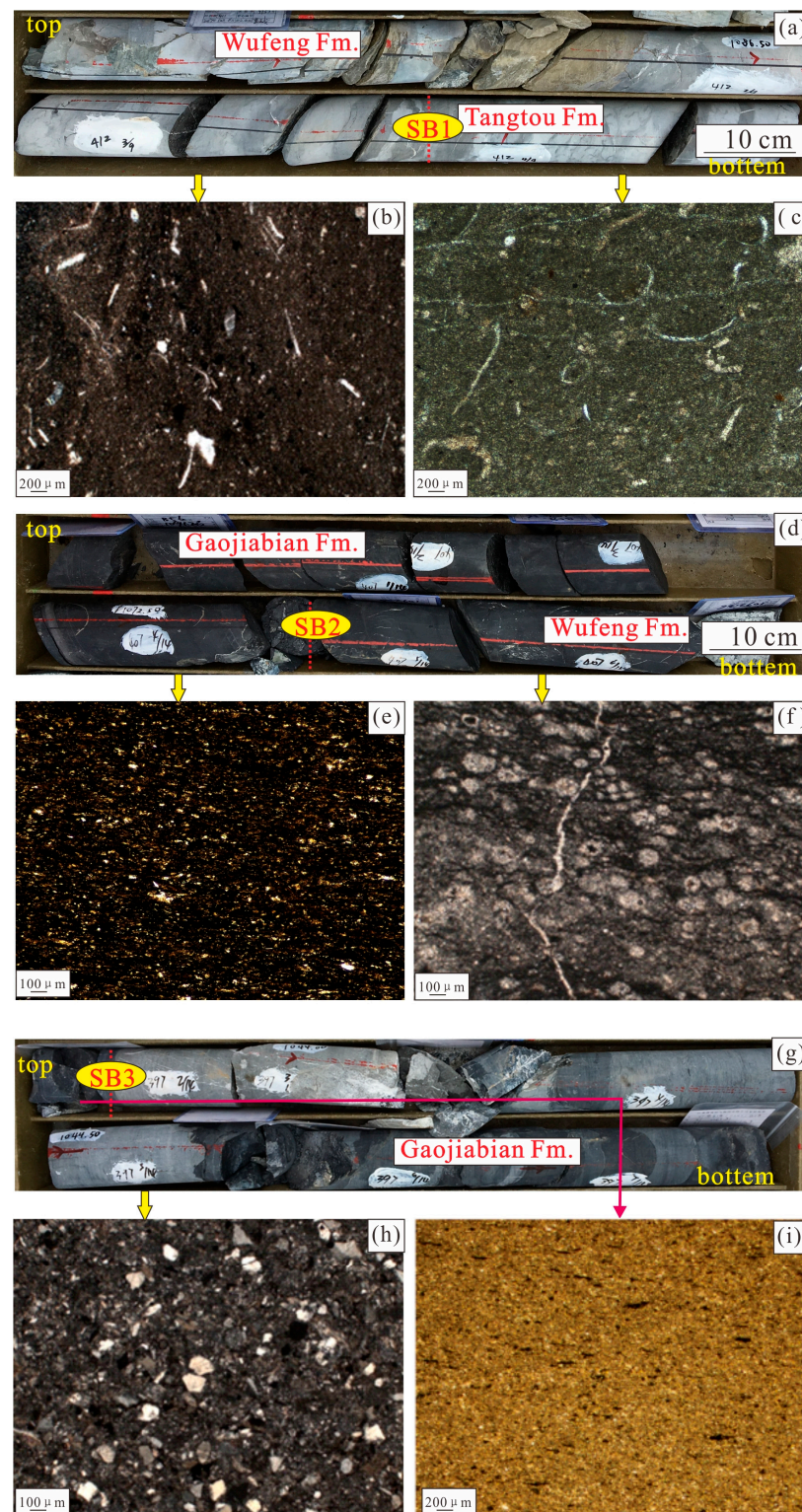


Figure 3. Sequence boundary and sedimentary characteristics showing lithological variations in the study area. (a) SB1 between the underlying Taotou Formation (O_3t) and the overlying Wufeng Formation (O_3w); (b) Calcareous mudstone in the lower part of O_3w . (c) Thin section micrograph of nodular limestone in O_3t . (d) SB2 between the underlying Wufeng Formation and the overlying Gaojiabian Formation (S_{1g1}). (e) Carbonaceous shale in the lower part of S_{1g1} . (f) Siliceous shale that contains abundant radiolarians of different sizes of O_3w . (g) SB3 is the boundary between the lower and the middle of S_{1g1} . (h) Thin section micrograph of the gray siltstone. (i) Thin section micrograph of the dark gray mudstone.

Based on the three sequence boundaries, we interpreted the succession of O_3w and S_{1g1} as two third-order sequences. Each sequence was deposited over 1–2 Myr with a lower transgressive systems tract (TST) and an upper regressive systems tract (RST). In general, SQ1 is composed of calcareous shale (TST1) and siliceous shale (RST1) of O_3w . SQ2 consists of black carbonaceous shale (TST2) and dark gray mudstone intercalated with siltstone (RST2) of S_{1g1} .

4.2. TOC

TOC is a common index to assess the abundance of organic matter in source rocks and can be used to reflect the preservation degree of organic matter. The TOC in well SY1 ranges from 0.14% to 5.70%, with an average of 2.42%. There are great differences in the TOC in different stages (Figure 4). The average TOC of TST 1 to RST2 is 1.12%, 4.38%, 3.94%, and 1.46%, respectively. The high-TOC segments mainly focus on RST1 and TST2, in which black shale is the main lithology. The relatively lower TOC segments are primarily developed in the TST1 and RST2, which is mainly composed of gray shale or gray mudstone and siltstone.

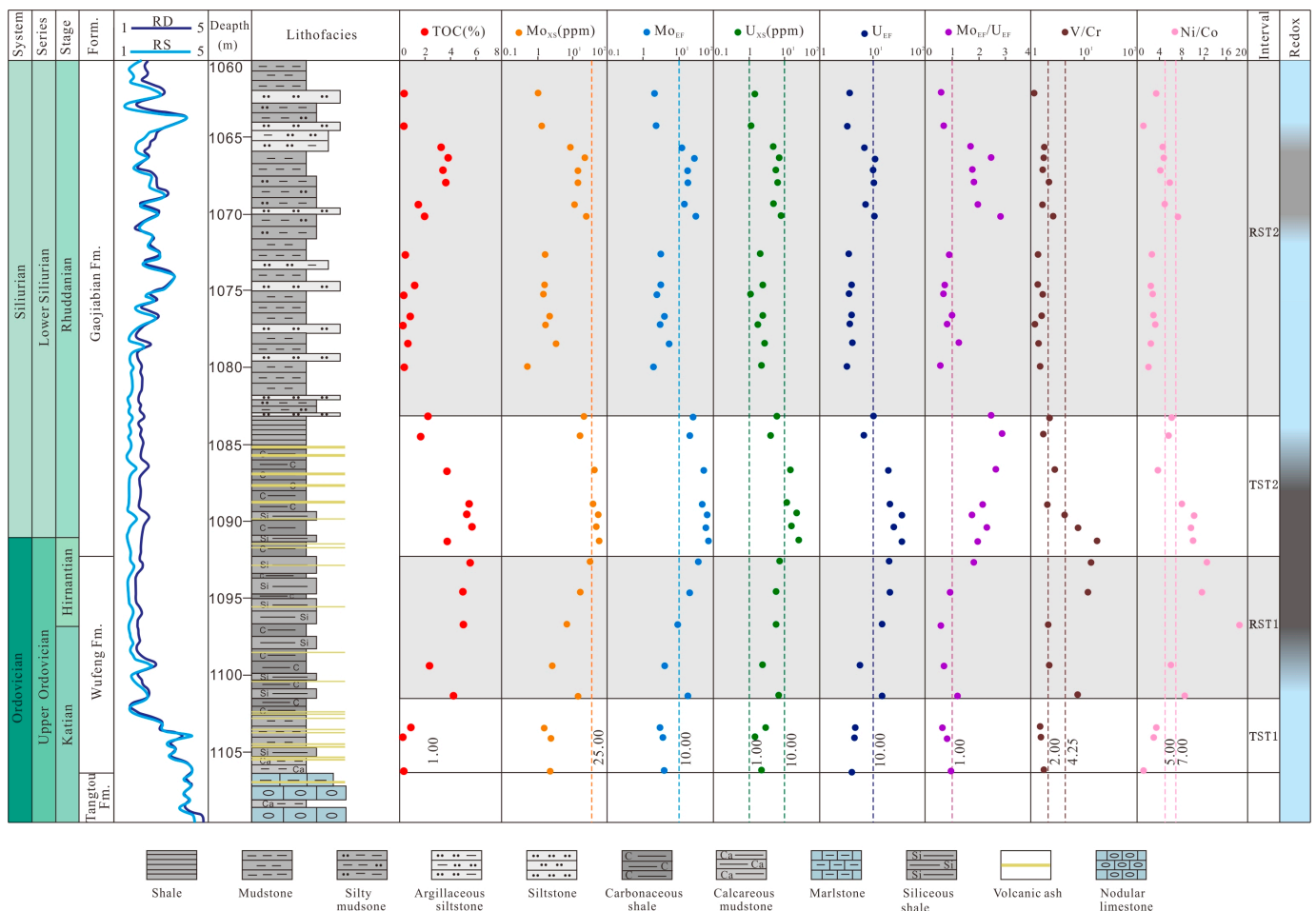


Figure 4. Vertical variations of TOC and redox proxies in Well SY1. Vertical dashed lines in each column mark key threshold values of redox-sensitive trace element proxies.

4.3. Major Elements and Trace Element Contents

Mo_{XS} concentrations ranged from 0.5 to 55.4 ppm (average 15.0 ppm) (Figure 4). The value of Mo_{EF} fluctuated between 1.9 and 68.7 (average 19.2). In addition, U_{XS} varied from 1.1 to 25.5 ppm (average 6.2 ppm), U_{EF} from 3.3 to 35.8 (average 11.1), V/Cr from 0.82 to 17.40 (average 3.38), and Ni/Co from 1.13 to 18.28 (average 5.78). These indicators present a similar variation pattern with TOC, which shows relatively high values in RST1 and TST2 (Figure 4).

The nutrient elements Zn_{XS}, Cu_{XS}, and Ni_{XS} ranged from 0.0 to 94.0 ppm, 0.0 to 354.8 ppm, and 0.0 to 129.5 ppm, respectively (Figure 5), which showed a roughly similar trend with TOC with relative high values in RST1 and TST2. The variation of Si_{XS} ranges from 0.01 to 29.84 wt%, with its content highest in RST1. The inactive trace element Zr varies from 71.4 to 344.0 ppm (average 172.7 ppm), and Zr/Al₂O₃ ranges from 9.15 to 22.20 ppm/wt% with an average value of 13.04 ppm/wt%. Besides, the content of Al₂O₃ ranged from 5.84 to 19.85 wt%, and generally showed high value in TST2. Co × Mn values ranged from 0.15 to 4.62 ppm·wt% (average 1.04 ppm·wt%), and exhibited low RST1.

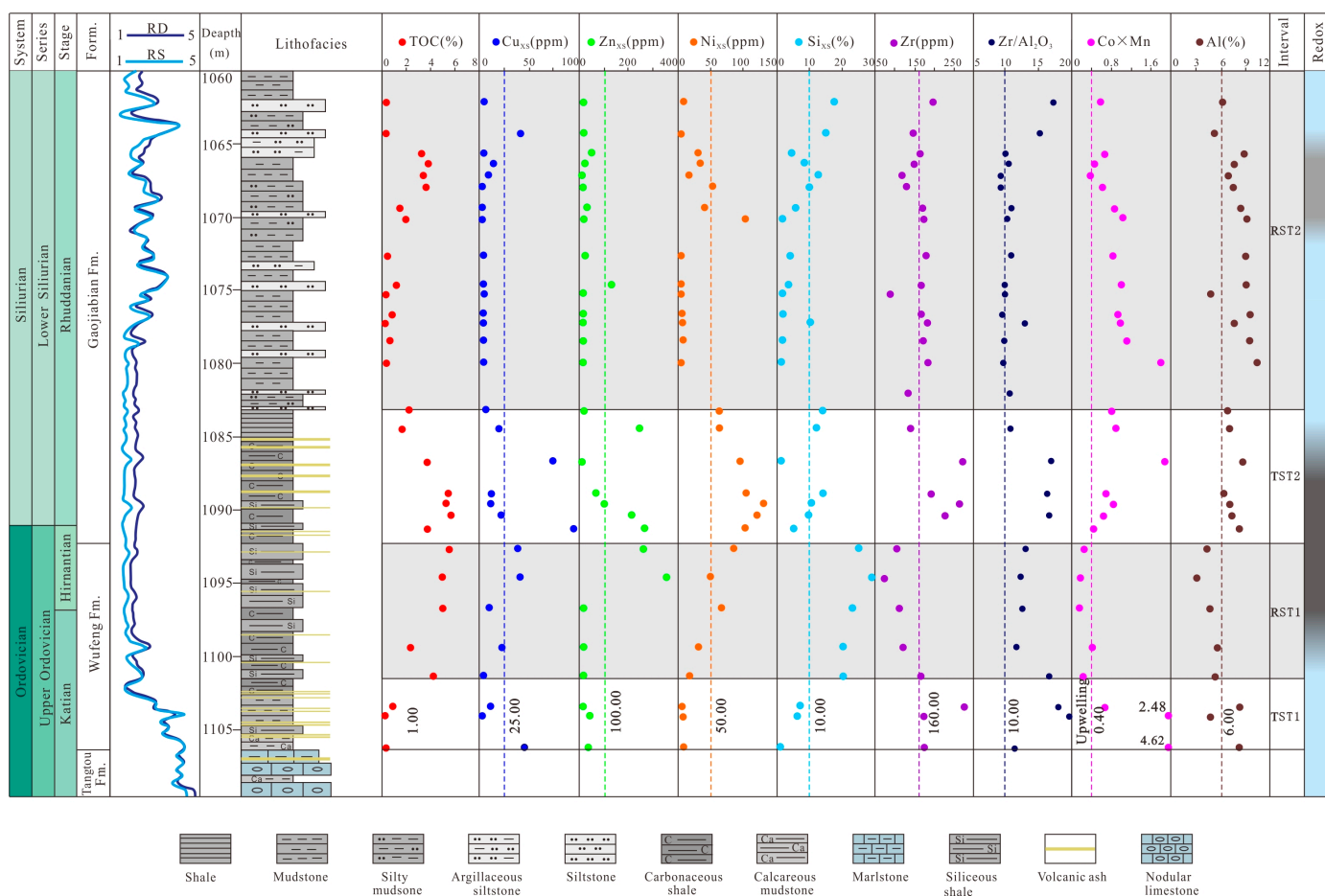


Figure 5. Vertical variations of proxies of primary productivity (TOC, Zn_{XS}, Cu_{XS}, Ni_{XS}, and Si_{XS}), volcanic activity (Zr and Zr/Al₂O₃ ratios), terrigenous input (Al contents), and upwelling currents (Co × Mn) in Well SY1.

5. Discussion

5.1. Marine Redox Conditions of the O/S Transition

The redox conditions of the ancient ocean have a significant impact on the migration, circulation, differentiation, and enrichment of redox-sensitive elements. Therefore, redox-sensitive elements can indicate changes in the redox environment of the ancient oceans [30,33].

The redox environment of the paleo-ocean during the O/S transition in the Upper Yangtze region has been extensively evaluated by previous researchers [34,35].

Redox-sensitive elements such as Mo, U, and V are generally enriched in sediments under anoxic conditions. Among them, the characteristics of Mo and U make their content extremely low in the oxidizing environment. Near the oxidation-reduction interface of Fe^{3+} and Fe^{2+} , the enrichment rate of U is faster than that of Mo, and in the anoxic or sulfurized environment, the enrichment rate of Mo exceeds U [36]. For black shale, Mo content characterizes the sulfidation degree of bottom water to a certain extent. Mo content < 25 ppm indicates a non-sulfiding environment, Mo content > 100 ppm implies a stable sulfidation environment, and Mo content is between 25–100 ppm, showing an intermittent euxinic environment [37]. $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ is often used to distinguish the suboxic, anoxic, and euxinic environments of ocean water and has achieved good results in the restoration of paleoenvironment in geological history [38,39]. In addition, V/Cr and Ni/Co values are also widely used to judge the oxidation-reduction degree of bottom water. Previous studies have shown that a V/Cr ratio greater than 4.25 indicates an anoxic or euxinic environments; from 2 to 4.25, suboxic conditions; and less than 2, oxic environments [40]. Ni/Co ratios >7.00 are anoxic environments, 5.00–7.00 are suboxic environments, and <5.00 are oxic environments [41]. In this paper, multiple geochemical indicators of Mo_{XS} , Mo_{EF} , U_{XS} , U_{EF} , V/Cr, and Ni/Co are used to discuss the redox characteristics of different stages [41] (Figure 4), which can effectively avoid the uncertainty of a single indicator.

During the stage of TST1, U and Mo were only weakly enriched in this interval, and both U_{EF} and Mo_{EF} remained low (U_{EF} average 4.4, Mo_{EF} average 3.4), consistent with low U_{XS} (average 2.2 ppm) and low Mo_{XS} (average 2.1 ppm) (Figure 4). The V/Cr ratio is 1.40–1.69, with an average value of 1.56 (less than 2.00); the Ni/Co ratio is 1.13–3.51, with an average value of 2.56 (less than 5.00). All Paleoredox indicators display that the seawater environment is more likely to be oxic at this stage.

For RST 1, all samples show $\text{TOC} > 2.0\%$, U_{EF} and Mo_{EF} increase significantly to more than 10 (U_{EF} average 15.3, Mo_{EF} average 17.3), and Mo_{XS} content gradually increases but still lower than 25 ppm (2.6–29.5 ppm, 13.7 ppm average) (Figure 4). Furthermore, the V/Cr ratio is 2.04–13.27, and the average value is 7.22 (greater than 4.25); the Ni/Co ratio is 6.07–18.28, and the average value is 11.38 (greater than 7.00). Various geochemical indicators suggest the transition from an oxygen-poor to an anoxic state at this stage.

In the interval of TST2, the average TOC was 3.94%, and it gradually decreased from the bottom to the top. U and Mo were strongly enriched at this stage (U_{EF} average 22.0, Mo_{EF} average 47.5). In addition, Mo_{XS} content increased significantly and peaked at 55.4 ppm (average 38.2 ppm), implying intermittent incursions of euxinic watermasses into the anoxic water column (Figure 4). The V/Cr value is 1.71–17.40, and the mean value is 5.43 (greater than 4.25); the Ni/Co ratio is 3.75–10.12, and the mean value is 7.62 (greater than 7.00). As a whole, deposition of TST2 likely experienced anoxic condition with intermittent incursions of euxinic water.

During the stage of RST2, the TOC value is 0.16%–3.78% with an average of 1.46%, which is generally low. Mo_{EF} dropped to 9.7, and Mo_{XS} content decreased (0.5–23.9 ppm, average 7.2 ppm), with an average value below 25 ppm. The V/Cr value is 1.01–2.48, and the average value is 1.51 (less than 2.00); the Ni/Co ratio is 1.20–5.85, the average value is 3.71 (less than 5.00) (Figure 4), showing that the bottom water is overall in an oxic state, except the transient anoxic state in the section of relatively high TOC (1065–1070 m).

Furthermore, the strong correlations between Mo_{XS} , U_{XS} , and Ni/Co ratios and TOC content (correlation coefficients 0.555, 0.466, and 0.655) (Figure 6) suggest that the redox conditions of bottom water during the O/S transition make a significant contribution to organic matter preservation and accumulation.

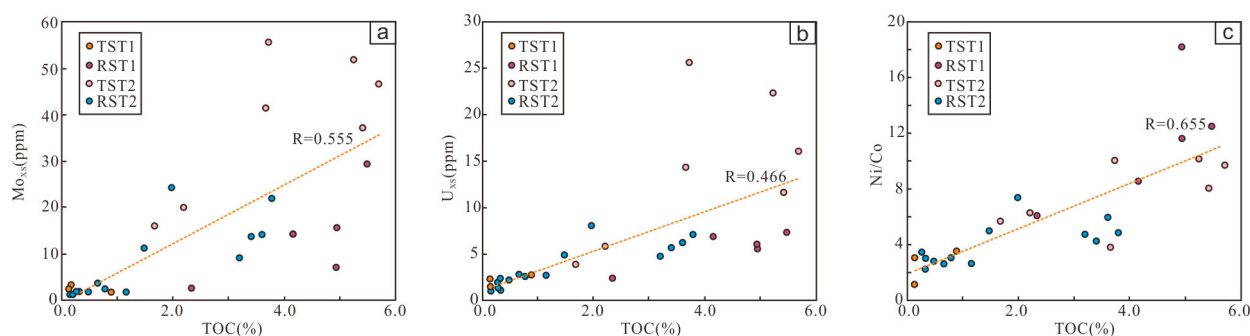


Figure 6. Crossplots of TOC vs. (a) Mo_{XS}, (b) U_{XS}, and (c) Ni/Co of samples from Well SY1.

5.2. Primary Productivity

Primary productivity plays a vital role in the global biochemical cycle and, to a certain extent, can reflect the chemical state of ocean surface water, the input of terrestrial materials, and the development of upwelling [42]. Several geochemical indicators such as Zn, Cu, and Ni in organic matter are related to the primary biological productivity of phytoplankton to some extent and are therefore used as proxies to assess primary productivity in many cases [26,43]. Zn, Cu, and Ni are released during organic matter degradation and are captured and preserved by pyrite in sediments under sulfate-reducing conditions [38]. Accordingly, Zn, Cu, and Ni are ideal indicators of organic matter fluxes into sediments under reducing conditions [26]. Here we used Zn_{XS}, Cu_{XS}, and Ni_{XS} contents that exclude the influence of terrigenous debris by the calculation formula described above to assess changes in primary productivity. In addition, Si_{XS} (excess silicon) represents the bio silicon produced under high productivity. By identifying the Late Ordovician–Early Silurian radiolarian assemblage in the Middle and Upper Yangtze region, previous researchers found that the bio silicon content is significantly higher in the organic-rich layers than the organic-poor layers [44,45], suggesting that Si_{XS} can be used as a reliable indicator of primary productivity.

In the interval of TST1, Zn_{XS} is 3.3–43.6 ppm (average 28.1 ppm); Cu_{XS} is 1.1–45.9 ppm (average 18.8 ppm); Ni_{XS} is 2.6–7.4 ppm (average 4.8 ppm); Si_{XS} value is 0.01%–7.25% (average 4.46%). All these indicators imply the low primary productivity in the surface water during the deposition of this stage (Figure 5). For RST1, Zn_{XS} (average 126.5 ppm), Cu_{XS} (average 22.0 ppm), Ni_{XS} (average 49.9 ppm), Si_{XS} (average 23.66%), and corresponding TOC value increased sharply, showing that the primary productivity of RST1 increased suddenly and a large amount of organic matter accumulated. During the deposition period of TST2, the content of Zn_{XS} (average 130.9 ppm), Cu_{XS} (average 33.5 ppm), Ni_{XS} (average 95.5 ppm) continued to rise (Figure 5). The rise of these elements was likely related to the occurrence of intermittent euxinic water column, which was favorable for capturing Zn, Cu and Ni. The decrease of Si_{XS} (average 9.35%) was probably related to the follow-up biological effect of the late Ordovician mass extinction that decreased the number of siliceous organisms [45]. The corresponding TOC value remained basically unchanged, indicating that the flux of organic matter into the sediments remained almost stable at this stage [27]. In RST2, the levels of Zn_{XS} (19.4 ppm), Cu_{XS} (4.5 ppm), and Ni_{XS} (19.9 ppm) showed rapid fall (Figure 5), indicating the decrease in primary productivity during this stage.

The correlation coefficients of Zn_{XS} and Si_{XS} with TOC are 0.24 and 0.27 (Figure 7a,b), respectively, which are weakly correlated. However, the correlation coefficient of Ni_{XS} with TOC reaches 0.60 (Figure 7c). Such a high correlation was probably associated with the reason that Ni_{XS} is more likely to enrich in euxinic and anoxic water column water [46,47]. In general, there is a weak to moderate correlation between the primary productivity and enrichment of organic matter during the O/S transition.

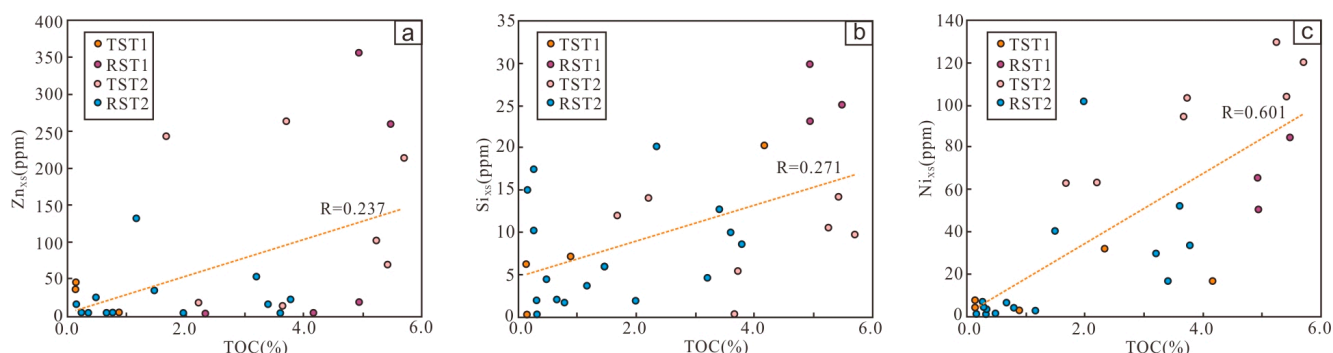


Figure 7. Crossplots of TOC vs. (a) Zn_{XS} , (b) Si_{XS} , and (c) Ni_{XS} of samples from Well SY1.

5.3. Influence of Volcanic Activities

Intense volcanic activity can import toxic substances and nutrients into the biosphere and release greenhouse gases (CO_2 , CH_4 , SO_2 , etc.), thus causing major disturbances of the terrestrial and marine ecosystems and global biogeochemical cycles [48]. Intense volcanic activity is widely recognized as a predisposing factor for oceanic anoxic events (OAEs) in geological history [49]. Inactive trace elements (e.g., Zr) can record the clue of volcanism, effectively identify volcanic material from mud shale, and are not easily affected by deposition and diagenesis [50].

In TST1, Zr value is 173.0–278.0 ppm, average 208.7 ppm (greater than 160 ppm), Zr/Al_2O_3 value is 11.31–19.65 ppm/wt%, average 16.29 ppm/wt% (greater than 15.00 ppm/wt%) (Figure 5). Multiple layers of volcanic ash were observed in the core, indicating that the volcanic activity was greater at this stage. In RST1, the Zr value was 71.3–166.0 ppm, with an average of 114.3 ppm (less than 160 ppm), and the Zr/Al_2O_3 value was 11.51–16.61 ppm/wt%, with an average of 13.13 ppm/wt% (less than 15.00 ppm/wt%) (Figure 5). The volcanic ash interlayer decreased in the core, implying that the volcanic activity weakened during this stage. The Zr value (average 225.3 ppm) and the Zr/Al_2O_3 value (average 16.14 ppm/wt%) (Figure 5) in TST2 increased significantly, and the volcanic ash interlayer in the core obviously increased, showing that the volcanic activity intensified during the deposition period of this stage. In RST2, Zr value (average 159.4 ppm) and Zr/Al_2O_3 (average 10.9 ppm/wt%) and the volcanic ash interlayer in the core decreased (Figure 5), indicating that the volcanic activity in this stage gradually weakened. There is little correlation between Zr value and TOC (correlation coefficient 0.001) (Figure 8a), and the correlation with Zn_{XS} and Ni_{XS} is extremely weak (correlation coefficients 0.001 and 0.104) (Figure 8b,c). It is suggested that volcanism contributed in a limited way in primary productivity and organic matter enrichment during the O/S transition.

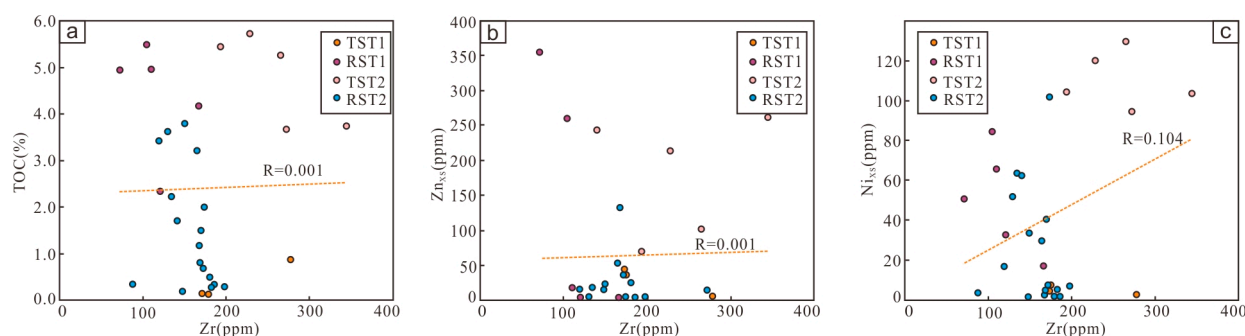


Figure 8. Crossplots of Zr vs. (a) TOC, (b) Zn_{XS} , and (c) Ni_{XS} of samples from Well SY1.

5.4. Upwelling

Upwelling is an important source of nutrient supply. It can bring essential nutrients for life in the deep waters of the ocean to shallow waters and stimulate the flourishing of

phytoplankton, thereby increasing primary productivity [27]. Generally, the combination of high phosphorus and silicon content is considered to have a genetic relationship with upwelling [30]. $\text{Co} \times \text{Mn}$ has recently been used as a proxy for upwelling in modern and ancient coastal systems, where $\text{Co} \times \text{Mn}$ values are typically low (<0.4) [51,52]. The $\text{Co} \times \text{Mn}$ values of Well SY1 are higher in the intervals of TST1, TST2, and RST2 (average values of 2.59, 0.89, and 1.57, respectively) (Figure 5), implying upwelling weak (or limited). In comparison, the upwelling was significantly enhanced in RST1 (average 0.24). In addition, the correlation between $\text{Co} \times \text{Mn}$ value and Si_{XS} and Ni_{XS} (correlation coefficients 0.299 and 0.097) (Figure 9a,b) suggest that nutrients brought by upwelling promoted the prosperity of siliceous organisms to a certain extent, and the content of biogenic silicon increased significantly in RST1. TOC also showed a moderate correlation with $\text{Co} \times \text{Mn}$ values (correlation coefficient 0.309) (Figure 9c), indicating that the development of upwelling played an important role in the enrichment of organic matter during the deposition of RST1.

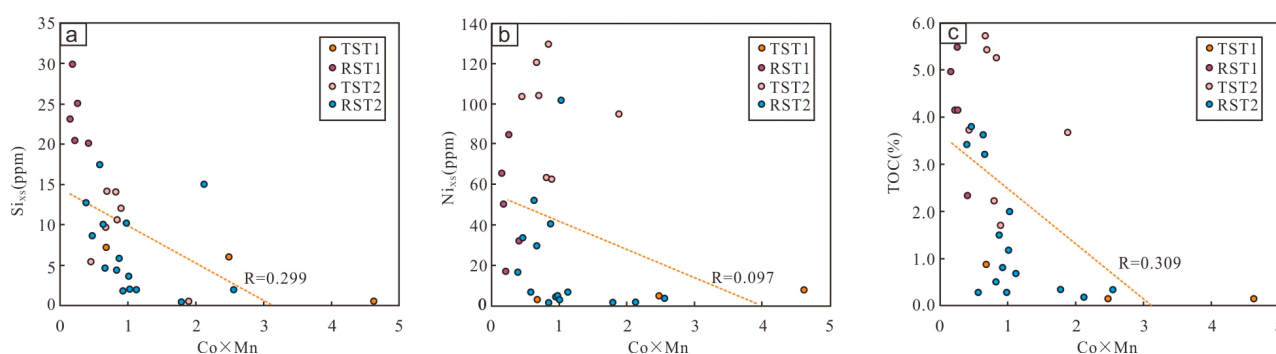


Figure 9. Crossplots of $\text{Co} \times \text{Mn}$ vs. (a) Si_{XS} , (b) Ni_{XS} , and (c) TOC of samples from Well SY1.

5.5. Terrigenous Input

Terrestrial material is mainly input into the ocean by rivers or wind and provides essential nutrients for life. On one hand, terrigenous input plays an important role in the production and accumulation of organic matter [53]. On the other hand, the clastic material has a significant impact on the organic and mineral compositions of shale and decreases the accumulation of organic matter by dilution [54].

Al mainly originates from terrigenous input. Because the influence of diagenesis can be almost negligible, Al can be used to indicate the change of terrigenous input [55]. The Al content of Well SY1 was relatively low in RST1, implying that the terrigenous input flux was weak in this stage. In contrast, the Al content in TST1, TST2, and RST2 increased significantly, reflecting enhance of terrigenous material input (Figure 5). Figure 10 shows the weak negative correlations (correlation coefficients 0.118, 0.102, and 0.014) between Al and TOC, Zn_{XS} , and Ni_{XS} . We suggest that the input of terrigenous material is not the main controlling factor for the high primary productivity and the accumulation of organic matter in the study interval but played the role of increasing the deposition rate and diluting the organic matter especially during the stage of RST2.

5.6. Controls on Organic Matter Accumulation during the O/S Transition

In the Lower Yangtze region, four system tracts were discriminated in terms of sea level changes during the O/S transition. RST1 corresponded to the intensification of compression between Yangtze and Cathaysia sub-blocks. The early passive continental margin with ‘platform-slope-basin’ pattern was transformed into a tectonic evolution stage of a foreland basin, accompanied by strong volcanic activity [56,57]. Under the effect of compression, the basin experienced quick subsidence. Its sedimentary records changed from nodular limestone in O_3t to calcareous mudstone in O_3w , accompanied by the deepening of water column. However, the overall depth of the water is still not too deep, as multiple redox geochemical indicators reveal that the water column in this stage

was oxic environment. Excessive O_2 tended to accelerate the decomposition and dilution of organic matter and hinder the accumulation of organic matter. Low levels of essential nutrients for life (i.e., Zn, Ni, and Cu) content may significantly limit primary productivity. Meanwhile, strong tectonic movement increases terrigenous input flux (Al content), which accelerated sediment deposition rate and diluted organic matter (Figure 11a).

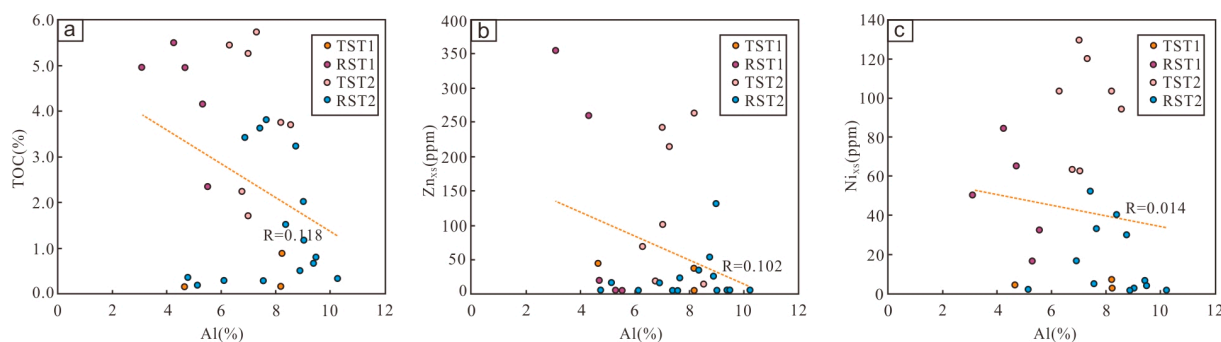


Figure 10. Crossplots of Al vs. (a) TOC, (b) Zn_{XS} , and (c) Ni_{XS} of samples from Well SY1.

RST1 developed in the Hirnantian ice age. The formation of polar glaciers led to the fall of the global sea level and caused a large-scale sea regression in the Yangtze region [34,35]. The temperature drop caused an increase in upwelling in the equatorial region where the Lower Yangtze region is located (Co $\times$ Mo index). A large number of essential nutrients for life (Zn, Ni, and Cu) were brought by the upwelling, and therefore phytoplankton flourished rapidly, and the primary productivity sharply increased. High productivity promoted the production of large amounts of organic matter, and meanwhile the degradation of some organic matter also increases oxygen consumption. The anoxic environment intensified the enrichment of redox sensitive elements. The terrigenous detrital input flux decreased (Al content), which slowed down the deposition rate (Figure 11b). High productivity, anoxic water column, and low deposition rates are the main controlling factors of organic matter enrichment in RST1.

During the deposition period of TST2, the end of glaciers age resulted in extensive transgression in the Yangtze region and rapid deepening of the water column, making the bottom water anoxic. Many volcanic ash interlayers in the black shale indicate an increase in volcanic eruptions during this period. Volcanic eruptions brought a large amount of nutrients into the water column, which would promote the prosperity of algae. The oxygen content in seawater further dropped sharply, resulting in anoxic conditions with intermittent incursions of euxinic water. In addition, volcanic ash hydrolysis and radiolarian skeletal dissolution can increase the content of dissolved silica and silica-clay colloids in seawater. These colloids absorb organic matter particles and rapidly deposit so that the organic matter is well preserved [58,59]. High productivity and anoxic condition with intermittent incursions of euxinic water is the main controlling factor for organic matter enrichment in this stage (Figure 11c).

During the deposition period of RST2, the depth of the water column began to decline significantly. The deposition of the carbonaceous shale gradually decreased, and that of the siltstone gradually increased. The climate is relatively warm and humid, which accelerates the chemical weathering and increases the terrigenous input flux [45]. Excessive terrigenous material injection diluted the enrichment of organic matter in sediments, resulting in the decrease of TOC (Figure 11d).

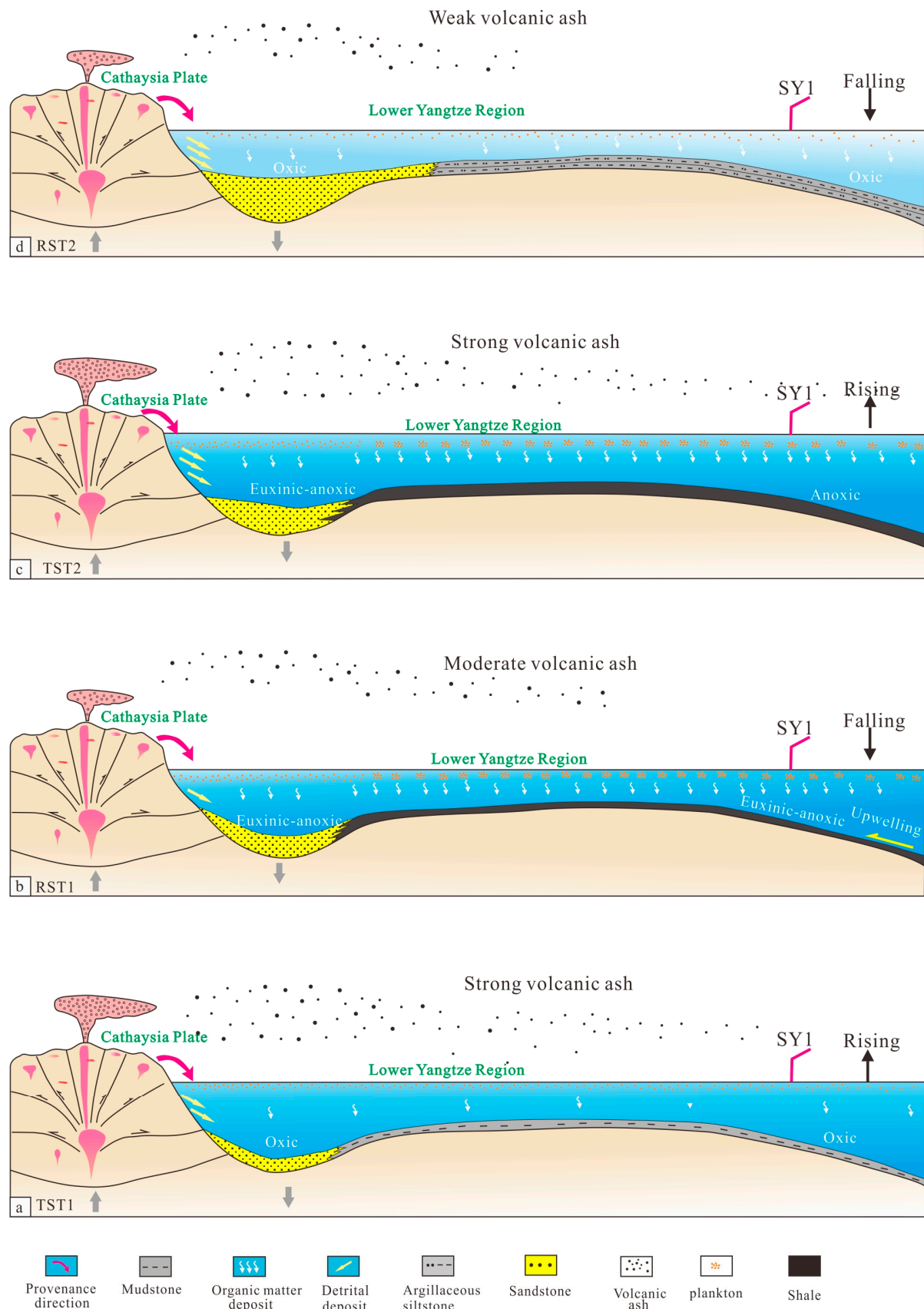


Figure 11. Schematic diagrams demonstrating the distinct OM accumulation models patterns of different systems tract in the Lower Yangtze region during O/S transition. (a) Stage of TST1, (b) Stage of RST1, (c) Stage of TST2, and (d) Stage of RST2.

6. Conclusions

Stratigraphic frameworks of the O/S transition in the Lower Yangtze region are composed of two third-order sequences, each of which can be subdivided into a lower TST (transgressive systems tract) and an upper RST (regressive systems tract). The high-TOC intervals mainly developed in RST1 of O_3w and TST2 of S_{1g} .

The deposition of TST1 represented an evident transition stage, which was marked by the ending of the underlying carbonate sediments and the initiation of the terrigenous clastic-dominated sediments. The oxic environment, low paleoproductivity and high terrestrial input fluxes are not favorable for organic matter enrichment in the stage of TST1. During the depositional period of RST1, the global sea level declined due to the Hirnantian glaciation age. High paleoproductivity, anoxic water column environment, and low sediment supply flux caused the deposition of organic-rich shale. During the stage of TST2, the sea level rose due to the ending of the ice age. The relatively large water depth and high paleoproductivity associated with volcanic eruptions are the main factors that caused the enrichment of organic matter. During the deposition of RST2, the increase of sediment supply flux resulted in a decrease in accommodation space, water depth, and the dilution of organic matter in sediments, which was the primary constraint of organic matter accumulation.

Author Contributions: Conceptualization, C.Z. and C.F.; methodology, C.Z.; formal analysis, C.Z. and C.F.; investigation, C.Z., C.F., D.Z. and W.S.; writing—original draft preparation, C.Z., C.F. and Q.Z.; visualization, C.Z., C.F., Q.Z., G.M. and W.S.; project administration, J.L. and D.Z.; funding acquisition, J.L. and D.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the China Geological Survey Oil and Gas Program (DD20221662), the Open Fund of Hubei Key Laboratory of Paleontology and Geological Environment Evolution (PEL-202206), and Geological Society of Jiangsu Province Funding Project (DZXHP2022-05).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Chen, X.; Melchin, M.J.; Sheets, H.D.; Mitchell, C.E.; Fan, J.X. Patterns and processes of latest Ordovician graptolite extinction and recovery based on data from South China. *J. Paleontology* **2005**, *79*, 842–861. [\[CrossRef\]](#)
- Yan, D.; Chen, D.; Wang, Q.; Wang, J. Geochemical changes across the Ordovician-Silurian transition on the Yangtze platform, South China. *Sci. China Ser. D Earth Sci.* **2009**, *52*, 38–54. [\[CrossRef\]](#)
- Yan, D.; Chen, D.; Wang, Q.; Wang, J.G. Predominance of stratified anoxic Yangtze Sea interrupted by short-term oxygenation during the Ordo-Silurian transition. *Chem. Geol.* **2012**, *291*, 69–78. [\[CrossRef\]](#)
- Algeo, T.J.; Marenco, P.J.; Saltzman, M.R. Co-evolution of oceans, climate, and the biosphere during the ‘Ordovician Revolution’: A review. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2016**, *458*, 1–11. [\[CrossRef\]](#)
- Finnegan, S.; Bergmann, K.; Eiler, J.M.; Jones, D.S.; Fike, D.A.; Eisenman, I.; Hughes, N.C.; Ripati, A.K.; Fischer, W.W. The magnitude and duration of Late Ordovician-Early Silurian glaciation. *Science* **2011**, *331*, 903–906. [\[CrossRef\]](#)
- Fan, J.X.; Chen, X. Preliminary report on the Late Ordovician graptolite extinction in the Yangtze region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2007**, *245*, 82–94. [\[CrossRef\]](#)
- Wang, G.; Zhan, R.B.; Percival, I.G. The end-Ordovician mass extinction: A single-pulse event? *Earth Sci. Rev.* **2019**, *192*, 15–33. [\[CrossRef\]](#)
- Dowey, P.J.; Hodgson, D.M.; Worden, R.H. Pre-requisites, processes, and prediction of chlorite grain coatings in petroleum reservoirs: A review of subsurface examples. *Mar. Pet. Geol.* **2012**, *32*, 63–75. [\[CrossRef\]](#)
- Yang, S.; Hu, W.; Wang, X.; Jiang, B.; Yao, S.; Sun, F.; Huang, Z.; Zhu, F. Duration, evolution, and implications of volcanic activity across the Ordovician-Silurian transition in the Lower Yangtze region, South China. *Earth Planet. Sci. Lett.* **2019**, *518*, 13–25. [\[CrossRef\]](#)
- Zou, C.; Qiu, Z.; Poulton, S.W.; Dong, D.; Wang, H.; Chen, D.; Lu, B.; Shi, Z.; Tao, H. Ocean euxinia and climate change “double whammy” drove the Late Ordovician mass extinction. *Geology* **2018**, *46*, 535–538. [\[CrossRef\]](#)
- Melchin, M.J.; Mitchell, C.E.; Holmden, C.; Storch, P. Environmental changes in the Late Ordovician-early Silurian: Review and new insights from black shales and nitrogen isotopes. *Bull. Geol. Soc. Am.* **2013**, *125*, 1635–1670. [\[CrossRef\]](#)

12. Zou, C.; Zhu, R.; Chen, Z.; Ogg, J.G.; Wu, S.; Dong, D.; Qiu, Z.; Wang, Y.; Wang, L.; Lin, S. Organic-matter-rich shales of China. *Earth-Sci. Rev.* **2019**, *189*, 51–78. [\[CrossRef\]](#)
13. Wang, K.; Orth, C.J.; Attrep, J.M.; Chatterton, B.D.; Wang, X.; Li, J. The great latest Ordovician extinction on the South China Plate: Chemostratigraphic studies of the Ordovician-Silurian boundary interval on the Yangtze Platform. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **1993**, *104*, 61–79. [\[CrossRef\]](#)
14. Wu, J.; Xu, J. Characteristics of Silurian sequence stratigraphy around the Jiangnan fault zone and analysis of shale gas potential. *East China Geol.* **2020**, *41*, 177–194. (In Chinese with English Abstract) [\[CrossRef\]](#)
15. Li, N.; Li, C.; Fan, J.; Algeo, T.J.; Yan, D.; Zhu, G.; Wu, S.; Tang, S.; Cheng, M.; Jin, C. Sulfate-controlled marine euxinia in the semi-restricted inner Yangtze Sea (South China) during the Ordovician-Silurian transition. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2019**, *534*, 109281. [\[CrossRef\]](#)
16. Li, N.; Li, C.; Algeo, T.J.; Cheng, M.; Jin, C.; Zhu, G.; Fan, J.; Sun, Z. Redox changes in the outer Yangtze Sea (South China) through the Hirnantian Glaciation and their implications for the end-Ordovician biocrisis. *Earth-Sci. Rev.* **2021**, *212*, 103443. [\[CrossRef\]](#)
17. Wang, K.; Chatterton, B.; Wang, Y. An organic carbon isotope record of Late Ordovician to Early Silurian marine sedimentary rocks, Yangtze Sea, South China: Implications for CO₂ changes during the Hirnantian glaciation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **1997**, *132*, 147–158. [\[CrossRef\]](#)
18. Chen, X.; Rong, J.; Li, Y.; Boucot, A.J. Facies patterns and geography of the Yangtze region, south China, through the Ordovician and Silurian transition. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2004**, *204*, 353–372. [\[CrossRef\]](#)
19. Huang, Z.; Fang, C.; Li, J.; Zhang, C.; Wang, Y.; Liu, L.; Zhao, S. U-Mo covariation in marine shales of Wufeng—Gaojiabian Formations in Ningjing-Zhenjiang area and its implication for identification of watermass restriction. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* **2021**, *47*, 443–450. (In Chinese with English Abstract)
20. Yin, Q.; Fang, C.; Zheng, H.; Wang, J.; Wang, F. Geological conditions of Ordovician shale gas and optimization for prospective areas in the Lower Yangtze region. *East China Geol.* **2020**, *41*, 70–78. (In Chinese with English Abstract) [\[CrossRef\]](#)
21. Zhang, Y. Huangqiao transform event in tectonic evolution of Lower Yangtze region and the meso-paleozoic hydrocarbon exploration. *Oil Gas Geol.* **1991**, *12*, 439–448. (In Chinese with English Abstract)
22. Yao, B.; Lu, H.; Guo, N. The multi-stage structure frame of Lower Yangtze basin evolution and its significance in petroleum geology. *Pet. Explor. Dev.* **1999**, *26*, 10–13. (In Chinese with English Abstract)
23. Zhang, G.; Guo, A.; Wang, Y.; Li, S.; Dong, Y.; Liu, S.; He, D.; Cheng, S.; Lu, R.; Yao, A. Tectonics of South China continent and its implications. *Sci. China Earth Sci.* **2013**, *56*, 1804–1828. [\[CrossRef\]](#)
24. Shu, L.S.; Chen, X.Y.; Lou, F.S. Pre-Jurassic tectonics of the South China. *Acta Geol. Sin.* **2020**, *94*, 333–360. (In Chinese with English Abstract)
25. Li, Y.; Zhang, T.; Ellis, G.S.; Shao, D. Depositional environment and organic matter accumulation of Upper Ordovician–Lower Silurian marine shale in the Upper Yangtze Platform, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2017**, *466*, 252–264. [\[CrossRef\]](#)
26. Chen, X.; Fan, J.; Zhang, Y.; Wang, H.; Chen, Q.; Wang, W.; Liang, F.; Guo, W.; Zhao, Q.; Nie, H.K.; et al. Subdivision and delineation of the Wufeng and Lungmachi black shales in the subsurface areas of the Yangtze Platform. *J. Stratigr.* **2015**, *39*, 351–358. (In Chinese with English Abstract)
27. Yang, S.; Hu, W.; Yao, S.; Wang, X.; He, W.; Wang, Y.; Zhu, F.; Sun, F. Constraints on the accumulation of organic matter in Upper Ordovician-lower Silurian black shales from the Lower Yangtze region, South China. *Mar. Pet. Geol.* **2020**, *120*, 104544. [\[CrossRef\]](#)
28. Hart, B.S.; Hofmann, M.H. Revisiting paleoenvironmental analyses and interpretations of organic-rich deposits: The importance of TOC corrections. *Org. Geochem.* **2022**, *170*, 104434. [\[CrossRef\]](#)
29. Taylor, S.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publications: Oxford, UK, 1985.
30. Ge, X.; Chen, D.; Zhang, G.; Huang, T.; Liu, M.; El-Shafeiy, M. Marine redox evolution and organic accumulation in an intrashelf basin, NE Sichuan Basin during the Late Permian. *Mar. Pet. Geol.* **2022**, *140*, 105633. [\[CrossRef\]](#)
31. Tribouillard, N.; Algeo, T.J.; Lyons, T.; Riboulleau, A. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* **2006**, *232*, 12–32. [\[CrossRef\]](#)
32. Catuneanu, O.; Abreu, V.; Bhattacharya, J.P.; Blum, M.D.; Dalrymple, R.W.; Eriksson, P.G.; Fielding, C.R.; Fisher, W.L.; Galloway, W.E.; Gibling, M.R.; et al. Towards the standardization of sequence stratigraphy. *Earth-Sci. Rev.* **2009**, *92*, 1–33. [\[CrossRef\]](#)
33. Wei, H. Productivity and redox proxies of palaeo-oceans: An overview of elementary geochemistry. *Sediment. Geol. Tethyan Geol.* **2012**, *32*, 76–88. (In Chinese with English Abstract)
34. Li, Y.; Shao, D.; Lv, H.; Zhang, Y.; Zhang, X.; Zhang, T. A relationship between element geochemical characteristics and organic matter enrichment in marine shale of Wufeng Formation-Longmaxi Formation, Sichuan Basin. *Acta Pet. Sin.* **2015**, *36*, 1470–1483. (In Chinese with English Abstract)
35. He, L.; Wang, Y.; Chen, D.; Wang, Q.; Wang, C. Relationship between sedimentary environment and organic matter accumulation in the black shale of Wufeng-Longmaxi Formations in Nanchuan area, Chongqing. *Nat. Gas Geosci.* **2019**, *30*, 203–218. (In Chinese with English Abstract) [\[CrossRef\]](#)
36. Algeo, T.J.; Maynard, J.B. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* **2004**, *206*, 289–318. [\[CrossRef\]](#)
37. Scott, C.; Lyons, T.W. Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chem. Geol.* **2012**, *324*, 19–27. [\[CrossRef\]](#)

38. Algeo, T.J.; Tribouillard, N. Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. *Chem. Geol.* **2009**, *268*, 211–225. [\[CrossRef\]](#)
39. Qiu, Z.; Wei, H.; Liu, H.; Shao, N.; Wang, Y.; Zhang, L. 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 with English Abstract)
40. 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. [\[CrossRef\]](#)
41. Zeng, S.; Wang, J.; Fu, X.; Chen, W.; Feng, X.; Wang, D.; Song, C.; Wang, Z.; Wang, Z. Geochemical characteristics, redox conditions, and organic matter accumulation of marine oil shale from the Changliang Mountain area, northern Tibet, China. *Mar. Pet. Geol.* **2015**, *64*, 203–221. [\[CrossRef\]](#)
42. Liu, H.; Lai, C.; Ting, H. Late Pleistocene nutrients and sea-surface productivity in the South China Sea: A record of the connections with northern hemisphere events. *Mar. Geol.* **1999**, *156*, 197–210. [\[CrossRef\]](#)
43. Piper, D.Z.; Calvert, S. A marine biogeochemical perspective on black shale deposition. *Earth-Sci. Rev.* **2009**, *95*, 63–96. [\[CrossRef\]](#)
44. Wang, S.; Zou, C.; Dong, D.; Wang, Y.; Huang, J.; Guo, Z. Biogenic Silica of Organic-Rich Shale in Sichuan Basin and Its Significance for Shale Gas. *Acta Sci. Nat. Univ. Pekin.* **2014**, *50*, 476–486. (In Chinese with English Abstract)
45. Guo, W.; Feng, Q.; Maliha, Z. Organic Matter Enrichment Mechanism of Black Shale in Wufeng-Longmaxi Formations: A Case Study from Jiaoye 143-5 Well at Chongqing. *Earth Sci.* **2021**, *46*, 572–582. (In Chinese with English Abstract)
46. Haraldsson, C.; Westerlund, S. Trace-metals in the water columns of the Black Sea and Framvaren Fjord. *Mar. Chem.* **1988**, *23*, 417–424. [\[CrossRef\]](#)
47. Morse, J.W.; Luther III, G.W. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim. Et Cosmochim. Acta* **1999**, *63*, 3373–3378. [\[CrossRef\]](#)
48. Grasby, S.E.; Shen, W.; Yin, R.; Gleason, J.D.; Blum, J.D.; Lepak, R.F.; James, P.H.; Benoit, B. Isotopic signatures of mercury contamination in latest Permian oceans. *Geology* **2017**, *45*, 55–58. [\[CrossRef\]](#)
49. Charbonnier, G.; Godet, A.; Bodin, S.; Adatte, T.; Föllmi, K.B. Mercury anomalies, volcanic pulses, and drowning episodes along the northern Tethyan margin during the latest Hauterivian-earliest Aptian. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2018**, *505*, 337–350. [\[CrossRef\]](#)
50. Yang, S.; Hu, W.; Fan, J.; Deng, Y. New geochemical identification fingerprints of volcanism during the Ordovician-Silurian transition and its implications for biological and environmental evolution. *Earth-Sci. Rev.* **2022**, *228*, 104016. [\[CrossRef\]](#)
51. Sweere, T.; van den Boorn, S.; Dickson, A.J.; Reichart, G.-J. Definition of new trace-metal proxies for the controls on organic matter enrichment in marine sediments based on Mn, Co, Mo and Cd concentrations. *Chem. Geol.* **2016**, *441*, 235–245. [\[CrossRef\]](#)
52. Zhang, L.; Buatois, L.A.; Mángano, M.G.; Gong, Y.; Feng, Q.; Qi, Y.; Luo, M.; Zhang, X. Uppermost Permian trace fossils along a shelf to slope transect in South China and their implications for oceanic redox evolution and extinction pattern. *Glob. Planet. Chang.* **2018**, *167*, 74–86. [\[CrossRef\]](#)
53. Canfield, D.E. Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* **1994**, *114*, 315–329. [\[CrossRef\]](#)
54. Yan, D.; Wang, H.; Fu, Q.; Chen, Z.; He, J.; Gao, Z. Geochemical characteristics in the Longmaxi Formation (Early Silurian) of South China: Implications for organic matter accumulation. *Mar. Pet. Geol.* **2015**, *65*, 290–301. [\[CrossRef\]](#)
55. Yarincik, K.M.; Murray, R.W.; Peterson, L.C. Climatically sensitive eolian and hemipelagic deposition in the Cariaco Basin, Venezuela, over the past 578,000 years: Results from Al/Ti and K/Al. *Paleoceanography* **2000**, *15*, 210–228. [\[CrossRef\]](#)
56. Chen, Q.; Fan, J.X.; Zhang, L.N.; Chen, X. Paleogeographic evolution of the Lower Yangtze region and the break of the “platform-slope-basin” pattern during the Late Ordovician. *Sci. China Earth Sci.* **2018**, *48*, 767–777. [\[CrossRef\]](#)
57. Fang, C.; Huang, Z.; Teng, L.; Xu, F.; Zhou, D.; Yin, Q.; Shao, W.; Shi, G. Lithofacies palaeogeography of the Late Ordovician Kaitian Stage-the early Silurian Rhuddanian Stage in Lower Yangtze region and its petroleum geological significance. *Geol. China* **2020**, *47*, 144–160. (In Chinese with English Abstract)
58. Zhang, Y.; Zheng, S.; Gao, B.; Fen, Q. Distribution Characteristics and Enrichment Factors of Organic Matter in Upper Permian Dalong Formation of Shangsi Section, Guangyuan, Sichuan Basin. *Earth Sci.* **2017**, *42*, 1008–1025.
59. Khan, M.Z.; Feng, Q.; Zhang, K.; Guo, W. Biogenic silica and organic carbon fluxes provide evidence of enhanced marine productivity in the Upper Ordovician-Lower Silurian of South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2019**, *534*, 109278. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.