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Research Article

Difference Analysis of Organic Matter Enrichment Mechanisms in Upper Ordovician-Lower Silurian Shale from the Yangtze Region of Southern China and Its Geological Significance in Shale Gas Exploration

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The upper Ordovician-lower Silurian shale has always been the main target of marine shale gas exploration in southern China. However, the shale gas content varies greatly across different regions. The organic matter content is one of the most important factors in determining gas content; therefore, determining the enrichment mechanisms of organic matter is an important problem that needs to be solved urgently. In this paper, upper Ordovician-lower Silurian shale samples from the X-1 and Y-1 wells that are located in the southern Sichuan area of the upper Yangtze region and the northwestern Jiangxi area of the lower Yangtze region, respectively, are selected for analysis. Based on the core sample description, well logging data analysis, mineral and elemental composition analysis, silicon isotope analysis, and TOC (total organic carbon) content analysis, the upper Ordovician-lower Silurian shale is studied to quantitatively calculate its content of excess silicon. Subsequently, the results of elemental analysis and silicon isotope analysis are used to determine the origin of excess silicon. Finally, we used U/Th to determine the characteristics of the redox environment and the relationship between excess barium and TOC content to judge paleoproductivity and further studied the mechanism underlying sedimentary organic matter enrichment in the study area. The results show that the excess silicon from the upper Ordovician-lower Silurian shale in the upper Yangtze area is derived from biogenesis. The sedimentary water body is divided into an oxygen-rich upper water layer that has higher paleoproductivity and a strongly reducing lower water that is conducive to the preservation of sedimentary organic matter. Thus, for the upper Ordovician-lower Silurian shale in the upper Yangtze region, exploration should be conducted in the center of the blocks with high TOC contents and strongly reducing water body. However, the excess silicon in the upper Ordovician-lower Silurian shale of the lower Yangtze area originates from hydrothermal activity that can enhance the reducibility of the bottom water and carry nutrients from the crust to improve paleoproductivity and enrich sedimentary organic matter. Therefore, for the upper

Ordovician-lower Silurian shale in the lower Yangtze region, exploration should be conducted in the blocks near the junction of the two plates where hydrothermal activity was active.

1. Introduction

Shale gas is an important unconventional gas resource that is a current research focus in the petroleum geology field [1, 2]. The study of shale gas began in the United States. The drilling of the first shale gas well by the United States in eastern Devonian shale in 1821 served as the prelude to the global natural gas industry. Since 2005, the development of horizontal well drilling and hydraulic fracturing technology has enabled the extraction of gas from shale at shallow depths in the United States and large-scale gas exploration and development in North America [3, 4]. China also contains large shale gas resources. Since the Wei-201 well (the first shale gas exploration well in China) obtained industrial gas in the upper Ordovician Wufeng-lower Silurian Longmaxi Formation (in accordance with the International Stratigraphic Code, the upper Ordovician Wufeng Formation corresponds to the upper Ordovician Hirnantian Formation and the no. 1 member of the Longmaxi Formation corresponds to the lower Silurian Rhuddanian Formation) marine shale in 2010, China began to develop shale gas vigorously and initially obtained commercial development in some shale gas blocks, including the Changning, Zhaotong, Fushun-Yongchuan, Fuling, and Dingshan blocks [5–7].

The content of organic matter in shale determines the hydrocarbon generation capacity, reservoir space, and adsorption capacity of shale, which play a decisive role in the shale gas content [8–11]. According to previous studies, there is a positive correlation between the organic carbon content and adsorbed gas content; the higher the content of organic matter is, the greater the total gas content is [12]. Therefore, research on the organic matter enrichment mechanisms and the spatial distribution characteristics of organic matter in a shale gas exploration area can provide a theoretical basis for shale gas exploration [13, 14]. A series of investigations have been carried out to study the organic matter enrichment mechanism of marine shale in the Yangtze region. Zhang et al. [15] studied the sedimentary environment and evolution of the lower Silurian Longmaxi Formation in the southeastern Sichuan and northern Chongqing regions. They posited that the argillaceous deep-water shelf served as the main sedimentary environment for the formation of source rocks in the Longmaxi Formation. Moreover, they thought that the anoxic environment and slow sedimentation rate present at the bottom of the Longmaxi Formation are the main factors necessary for the development of high-quality source rocks in the study area. Wang et al. [16] used redox-sensitive elements in trace elements as important proxies to determine the redox environment of the ancient ocean and to further study the mechanism underlying organic matter enrichment. They found that the organic-rich shale present at the bottom of the Longmaxi Formation was deposited in an anoxic environment and that organic C content is positively correlated with V/Cr and Ni/Co ratios. This relationship indicates that organic matter enrichment is associated with an anoxic environment. Zhao et al. [17] categorized different lithofacies types by combining field surveys and drilling core descriptions of the Wufeng-Longmaxi Formation shale obtained at four different wells in the Sichuan Basin with observations of rock thin section. They discovered that Wufeng-Longmaxi shale contains a variety of elements, such as Si, Ca, Al, U, Fe, and Mn, as well as siliceous minerals that are closely related to organic matter enrichment. Therefore, a large amount of research on siliceous minerals has been conducted. Siliceous minerals are generally derived from terrigenous clastic sediment, biogenic deposits, and hydrothermal sediment [18]. Holdaway and Clayton [19] defined the concept of excess silicon, which refers to the portion of siliceous minerals that exceeds normal terrigenous clastic sources, and they proposed a method for quantitatively calculating the excess silicon content. Wedepohl [20], Adachi et al. [21], and Yamamoto [22] proposed the use of the Al-Fe-Mn ternary diagram to determine whether siliceous minerals are hydrothermal or biogenic in origin.

In this paper, two of the aforementioned methods are combined in order to determine the existence and content of excess silicon in the shale. Next, the origins of the excess silicon are determined by the Al-Fe-Mn ternary diagram and silicon isotope analysis and trace element proxies are used to determine the sedimentary environment characteristics and paleoproductivity in order to analyze the enrichment mechanism of organic matter. Finally, the difference in the organic matter enrichment between the upper and lower Yangtze regions during the late Ordovician-early Silurian period is analyzed.

2. Geological Settings

2.1. Sedimentary Evolution History of the Study Area. The X-1 well in the upper Yangtze area is located in the southern part of the Sichuan Basin (Figure 1), which became an important part of the Yangtze platform after the Jinning movement (800 Ma). Marine sedimentation began after the consolidation of the basin basement, and subsequent multistage tectonic movements continued to transform the Sichuan Basin [23, 24]. The Chuanzhong Uplift began to form in the west-central Sichuan Basin during the late Ordovician-early Silurian period. The Xuefeng Uplift and central Guizhou Uplift formed in the eastern and southern parts of the Sichuan Basin, respectively. The formation of these uplifts caused the Sichuan Basin to change from an open sea environment to a restricted sea environment that was surrounded by the Chuanzhong, Xuefeng, and central Guizhou Uplifts. The Sichuan Basin transformed into a cratonic depression basin after compression. During the late Ordovician-early Silurian, the sedimentary environment of the upper Yangtze area was dominated by deep-water shelf deposits, whereas that at the edge of the uplift was mainly dominated by

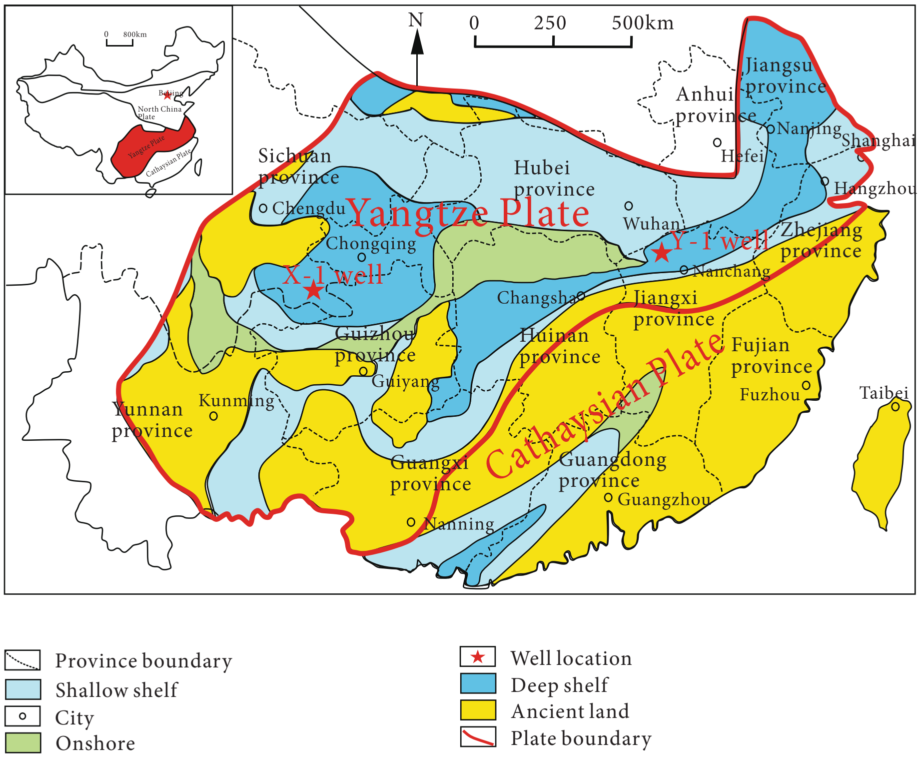

Figure 1: Sedimentary characteristics of the late Ordovician-early Silurian in southern China. The X-1 well is located in the upper Yangtze region, which is a deep-water shelf environment that is surrounded by ancient land; the Y-1 well is located in the lower Yangtze region, close to the junction of the Yangtze Plate and the Cathaysian Plate [24, 25, 29].

shallow shore shelves (Figure 1) [25]. Under the influence of the Caledonian movement, large-scale tectonic uplift occurred at the end of the Silurian period, which formed a large paleouplift in the middle and upper Yangtze regions. This uplift caused the Sichuan Basin to be entirely eroded, contributing to the widespread absence of the Devonian and Carboniferous systems in the Sichuan Basin [26]. During the early Permian, the large-scale invasion of Tethyan sea water from the southwest resulted in the formation of a vast epicontinental sea. The Sichuan Basin became a part of the massive shallow-sea carbonate platform in the upper Yangtze, in which the sea water was clear with normal salinity and flourishing biota [27]. The Sichuan Basin was once again deposited in the Permian until the end of the middle Triassic, when the end of a large-scale transgression was nearly reached and the basin transformed from a region of marine sedimentation to one of continental sedimentation. At the end of the Jurassic, intensive folding occurred in the basin margin, causing uplift in the basin, which led to the large-scale denudation of the Jurassic strata. In the Paleogene and Neogene periods, the Sichuan Basin was reshaped and nearly formed its current appearance [28].

The Y-1 well in the lower Yangtze region is located in the western part of the Xiushui-Wuning syncline in the Xiuwu Basin, which formed through structural compression during the Early-middle Jurassic. The Mesoproterozoic Shuangqiaoshan metamorphic rock group constitutes the basement of the Xiuwu Basin. With the occurrence of a marine regression at the end of the Ediacaran period, the sedimentary environment in the Xiuwu Basin became a shallow sea [29]. However, a major transgression occurred during the early Cambrian, which caused the sedimentary environment to evolve into a deep-water environment, where organic-rich shale with a high TOC content (average TOC content > 8 wt%) was deposited. Subsequently, the water body gradually became shallower and the TOC content gradually decreased. The sedimentary environment evolved into a shallow-water shelf environment in the Late-early Cambrian [30, 31]. During the Middle-late Cambrian, the sedimentary system of the Xiuwu Basin evolved from a detrital sedimentary system to a carbonate sedimentary system. Until the early stage of middle Ordovician, it was reforming into a detrital sedimentary system. Due to the compression of two plates (Yangtze Plate and Cathaysian Plate) during the late Ordovician-early Silurian period, the Xiuwu Basin was crushed to form a foreland basin. The water body in the area became deeper, and approximately 20-30 m of organic-rich shale was deposited [32]. Under the influence of the Caledonian movement in the Late Silurian period, the Xiuwu Basin was uplifted to become ancient land. In the Devonian and Carboniferous periods, the frequent uplift and subsidence alternated with each other and deposited thin strata. The Permian and Early-middle Triassic periods were the main subsidence periods of the Xiuwu Basin, in which the sedimentary environment was a carbonate platform. In the late Triassic, the North China plate collided with the South China plate, which caused the uplift of the Xiuwu Basin and seawater withdrawal from this area, which indicated the end of the marine deposition period [31, 33].

2.2. Lithology and Lithofacies Characteristics. In this paper, our target layer is a set of strata that was widely deposited through the Yangtze plate in the late Ordovician-early Silurian. Due to its wide distribution, these strata have different names in different regions. A unit in the upper Yangtze region was designated as the Wufeng- no. 1 member of the Longmaxi Formation. Another unit in the lower Yangtze region was called as the Xinkailing- no. 1 member of the Lishuwo Formation. The upper Ordovician Wufeng Formation corresponds to the upper Ordovician Hirnantian Formation, and the no. 1 member of the Longmaxi Formation corresponds to the lower Silurian Rhuddanian Formation. The focus of this paper is on the Xinkailing Formation- no. 1 member of the Lishuwo Formation in the lower Yangtze region and the Wufeng Formation- no. 1 member of the Longmaxi Formation in the upper Yangtze region.

The sea area shrank, and a thin deposit of the Wufeng Formation formed during the late Ordovician when the study area in the upper Yangtze became surrounded by paleouplifts. A black clastic rock series mainly developed in the Wufeng Formation. The lithology of the formation is dominated by black siliceous shale with a small amount of marl in the upper part and abundant graptolites (Figures 2(b) and 2(d)). A restricted deep shelf water mainly constituted the sedimentary environment in the study area during the Early Silurian. The no. 1 member of the Longmaxi Formation (the lowest part) developed a graptolite-rich black clastic rock series (Figure 2(f)). Its lithology is mainly black organic siliceous shale. Because the relative sea level decreased and sedimentary water body became shallow, the lithology of the upper Longmaxi Formation is gray silty shale.

The lithological characteristics of the upper Ordovician-lower Silurian in the lower Yangtze region are similar to those in the upper Yangtze region. The upper Ordovician Xinkailing Formation mainly comprises gray and black siliceous shale (Figures 2(a) and 2(c)) and is similar to the Wufeng Formation in the upper Yangtze area. The no. 1 member of the lower Silurian Lishuwo Formation consists of black siliceous shale and is similar to the no. 1 member of the Longmaxi Formation (Figure 2(e)).

3. Samples and Experimental Data Sources

3.1. Elemental Logging Data. In this study, the X-1 and Y-1 wells in the upper Yangtze and lower Yangtze regions, respectively, were selected for the analysis of the mechanism underlying sedimentary organic matter enrichment during the late Ordovician-early Silurian. We collected elemental logging data for U, Si, Al, and Th from two wells, which are provided by the Schlumberger Corp., and took a data point every 0.125 m.

3.2. Elemental Analysis. In this paper, we took 15 core samples from the Wufeng Formation- no. 1 member of the Longmaxi Formation in the X-1 well and collected 85 core samples from the Xinkailing Formation- no.1 member of the Lishuwo Formation in the Y-1 well for elemental analysis. All core samples were taken every 0.5 m~1 m. The element analysis of cores from two wells was carried out by an X-ray fluorescence spectrometer (Axios mAX), and the volume percentage of Al, Fe, and Mn was obtained.

3.3. TOC Content Analysis. A total organic carbon analyzer (OG-2000 V) was used to test the TOC of 63 core samples from the Wufeng Formation- no. 1 member of the Longmaxi Formation in the X-1 well and 93 core samples from the Xinkailing Formation- no. 1 member of the Lishuwo Formation in the Y-1 well, in which some of the data comes from Zhang et al. [14]. All of the samples were ground to 200 mesh before TOC analysis.

3.4. Silicon Isotope Analysis. Three core samples from the upper Ordovician Xinkailing Formation-lower Silurian no.1 member of the Lishuwo Formation in Y-1 well were selected for silicon isotope analysis by MC-ICP-MS in the Chinese Academy of Sciences. The sample numbers and depth can be shown in Table 1. The silicon isotope analysis method is SiF_4 method, by which the samples were ground into 200 mesh, calcined, and then soaked in HCl to remove siderite and other sulfides and then organic matter was removed. Then the purified sample (SiO_2) was reacted with BrF_5 at a constant temperature of 550°C to form SiF_4 gas. Finally, the purified SiF_4 gas, which was obtained through N_2 trap purification process, was measured by mass spectrometry based on international standard NBS-28 and the analytical accuracy was (+0.1).

4. Results and Discussion

4.1. Proxies of Redox Environment and Paleoproductivity

4.1.1. Redox Environment Proxies. The use of trace elements to determine the sedimentary environment is a commonly applied method [34–36]. Based on previous studies, the ratio of U/Th can be used to determine the water redox environment because U exists in a strongly reducing environment as insoluble U^{4+}, resulting in the enrichment of U in the sediments, where in an oxidation environment, U exists in the form of soluble U^{6+}; because Th is not affected by the redox environment of the water body, the U/Th ratio can be used to reflect the sedimentary redox environment [34]. In this study, the selected U/Th ratio varies continuously and can reflect changes in the water redox environment. Generally, when U/Th > 1.25, the water body is an anaerobic environment; when the ratio of U/Th is between 0.75 and 1.25, the water represents an oxygen-deficient environment; when U/Th < 0.75, the water represents an oxidation environment (Figure 3) [36].

The U/Th ratio was used to characterize the redox environment of the water body. The test results showed that the bottom of the X-1 well had the highest U/Th ratio. The U/Th ratio at this location reached a value of 2, which is more than 1.25. This result confirms that the water body in the upper Yangtze region was strongly reducible during the late Ordovician-early Silurian periods. The gradual decrement in the U/Th ratio to 0.3 from the bottom to the upper parts

(a) (b) (c) (d) (e) (f)

Figure 2: Shale cores from the X-1 well and Y-1 well. (a) Upper Ordovician Xinkailing Formation, 1360 m, Y-1 well, black siliceous shale; (b) upper Ordovician Wufeng Formation, 2523 m, X-1 well, black siliceous shale; (c) upper Ordovician Xinkailing Formation, 1362 m, Y-1 well, grey siliceous shale; (d) upper Ordovician Wufeng Formation, 2523 m, X-1 well, black siliceous shale with a large amount of graptolites; (e) no. 1 member of the lower Silurian Lishuwo Formation, 1336 m, Y-1 well, organic rich shale; (f) no. 1 member of the lower Silurian Longmaxi Formation, 2520 m, X-1 well, organic rich shale; see Figure 1 for the location of the outcrop and well site.

Table 1: Silicon isotope analysis of the upper Ordovician-lower Silurian shale in the Y-1 well. See Figure 1 for the well location.

Number	Well	Depth (m)	Formation	$\delta^{30}Si$
1	Y-1	1300	Lishuwo	-0.15
2	Y-1	1360	Xinkailing	-0.09
3	Y-1	1362	Xinkailing	-0.11

of the well indicates that the water environment in this area changed from an anoxic environment to a dysoxic environment and then to an oxic environment. The U/Th ratio of the Y-1 well in the Xinkailing Formation was high and ranged from 0.5 to 1. This U/Th ratio range is indicative of a dysoxic environment. The U/Th ratio of the upper part of the well was less than 0.25 and represents an oxic environment.

4.1.2. Paleoproductivity Proxies. The primary productivity of a water body can be measured by the two factors of nutrient abundance and organic carbon flux [37]. The more abundant nutrients are in the surface water, the stronger photosynthesis and greater productivity will enhance the organic carbon flux of the water body. The elements that can reflect the nutrient degree of the water body are C, N, P, Fe, Cu, Ni, and Zn. However, the contents of C, N, P, and Fe are greatly influenced by water recirculation and diagenesis, which makes it difficult to represent the content of those elements at a particular time [38]. Therefore, it is not reliable to use those elements as proxies of paleoproductivity. Nevertheless,

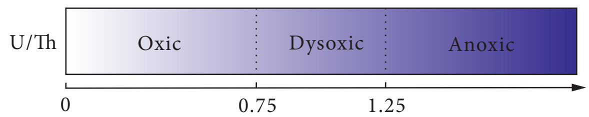

Figure 3: The correlation chart for U/Th identified as reliable indices of depositional conditions. The chart is modified from Jones and Manning [35]. See Figure 1 for the well location.

we can use Ba to reflect the paleoproductivity in the water body because there is a high concentration of SO_4^{2-} on the surface of rotted organic matter, which is formed by the oxidation of H_2S. This easily reacts with the Ba^{2+} in water to produce precipitation that leads to the high content of $BaSO_4$ in a high-paleoproductivity area [37, 38].

In this study, we use Ba as a proxy of paleoproductivity. This Ba has two source origins: terrestrial and biogenic. The Ba from biogenic sources is called excess barium (Ba_{XS}). To yield the Ba_{XS} and exclude the influence of terrestrial sources, we need to calibrate the Ba content using the following correction formula:

$$Ba_{XS} = Ba_{total} - Al_{total}\left(\frac{Ba}{Al}\right)_{PAAS}. \quad (1)$$

Ba_{XS} represents the excess value of Ba, Ba_{total} and Al_{total} are the total contents of Ba and Al in the tested samples, respectively, and $(Ba/Al)_{PAAS}$ is the ratio of Ba and Al in the standard Australian shale [39].

4.2. The Mechanism Underlying Sedimentary Organic Matter Enrichment in the Upper Yangtze Region

4.2.1. Silicon Source Analysis. The X-1 well is located in the Changning-Weiyuan shale gas block of the southern Sichuan Basin in the upper Yangtze region, where the exploration target is the upper Ordovician Wufeng-lower Silurian Longmaxi Formation. To accurately analyze the source of siliceous minerals, this study utilizes the concept of excess silicon. The siliceous sources can be classified as terrigenous clastic silicon, hydrothermal origin silicon, and biogenic silicon [40–43]. Excess silicon (abbreviated as Si_{ex}), which refers to all siliceous minerals except those from normal terrigenous clastic deposits, can be calculated by the following equation:

$$Si_{ex} = Si_s - \left[\left(\frac{Si}{Al}\right)_{bg} \times Al_s\right]. \quad (2)$$

Si_s represents the silicon content in the sample, Al_s is the content of aluminum in the sample, and $(Si/Al)_{bg}$ is the average content in shale, which is taken as 3.11 [19].

We use this equation to calculate the excess silicon content of the upper Ordovician Wufeng Formation-lower Silurian no.1 member of the Longmaxi Formation in the X-1 well. As shown in Figure 4, the Wufeng Formation and the lower part of the no. 1 member of the Longmaxi Formation contain a large amount of excess silicon. In more than half of the layers where excess silicon exists, the excess silicon content in more than half of the layers is between 5% and 15%, even reaching as high as 15% to 20% and as low as 0% to 5% in a few layers; while the excess silicon content in the upper part of the Longmaxi Formation gradually decreases, it generally ranges from 0% to 5% and even contains terrigenous clastic silicon.

Using the method of an Al-Fe-Mn triangular diagram to determine the source of siliceous minerals, we can determine whether the siliceous minerals in this area are hydrothermal or biogenic in origin [20–22]. In this paper, the test values of Al, Fe, and Mn in the Wufeng Formation- no. 1 member of the Longmaxi Formation, where there is excess silicon, are recorded on the triangular diagram. As shown in Figure 5, these values nearly plot in the biogenic zone, indicating that this excess silicon comes from biogenesis.

4.2.2. Analysis of Water Closure. According to previous studies, during the early stage of the late Ordovician-early Silurian, the water body in the upper Yangtze region was divided into upper and lower layers. The upper water body was an oxic zone, which was beneficial to the growth and reproduction of organisms, and it provided a rich source of organic matter for the sediment. In contrast, the lower water body was a suboxic zone that hindered the decomposition of sediments and was conducive to the preservation of organic matter. During the late stage of the early Silurian, the lower water body gradually mixed with warm water from the upper layer. Additionally, high sedimentation rates facilitated organic matter oxidation, which is not conducive for organic matter preservation. As a result, the reducing environment was damaged and sedimentary organic matter underwent oxidization and decomposition, causing the decrease of organic matter abundance [17, 44–46].

The above conclusion can be verified on the basis of the data shown in Figure 4. The trend exhibited by Ba_{XS} (excess Ba), which was used to characterize the paleoproductivity of the water body, is the same as that exhibited by the content of biogenic excess Si. This trend shows that high biological productivity is associated with high biogenic excess Si content. These trends decrease gradually from the bottom upwards, indicating that the paleoproductivity declined as the reducibility of the water body decreased. The U/Th ratio used to characterize the redox environment is largest at the bottom, up to 2, which is more than 1.25, indicating that the reducibility of the water body in the upper Yangtze region was very strong in the late Ordovician-early Silurian. Then the U/Th ratio gradually decreases to 0.3 from the bottom to the upper part, indicating that the water environment in the study area changed from an anaerobic environment to an oxygen-deficient environment and then to an oxidation environment and the reducibility of water gradually weakened. The changing trend of TOC content indicates that in the early stage of the late Ordovician-early Silurian period, the strong water closure resulted in high paleoproductivity and an anaerobic reduction environment and the TOC content in the lower part of the Wufeng Formation- no. 1 member of the Longmaxi Formation ranged from 2% to 5%. Subsequently, with the weakening of the water closure in

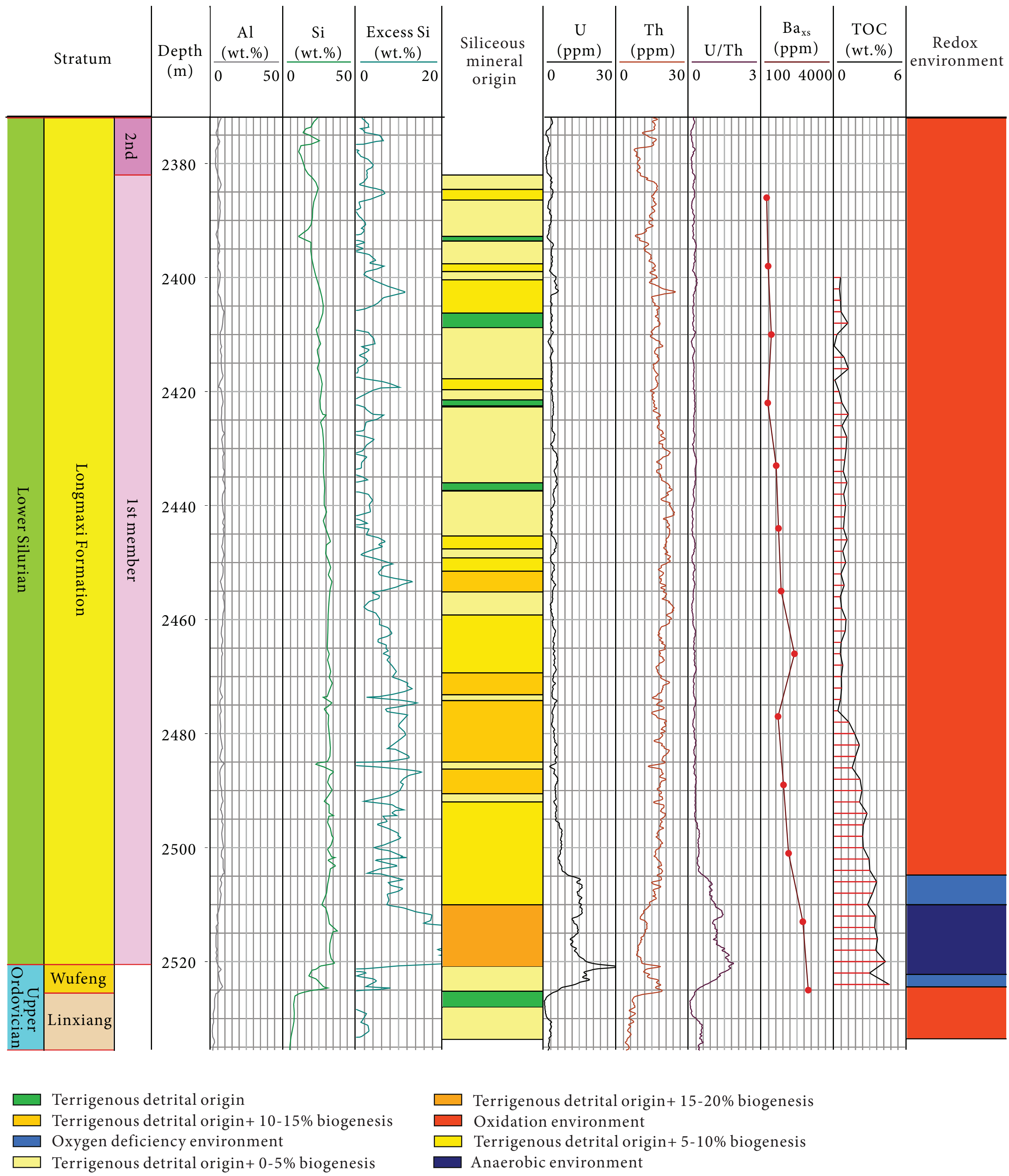

Figure 4: Excess silicon content, redox environment characteristics, paleoproductivity (Ba$_{xs}$) and TOC content of the upper Ordovician Wufeng Formation-lower Silurian no. 1 member of the Longmaxi Formation from the X-1 well in the upper Yangtze region. See Figure 1 for the well location.

the upper part of the no. 1 member of the Longmaxi Formation, the TOC content decreased to less than 2%.

4.3. The Mechanism Underlying Sedimentary Organic Matter Enrichment in the Lower Yangtze Region

4.3.1. Silicon Source Analysis. The Y-1 well is located in the shale gas block of the Xiuwu Basin in the lower Yangtze region, where the exploration target is the upper Ordovician Xinkailing Formation-lower Silurian no. 1 member of the Lishuwo Formation. We use the same method as described

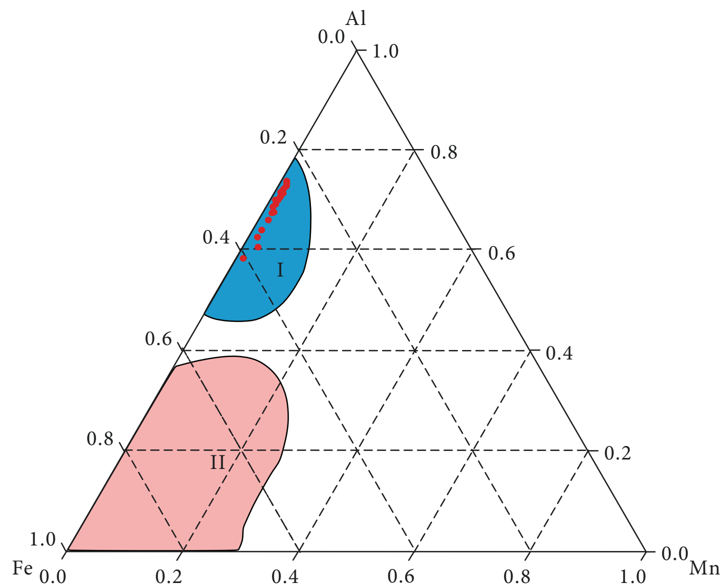

Figure 5: Al-Mn-Fe content and origin analysis diagram for the siliceous minerals from the upper Ordovician Wufeng Formation-lower Silurian no. 1 member of the Longmaxi Formation in the X-1 well. The values of excess silicon are nearly all in the biogenic zone, indicating that the excess silicon is derived from biogenesis. The base map is from Wedepohl [20], Adachi et al. [21], and Yamamoto [22]. See Figure 1 for the well location. I: bio-origin; II: hydrothermal origin.

above to calculate the excess silicon content. From Figure 6, it can be seen that the Xinkailing Formation and the lower part of the no. 1 member of the Lishuwo Formation contain a large amount of excess silicon. In the layers with excess silicon content, the layer with excess silicon content ranging from 0% to 5% accounts for more than 50%; in some layers, this content ranges from 5% to 15%, and even up to 20%. However, in the upper part of the no. 1 member of the Lishuwo Formation, most siliceous minerals originate from terrigenous debris and they have a small amount of excess silicon between 0% and 5%. Next, we record the values of Al, Fe, and Mn in the layers where there is excess silicon on a triangular diagram. As shown in Figure 7, the values of excess silicon are nearly all in the hydrothermal zone, which indicates that excess silicon is derived from a hydrothermal origin.

The conclusion mentioned above can also be proved by the results of silicon isotope analysis. Considering that the δ^{30}Si value in siliceous rocks has regular changes in different sedimentary environments, Si isotope analysis can be considered as a reliable method for judging the source of silica and its depositional environment. Based on the previous research, the δ^{30}Si value of quartz from the hydrothermal source is very small, only ranging from -1.5‰ to +0.8‰; the δ^{30}Si value of authigenic quartz in groundwater ranges from +1.1‰ to +1.4‰, while the δ^{30}Si value of quartz in metasomatism siliceous rock is higher, ranging from +2.4‰ to +3.4‰ [40, 47, 48]. In this study, the δ^{30}Si values of the three core samples from the upper Ordovician Xinkailing Formation-lower Silurian no. 1 member of the Lishuwo Formation shale in the Y-1 well were -0.15‰, -0.09‰, and -0.11‰, respectively, as shown in Table 1 (the samples are numbered from 1 to 3), indicating that in the late Ordovician-early Silurian period, the sedimentary environment of the study area was an oceanic basin affected by the hydrothermal activity between the Yangtze plate and the Cathaysian plate.

4.3.2. Hydrothermal Activity. The large amount of silicon that is hydrothermal in origin in the Xinkailing Formation no. 1 member of the Lishuwo Formation of the Y-1 well is related to the more active compressive movements of the Yangtze Plate and the Cathaysian Plate during the late Ordovician-early Silurian period [49–51]. This hydrothermal activity not only formed the siliceous minerals in the shale but also affected the redox environment and the paleoproductivity of the water body, thus affecting the organic matter abundance. According to previous studies, reducing hydrothermal fluid can form a dysoxic environment after entering the bottom of the sea, which is conducive to the preservation of organic matter [31, 52]. Additionally, hydrothermal activity in the Xiuwu Basin during the Late Ordovician-Early Silurian is related to the redox environment of the water body. As shown in Figure 6, the hydrothermal origin silicon contents in the Xinkailing Formation and the lower part of the no. 1 member of the Lishuwo Formation from the Y-1 well range from 5% to 20%. These values indicate that hydrothermal activity in the late Ordovician-early Silurian period was frequent. Additionally, the U/Th ratio of this area is relatively high, ranging from 0.5 to 1, which indicates an oxygen-deficient environment; however, in the upper part of the no. 1 member of the Lishuwo Formation, most siliceous minerals are derived from a terrigenous detrital origin. Here, the content of hydrothermal-origin silicon is small, ranging only from 0% to 5%. This indicates that the hydrothermal activity was weakened during the late depositional period of the no. 1 member of the Lishuwo Formation. The U/Th ratio in the upper part was less than 0.25, indicating an oxidation

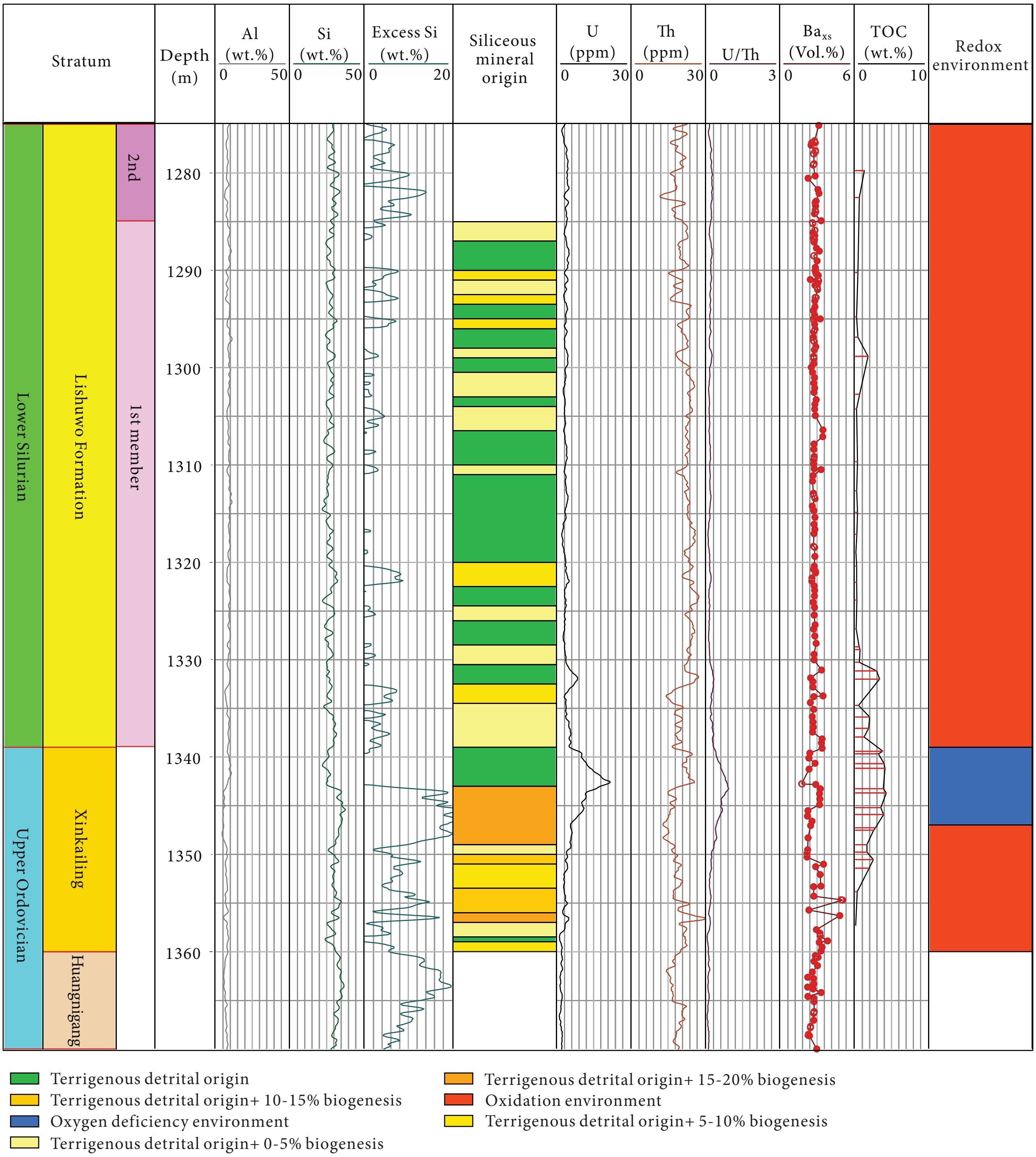

Figure 6: Excess silicon content, redox environment characteristics, paleoproductivity (Ba_{xs}) and TOC content of the upper Ordovician Xinkailing Formation-lower Silurian no. 1 member of the Lishuwo Formation from the Y-1 well in the lower Yangtze region. The figure is modified from Zhang et al. [14]. See Figure 1 for the well location.

environment. Thus, the above data strongly indicate that hydrothermal activity affected the redox conditions of the water body in this area.

Hydrothermal activity is also closely related to paleoproductivity. Based on previous research, Halbach et al. [53] found that the closer to the hydrothermal activity area the water body is, the greater the number of organisms and the greater their activity are. In addition, McKibben et al. [54] and Korzhinsky et al. [55] considered that hydrothermal fluid can carry many trace elements into the ocean, which are necessary for marine organisms. These trace elements can provide nutrients for marine organisms and promote their growth. After the death of these marine organisms, organic carbon in their bodies sinks to the bottom of the

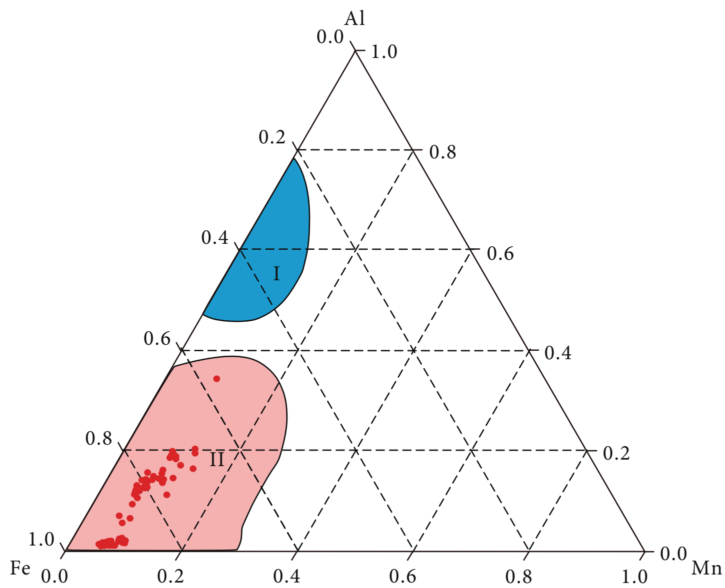

Figure 7: Al-Mn-Fe content and origin analysis diagram for the siliceous minerals from the upper Ordovician Xinkailing Formation-lower Silurian no. 1 member of the Lishuwo Formation in the Y-1 well. The values of excess silicon are nearly all in the hydrothermal zone, indicating that the excess silicon is derived from a hydrothermal origin. The base map is from Wedepohl [20], Adachi et al. [21], and Yamamoto [22]. See Figure 1 for the well location. I: bio-origin; II: hydrothermal origin.

ocean, providing material sources for the source rocks. According to Figure 6, the hydrothermal-origin silicon content in the Xinkailing Formation and the lower part of the no. 1 member of the Lishuwo Formation is high, reflecting that frequent hydrothermal activity occurred during the deposition period. In the layers with high hydrothermal-origin silicon contents, the excess barium content used to characterize paleoproductivity of the water body is higher than that in the upper part of the no. 1 member of the Lishuwo Formation. This section exhibits weak hydrothermal activity, which suggests that hydrothermal activity in the Xiuwu Basin promoted paleoproductivity during the late Ordovician-early Silurian period.

Based on the above analysis, we can conclude that in the lower Yangtze region, the active hydrothermal activity close to the junction of the two plates during the early stage of late Ordovician-early Silurian period led to high paleoproductivity and an oxygen-deficient environment. However, in the late stage of the early Silurian period, hydrothermal activity weakened, causing enhanced water oxidation. According to the TOC contents of shale samples from the region (the TOC content in the Xinkailing Formation and the lower part of the no. 1 member of the Lishuwo Formation ranges from 2% to 4%, and the TOC content in the upper part of the Lishuwo Formation falls below 2%; see Figure 6), hydrothermal activity in the lower Yangtze region controlled the enrichment of organic matter.

4.4. The Mechanism Underlying Sedimentary Organic Matter Enrichment in the Upper Ordovician-Lower Silurian Shale from the Yangtze Region

4.4.1. The Upper Yangtze Region. As shown in Figure 8, during the late Ordovician-early Silurian period, large-scale tectonic uplift occurred in the upper Yangtze region due to the compression of the Yangtze plate and the Cathaysian plate, resulting in a deep-water shelf environment surrounded by ancient land. Because this region was restricted by ancient land, the water closure in the upper Yangtze region was very strong. In this case, the water body in the upper Yangtze region was divided into upper and lower layers. The upper water body was an oxic zone, which was beneficial to the growth and reproduction of organisms. Meanwhile, the lower water body was a suboxic zone that hindered the decomposition of sediments, which was conducive to the preservation of organic matter from the upper layer, thereby contributing to the enrichment of sedimentary organic matter.

4.4.2. The Lower Yangtze Region. As shown in Figure 9, during the late Ordovician-early Silurian period, the lower Yangtze region was deformed to form a foreland basin due to the compression of the Yangtze plate and the Cathaysian plate. Meanwhile, seawater entered the fractures near the junction of the two plates and carried deep material from the crust, which was heated to form hydrothermal fluid with abundant minerals. Under the action of upwelling, hydrothermal fluid entered the deep-water shelf and it affected the redox environment and the paleoproductivity of the water body. On the one hand, the nutrients carried by the hydrothermal fluid contributed to the growth of marine organisms, which provided material sources for the source rocks. On the other hand, hydrothermal fluid can form an oxygen-deficient environment after entering the bottom of the sea, which is conducive to the preservation of organic matter. Thus, hydrothermal activity in the lower Yangtze region controlled the enrichment of organic matter.

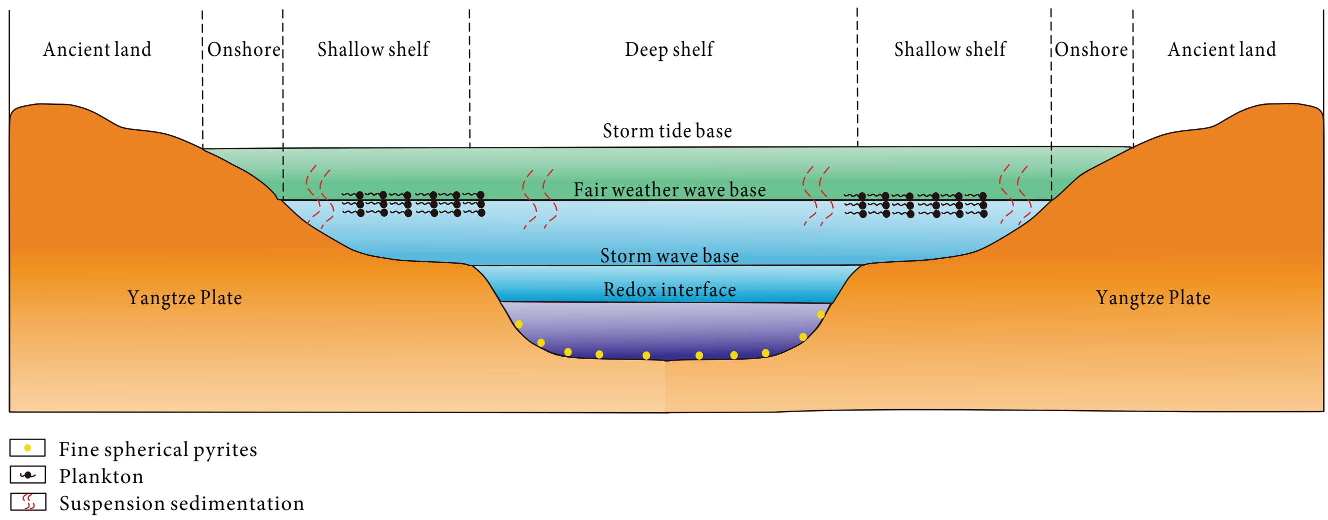

Figure 8: The mechanism underlying sedimentary organic matter enrichment in the upper Ordovician-lower Silurian shale from the upper Yangtze region. The water body was divided into upper and lower layers by a redox interface [55].

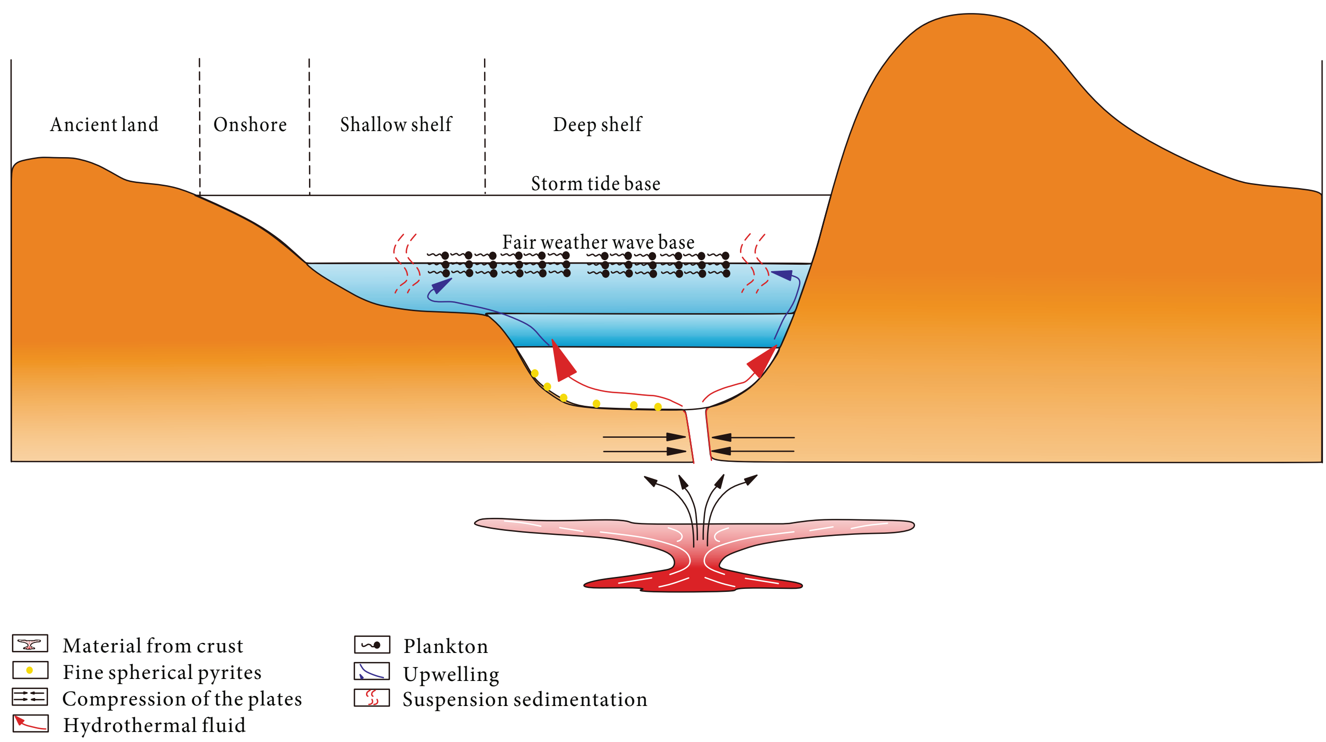

Figure 9: The mechanism underlying sedimentary organic matter enrichment in the upper Ordovician-lower Silurian shale from the lower Yangtze region. The active hydrothermal activity near the junction of the two plates (Yangtze Plate and Cathaysian Plate) led to high paleoproductivity and an oxygen-deficient environment [31, 44].

5. Conclusions

(1) Excess silicon in the upper Ordovician-lower Silurian shale in the upper Yangtze region is derived from biogenesis, while the shale in the lower Yangtze region is derived from a hydrothermal origin. Their content is positively correlated with TOC (total organic carbon) content

(2) In the upper Yangtze region, the strong water closure controlled the enrichment of organic matter during the late Ordovician-early Silurian. The strong water closure resulted in water delimitation. The upper water body was an oxic zone, which was beneficial for the growth of marine organisms. However, strong water oxidation resulted in organic matter decomposition and low TOC content. The lower water body

was a suboxic zone that hindered sediment decomposition. This effect was conducive for the preservation of organic matter from the upper layer. Organic matter preservation, in turn, resulted in high Ba_{XS} and TOC content and contributed to the enrichment of sedimentary organic matter. For the upper Ordovician-lower Silurian shale in the upper Yangtze region, exploration should be conducted in the center of the blocks with high TOC contents and strongly reducing water body

(3) In the lower Yangtze region, hydrothermal activity close to the junction of the two plates controlled the enrichment of organic matter. Hydrothermal activity not only carried nutrients into water, contributing to the growth of marine organisms that promoted paleoproductivity, but also formed an oxygen-deficient environment that was conducive to the preservation of organic matter, resulting in high TOC content in shale. During the sedimentary period of the upper part of the no. 1 member of the Lishuwo Formation, the hydrothermal activity was weakened, which caused a decrease in the TOC content of shale. For the upper Ordovician-lower Silurian shale in the lower Yangtze region, exploration should be conducted in the blocks near the junction of the two plates where hydrothermal activity was active

Data Availability

The well location data derived from drilling data in the study area are included in Figure 1. The contents of Al, Fe, and Mn which were analyzed by X-ray fluorescence (Axios mAX) and used to judge the genesis of excess > silicon (Si ex) and are included within the article (15 cores from the Wufeng Formation no. 1 section of the Longmaxi Formation in the X-1 well and 85 cores from the Xinkailing Formation no.1 section of the Lishuwo Formation in the Y-1 well; see Figures 5 and 7). The U/Th data used to support the findings of water redox environment are included within the article (the contents of U and Th elements were derived from logging data by Schlumberger Corp., which take a point at every 0.125 meters. The original data is shown in Figures 4 and 6). The contents of excess barium (Ba XS) were calculated by formula (1) and used to support the findings of paleoproductivity (the contents of Al and Ba were analyzed by X-ray fluorescence (Axios mAX)). (13 cores from the Wufeng Formation no. 1 section of the Longmaxi Formation in the X-1 well and 190 cores from the Xinkailing Formation no.1 section of the Lishuwo Formation in the Y-1 well. The original data is shown in Figures 4 and 6). The contents of excess silicon (Si ex) were calculated by formula (2) and used to support the source of siliceous mineral (the contents of Al and Si elements were derived from logging data by Schlumberger Corp., which take a point at every 0.125 meters. The original data is shown in Figures 4 and 6). The TOC content data used to support the findings of organic matter enrichment are included within the article (a total organic carbon > analyzer (OG-2000 V) was used to test the TOC of 63 cores from the Wufeng Formation no. 1 section of the Longmaxi Formation in the X-1 well and 93 cores from the Xinkailing Formation no. 1 section of the Lishuwo Formation in the Y-1 well. The original data is shown in Figures 2 and 4).

Additional Points

Highlights. (1) Excess silicon in the upper Ordovician-lower Silurian shale in the upper Yangtze is biogenic; excess silicon in the lower Yangtze region is derived from hydrothermal solution. (2) In the upper Yangtze region, strong water closure increased the paleoproductivity of the ancient ocean; additionally, it enhanced the reducibility of the bottom water in the ocean, which controlled the enrichment of sedimentary organic matter. (3) The hydrothermal activity in the lower Yangtze region increased the paleoproductivity by providing nutrients to the organisms and enhanced the reducibility of water, thus enriching the sedimentary organic matter.

Disclosure

Part of the work in this paper has been presented as an abstract at the GSA Annual Meeting in Indianapolis, Indiana, USA, 2018.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Ming Wen and Kun Zhang contributed equally to this work.

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