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Sedimentary Paleoenvironment and Organic Matter Enrichment of the Ying 4 Member in the Southern Shuangcheng Area, Songliao Basin

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Abstract: Based on organic carbon content measurement, kerogen microscopic examination, and the analysis of source rock maturity and major/trace elements, this study restores the sedimentary paleoenvironment of the Ying 4 Member in the southern Shuangcheng area, Songliao Basin, and determines the main controlling factors of the region's organic matter enrichment. The results indicate that the organic carbon content of the source rock in the study area is 0.51%–8.29%, with a mean value of 2.48%. The average total organic carbon (TOC) value of the source rock reaches 2.35%, and the kerogen type index (KTI) is mainly distributed between 1.6 and 39.5, with an average of 21.5. The organic matter type is II_2. The rock core test shows that the vitrinite reflectance (*Ro*) is 0.83%–0.97%, with an average of 0.90%, demonstrating that the source rock in the study area has entered the peak hydrocarbon-generation stage. During the deposition of Ying 4 Member, the paleoclimate was warm and humid, and the corresponding sedimentary paleoenvironment was brackish water, having a typical reducing condition with low oxygen content and good primary productivity. In addition, intense volcanic activity have occurred, and the generated volcanic ash and hydrothermal fluids have transported substantial nutrients to the lake basin, promoting the development of algae in the water. The crossplot of the TOC content of dark shale against multiple paleoenvironment indexes shows that the organic matter enrichment in the Ying 4 Member is mainly controlled by paleoproductivity and the paleoclimate, but not associated with redox conditions and paleosalinity. Only warm conditions with high paleoproductivity can lead to organic matter enrichment, and regional volcanic activity plays a significant role in increasing paleoproductivity. Overall, the organic matter enrichment in the study area can be described by the productivity model.

Keywords: southern Shuangcheng area; source rock; Ying 4 Member; organic matter enrichment; main controlling factors

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1. Introduction

High-quality source rock is the basis for oil and gas generation, and the formation mechanism and distribution of source rock are essential for oil and gas exploration. For small-scale faulted basins with rapid phase change, the deposition environment change exerts a strong influence on source rock [1]. The major and trace elements within sedimentary rocks are significant records that remained in strata during the evolution of the deposition environment. In recent years, researchers have established multiple indexes to identify and evaluate different sedimentary environments based on element geochemistry data [2]. Specifically, Sr/Cu was proposed to determine paleoclimate conditions, Sr/Ba was employed to recognize paleosalinity, and V/(V + Ni) and V/Cr were commonly used to identify oxidation and reducing environments. The element Mo and some biomarkers were also utilized to analyze paleoproductivity and the organic matter (OM) source [3–6]. Numerous studies have demonstrated that sedimentary environment factors, including paleosalinity, paleoproductivity, and redox conditions, affect the quality of source rock by controlling OM preservation and enrichment [7–10]. Furthermore, it is indicated that primary productivity and redox conditions are the main controlling factors for source rock formation [11,12], and two OM enrichment models have been proposed: the productivity model and the preservational model [13,14]. The productivity model considers that high productivity in surface waters is the essential condition for OM enrichment, while the preservational model emphasizes that the main reason for OM enrichment is the oxygen deficiency in oceans and lakes [15]. In addition to the two models, Xu [16] suggested that OM enrichment and the formation of high-quality source rocks are controlled by both productivity and anoxic conditions. Other factors, such as terrigenous detrital sediments, deposition rate, and the precipitation rate of carbonates, are also suggested to be responsible for OM enrichment [17].

Since 2019, the Denglouku Formation and Yingcheng Formation in the southern Shuangcheng region have made significant advancements in oil and gas development, demonstrating the area's potential for hydrocarbon resources. Several scientists have conducted a series of studies on the source rocks of the Ying 4 Member in the Shuangcheng Depression. The findings indicate that the average total organic carbon (TOC) of the source rocks in the Ying 4 Member of the Shuangcheng area is 2.46%, with type II organic matter predominating in these source rocks. The source rocks are in the mature phase, and the water predominantly represents a reducing environment. By reorganizing hopanes for the purpose of oil source comparability, the findings reveal that oil from the Deng 3 Member is derived from the Ying 4 Member when the source rock maturity is low, suggesting that the Ying 4 Member oil is predominantly near-source oil [18–20]. Prior researchers have examined the geochemical attributes of source rocks and the sedimentary environments of water bodies within the Ying 4 Member; however, the paleoclimate, paleoproductivity levels, relevant controlling factors, and OM enrichment models are still poorly understood. In this study, we conducted TOC measurements, kerogen microscopic examinations, and the analysis of source rock maturity and major/trace elements, aiming at exploring the formation environment of the source rock and deciphering the controlling factors and enrichment models of the OMs in the Ying 4 Member.

2. Geological Setting

The Shuangcheng area is located in the junction of Shuangcheng city, Zhaodong city, and Zhaoyuan county in Heilongjiang province. Tectonically, it is situated to the east of the Daqing placanticline and to the northwest of the southeast uplift area in Songliao Basin. This area includes three depressions (Shuangcheng, Miaotaizi, and Yingshan depressions), covering an area of 2367.7 km^2 (Figure 1). The study area, Shuangcheng depression, is located at the southeast fault depression in the northern Songliao Basin, structurally controlled by the Taipingzhuang and Chaoyang faults, with an area of 1031 km^2 (i.e., the area within the depression-controlling faults). From south to north, the shallow-to-medium structural units in the depression are the Qingshankou anticline, Binxian-Wangfu sag, Changchunling anticline, and Chaoyang terrace. The maximum thickness during the fault-depression stage reached 1800 m [21]. Under the influence of four S-shaped NNE-striking faults, the Yingshan depression, Shuangcheng depression, and Qingshan uplift are developed [18,22].

Since the Cretaceous, the study area has experienced four tectonic evolution stages: fault-depression stage, transformation stage, subsidence stage, and structural inversion stage [23]. The target layer of this study is the Ying 4 Member, corresponding to the late period of fault-depression stage when regional extension was weak. As a result, a variety of sedimentary systems were developed, including deep-to-semideep lake facies and fan deltas [23]. In terms of lithology, the Ying 4 Member is characterized by sand–shale interbedding, with some regionally developed glutenite (Figure 2) [23].

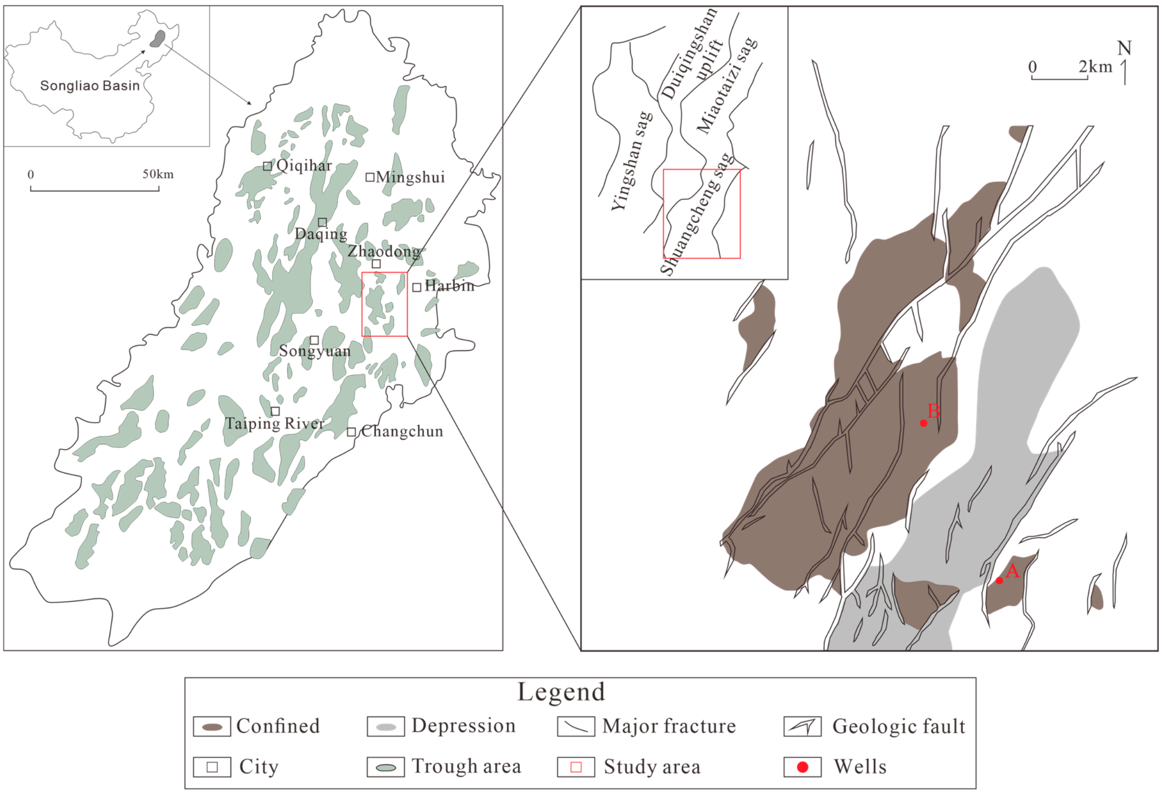

Figure 1. Tectonic map of the study area.

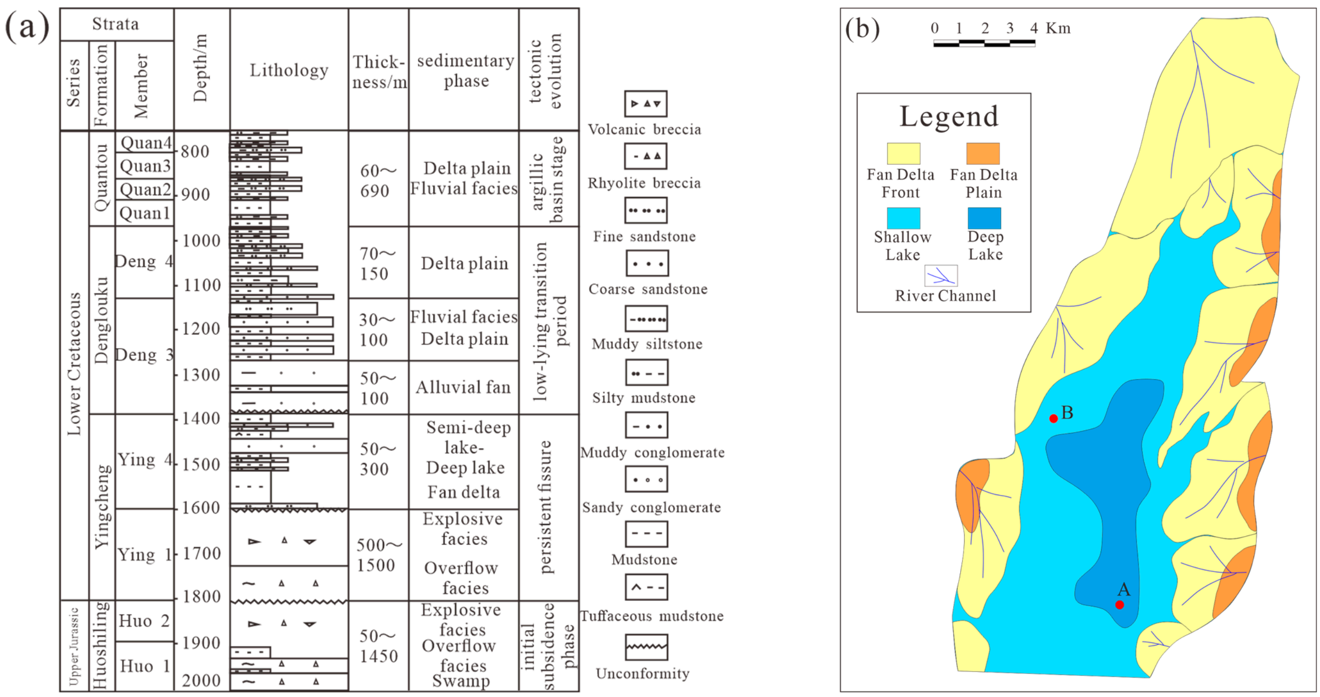

Figure 2. (**a**) Stratigraphy of southern Shuangcheng area (revised from [24]). (**b**) Sedimentary facies map of Ying 4 Member in the southern Shuangcheng area.

3. Sample and Method

To restore the sedimentary environment of the study area and identify the factors affecting organic matter enrichment, this research conducted systematic observations of the Ying 4 Member cores from key wells A and B and collected 69 mudstone samples. Among them, in well A, the Ying 4 Member is primarily characterized by deep lake facies, with the main deposits being black massive or laminated mudstone. A total of 37 samples were collected from depths of 1427.3 to 1443.95 m and 15 samples from 1486.24 to 1494.84 m. In well B, the Ying 4 Member is mainly characterized by shallow lake facies, with the main deposits being black massive mudstone. A total of 17 samples were collected from depths of 1286.04 to 1295.14 m.

The instrument used for measuring TOC content is the German CS580A infrared carbon-sulfur analyzer. To measure the TOC content of the samples, the samples were first ground to 100 mesh and then treated with 5.0% dilute hydrochloric acid. The residue was then washed with distilled water and dried. The Rock-Eval 6 pyrolysis instrument was used for rock pyrolysis analysis. Samples were ground to below 200 mesh, and the powdered samples were rapidly heated to 300 °C, held for 3 min, and the free hydrocarbon (S_1) content was measured. Then, the temperature was raised to 600 °C at a rate of 50 °C/min, held for 1 min, and the pyrolysis hydrocarbon (S_2) content and Tmax value were measured. To measure Ro, the sample needs to be cut into small pieces and then polished. The polished samples are measured for Ro using a CRAIC 508PV microspectrophotometer. The analysis of Ro was conducted based on the industry standard (SY/T 5124-2012) [25]. To analyze organic petrological characteristics, the samples were polished and then observed under an Axio ImagerM2 upright fluorescence microscope. The organic petrological analysis was conducted based on the energy industry standard (NB/T 11287-2023) [26]. To extract chloroform bitumen "A" from the samples, chloroform is used in a Soxhlet extractor to extract the powdered samples for 72 h at an extraction temperature of 72–80 °C. The extract is then evaporated and concentrated to obtain chloroform bitumen "A".

Major and trace element analyses were conducted at the Xi'an Mineral Resources Survey Center of the China Geological Survey. First, 69 selected samples were ground to 200 mesh, dried at 105 °C for 3 h, cooled to room temperature in a desiccator, and then precisely weighed to 0.70 g. The samples were mixed with 7.00 g of lithium borate ($Li_2B_2O_7$) flux to fuse into glass discs in a furnace. A major element analysis was performed using an Axiosmax X-ray fluorescence spectrometer with an analytical error of less than 3%. The dried 0.1 g sample was treated for desalting, and 40 mg of the sample was accurately weighed and added to a 1:10 HF-HNO_3 mixed solution. The solution was sealed and heated at 180 °C for 24 h, then evaporated to dryness. Deionized water and HNO_3 (1 mL each) were added, and the sample was redissolved at 180 °C for 12 h. The solution was diluted to 80 g with 2% HNO_3 and stored at 4 °C. Trace elements were analyzed using an ICPMS (ICAP Q) with an analytical error of less than 5%.

4. Results

4.1. Petrography

Core observations indicate that the hydrocarbon source rock types of the Ying 4 Member are mainly black laminated or massive mudstone (Figure 3g–i). Organic petrology research shows that algae (Figure 3f) and exinite components (Figure 3b) are commonly observed in most samples. In some samples, vitrinite derived from higher land plants was observed (Figure 3b–d). In addition, scattered pyrite particles were observed in most of the samples, manifesting as a bright globular aggregate (Figure 3a,e).

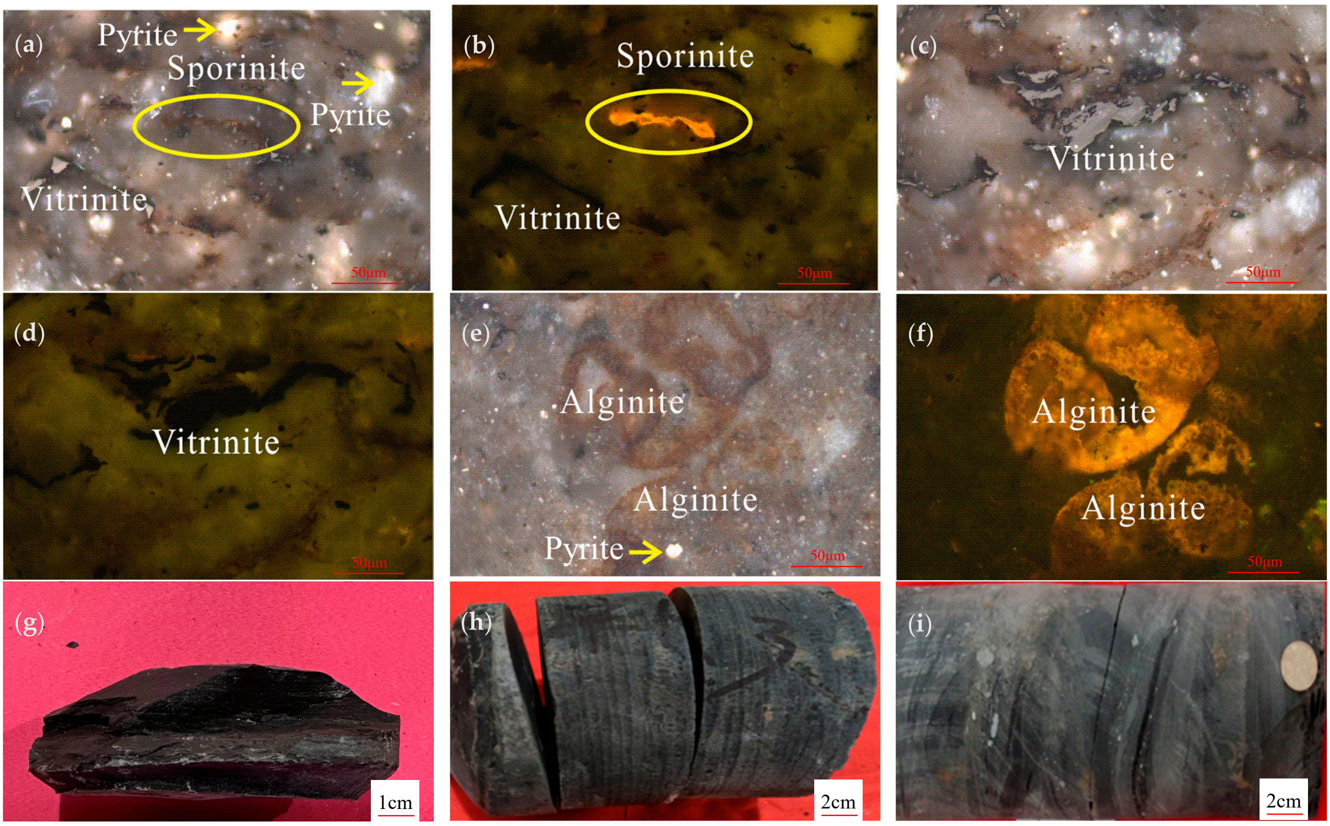

Figure 3. Photos showing the petrology features of the source rock in the Ying 4 Member. Different maceral components are marked in different thin sections (revised from [20]). (**a**–**d**) Vitrinite; (**b**) fusinite; (**a**,**e**) pyrite. (**a**,**b**) 1426.90 m, Well A; (**c**,**d**) 1432.40 m, Well A; (**e**,**f**) 1292.94 m, Well B; (**g**) core of black laminated mudstone (Well A, 1442.56 m); (**h**) core of black massive mudstone (Well A, 1493.68 m); (**i**) core of black massive mudstone (Well B, 1289.64 m).

4.2. Characteristics of Organic Geochemistry

The experimental results in this study have shown that the OM abundance in the Ying 4 Member is 0.51%–8.29%, with an average of 2.48%. The TOC value of Well A is 0.76%–8.29%, with an average of 2.28%, while that of Well B is 0.51%–4.67%, with a mean value of 2.98%. The hydrocarbon potential value is 0.44 mg/g–16.74 mg/g, with an average of 5.64 mg/g. The content of chloroform bitumen "A" is 0.028%–0.3%, with an average of 0.131%. Overall, the OM abundance in the study area is good.

The TI value (TI = (sapropelite × 100 + exinite × 50 − vitrinite × 75 − inertinite × 100)/100) can be used to classify organic matter types [27]. Generally, a TI value greater than 80 indicates kerogen type I, a TI value within 40~80 indicates kerogen type II_1, a TI value within 0–40 indicates kerogen type II_2, and a TI value less than 0 suggests kerogen type III. The TI value of the Ying 4 Member ranges from 1.6 to 39.5, with an average of 21.5, which indicates that the kerogen type is II_2. The Ro of the rock core test is 0.83%–0.97%, with an average of 0.90%, which indicates that the source rock in this area has entered the peak hydrocarbon-generation stage.

4.3. Characteristics of Major and Trace Elements

This study mainly restored paleoclimate, paleosalinity, redox conditions, and paleoproductivity by calculating the characteristic element ratio based on the content of major and trace elements in mudstone. Specifically, paleoclimate indexes include CIA and Sr/Cu values, paleosalinity indexes include Sr/Ba, MgO/Al_2O_3*100, Ca/(Ca + Fe), and Rb/K values, and redox indexes are V/(V + Ni) and Cu/Zn values. In addition, four indexes (P/Ti, Ni/Ti, Cu/Ti, and Zn/Ti) were employed to evaluate the paleoproductivity in the Ying 4 Member

(Table 1). The results of this study show that the CIA and Sr/Cu values are 69.69–82.6 and 2.23–9.59, respectively. The Sr/Ba, MgO/Al_2O_3*100, Ca/(Ca + Fe), and Rb/K values are 0.28–1.53, 0.62–4.04, 0.05–0.65, and 0.0021–0.0065, respectively. The V/(V + Ni) and Cu/Zn values are 0.62–0.90 and 0.06–1.38, respectively, and the P/Ti, Ni/Ti, Cu/Ti, and Zn/Ti values are 0.03–0.16, 0.0018–0.0083, 0.0023–0.0111, and 0.0034–0.1106, respectively.

Table 1. Paleoenvironment index of mudstone in the Ying 4 Member of southern Shuangcheng area.

Paleoenvironment Index		**Well A**	**Well B**
TOC (%)		0.76–8.29 (2.28)	0.51–4.67 (2.98)
Paleoenvironment and paleo-weathering conditions	CIA	74.05–82.60 (78.95)	69.69–79.01 (75.18)
	Sr/Cu	2.23–9.59 (4.60)	2.35–7.33 (4.51)
Paleosalinity	Sr/Ba	0.28–1.46 (0.90)	0.44–1.53 (0.85)
	MgO/Al_2O_3*100	0.62–3.67 (2.19)	2.30–4.04 (3.09)
	Ca/(Ca + Fe)	0.06–0.65 (0.14)	0.05–0.32 (0.11)
	Rb/K	0.0021–0.0059 (0.0040)	0.0028–0.0065 (0.0046)
Redox condition	V/(V + Ni)	0.67–0.90 (0.80)	0.62–0.82 (0.74)
	Cu/Zn	0.06–1.38 (0.16)	0.07–0.18 (0.12)
Paleoproductivity	P/Ti	0.03–0.16 (0.08)	0.04–0.16 (0.07)
	Ni/Ti	0.0018–0.0074 (0.0038)	0.0025–0.0083 (0.0051)
	Cu/Ti	0.0023–0.0111 (0.0059)	0.0044–0.0091 (0.0070)
	Zn/Ti	0.0034–0.1106 (0.0437)	0.0376–0.0764 (0.0591)

Note that the values in the parentheses are average values.

5. Discussion

5.1. Restoration of Sedimentary Paleoenvironment

The formation of sedimentary rocks is closely associated with the paleo sedimentary environment. Therefore, restoring and reconstructing the sedimentary paleoenvironment is critical for studying the origin of rocks and guiding oil and gas exploration [28]. At present, the paleoenvironment can be restored based on multiple features or indexes, including element geochemistry parameters, organic geochemistry parameters, biomarker characteristics, isotopes, paleontological index, petrological index, and mineralogical index. In this study, we restored the sedimentary paleoenvironment based on the characteristic element ratio.

5.1.1. Paleoclimate and Paleoweathering Conditions

The paleoclimate refers to the climatic environment over the course of geological history. Changes in paleoclimate can alter the sedimentary environment in the water and the number of primary producers, thereby affecting the OM enrichment in the source rock. A warm and humid climate is conducive to chemical weathering. Abundant water sources can bring more terrigenous debris supply, carrying extensive nutrients into the lake basin and thus improving the productivity of the lake. As a result, the number of primary producers further increases, leading to an oxygen-deficient environment at the bottom of the water, which is favorable for OM preservation [29,30]. Different climatic conditions can change the content of sensitive elements in the water, and thus, we can determine the paleoclimate based on the method of element geochemistry. The Sr/Cu ratio is sensitive to climate change, and no epigenesis Cu-bearing minerals have been found in the study area, so it can be used to reconstruct the paleoclimate of the area. Specifically, an Sr/Cu ratio between 1 and 10 indicates a warm and humid climate, and a value greater than 10 indicates a dry climate. The Sr/Cu value of the mudstone in Ying 4 Member is between 2.23 and 9.59, with an average value of 4.58, indicating a warm and humid climate (Figure 4).

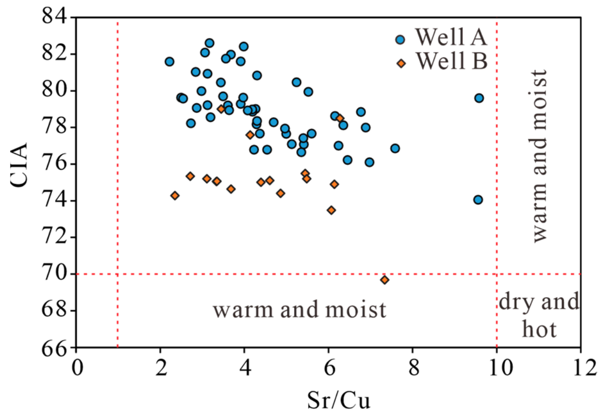

Figure 4. Correlation diagram of Sr/Cu and CIA.

The chemical index of alteration (CIA) is the ratio of Al_2O_3 to unstable oxides. It is a parameter used to quantitatively evaluate the intensity of feldspar chemical weathering, reflecting the degree of feldspar transforming into clay minerals [31]. In the chemical weathering process of the upper crustal rocks, potassium feldspar in the parent rock is the most abundant mineral, and alkali metals such as potassium (K), calcium (Ca), and sodium (Na) gradually diminish in the form of ions through surface runoff. In this process, the content of aluminum oxide (Al_2O_3), which has the most stable chemical composition, gradually increases. Therefore, CIA, as a parameter reflecting the intensity of chemical weathering, can accurately reflect the paleoclimate conditions during the deposition period. Particularly, when the CIA value is between 50 and 70, it indicates a cold and dry paleoclimate, reflecting a weak degree of weathering. When the CIA value is between 70 and 85, it denotes a warm and humid paleoclimate, which implies a moderate degree of weathering. When the CIA value has a range of 85–100, it denotes a hot and dry paleoclimate, indicative of a strong degree of weathering. The CIA value can be obtained through:

$$CIA = Al_2O_3/(Al_2O_3 + K_2O + Na_2O + CaO^*) \times 100 \quad (1)$$

In this formula, the oxides are measured in moles. CaO* refers to the CaO content in silicate minerals; however, non-silicate minerals (phosphates and carbonates) also contain CaO, and thus, the CaO in non-silicate minerals needs to be excluded when calculating the CIA value. The calculation method is $CaO = CaO\text{-}10/3P_2O_5$. If the calculated n (CaO) is higher than n (Na_2O), then n (CaO^*) = n (Na_2O), otherwise n (CaO^*) = n (CaO). The potassium content will gradually decrease during the sediment weathering process. If the potassium metasomatism occurs during diagenesis, the potassium content will increase, leading to a smaller-than-normal CIA value, which needs to be corrected. The triangular graph (Figure 5) shows that the CIA values of the samples are generally parallel to the ideal weathering trend line, indicating that the samples are not affected by potassium metasomatism. Therefore, it can be concluded that the CIA value can effectively determine the weathering degree of the source area. The CIA value ranges from 69.69 to 82.60, with an average of 78.02. Such a medium CIA value range reflects a moderate degree of weathering, indicating a warm and humid climate condition.

In addition, the crossplots of SiO_2-(Al_2O_3 + K_2O + Na_2O) and Ga/Rb-(K_2O/Al_2O_3) suggest that the Ying 4 Member was in a warm and humid sedimentary environment (Figure 6).

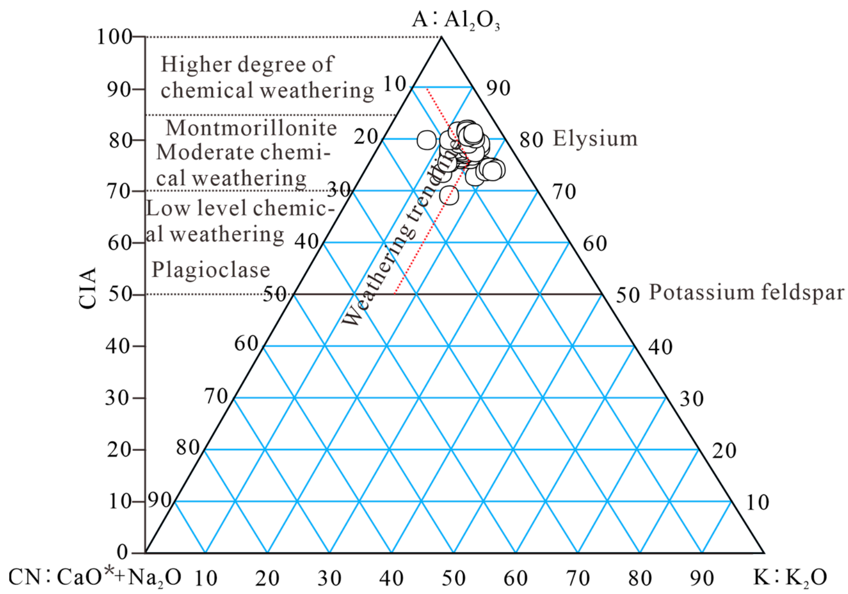

Figure 5. Triangular graph of Al_2O_3, CaO + Na_2O, and K_2O in the Ying 4 Member.

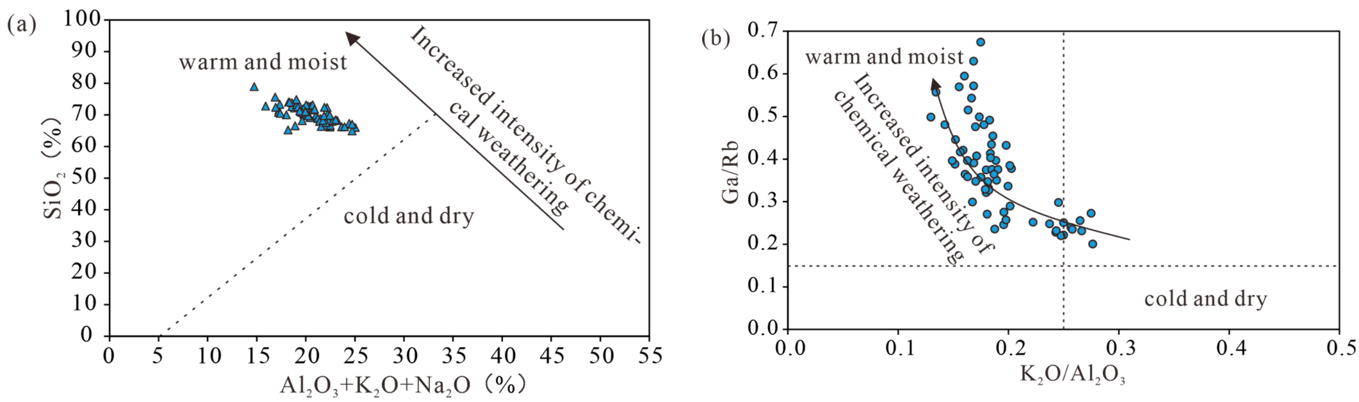

Figure 6. (**a**) Crossplot of SiO_2 against Al_2O_3 + K_2O + Na_2O in the Ying 4 Member; (**b**) crossplot of K_2O/Al_2O_3 against Ga/Rb in the Ying 4 Member.

5.1.2. Paleosalinity

Paleosalinity is a significant index in investigating sedimentary environment since it directly reflects climate and environment change. Different salinity values can result in different organism species and quantity, thereby affecting the formation of source rocks.

The Sr/Ba value is a common index used to determine paleosalinity. The elements Sr and Ba possess similar chemical properties and exist in the form of bicarbonate in water. As the salinity of seawater continues to rise, the two elements will precipitate in different orders due to the different migration abilities and solubilities. In particular, Ba precipitates in the form of barium sulfate, while Sr precipitates when the water salinity becomes higher. When Sr/Ba < 0.5, it represents a freshwater–brackish water environment. Sr/Ba between 0.5 and 1 indicates a brackish water environment. When Sr/Ba > 1, it indicates a saltwater environment [32]. MgO/Al_2O_3*100 is another index for estimating paleosalinity. When MgO/Al_2O_3*100 < 1, it represents a freshwater environment with low salinity. When the value is between 1 and 10, it denotes a marine–terrestrial transition environment. When MgO/Al_2O_3*100 > 10, it indicates a marine environment [33]. Additionally, previous studies have shown that the ratio of Rb/K can also effectively determine paleosalinity. Potassium is mainly distributed in the upper part of the continental crust. It is alkaline and has poor weathering resistance. After weathering, potassium ions drift with the river water, being adsorbed on the surface of clay minerals during the drifting process. Therefore, potassium has a tight relationship with the content of clay minerals, especially illite that adsorbs potassium the most. In general, Rb exists in the form of colloids. Under alkaline reducing conditions, Rb is easily adsorbed and precipitated by clay and organic matters. With the increase in salinity, the Rb/K value gradually increases. When Rb/K < 0.004, it indicates a freshwater environment. When the value has a range of 0.004–0.006, it indicates a brackish water environment. When Rb/K > 0.006, it denotes a saltwater environment [34]. In addition, Ca/(Ca + Fe) can be used to determine paleosalinity. When Ca/(Ca + Fe) < 0.4, it indicates freshwater sedimentation. When 0.4 < Ca/(Ca + Fe) < 0.8, it indicates brackish water sedimentation. When Ca/(Ca + Fe) > 0.8, it reflects saltwater sedimentation.

The distribution range of Sr/Ba values in the Ying 4 Member is 0.28–1.53, with an average value of 0.89. The MgO/Al_2O_3*100 values range from 0.62 to 4.04, with a mean value of 2.41. Rb/K has a range of 0.0021–0.0065, with an average of 0.0042. The Ca/(Ca + Fe) values are from 0.05 to 0.65, and the corresponding average value is 0.13 (Table 1). Overall, it can be concluded that the mudstone of Ying 4 Member was deposited in a freshwater–brackish marine–terrestrial transition environment (Figure 7).

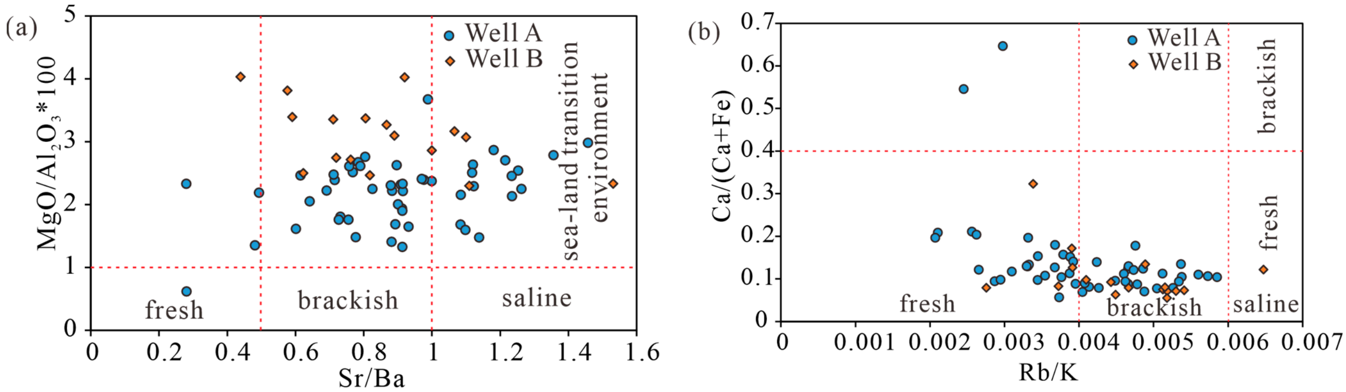

Figure 7. (**a**) Correlation diagram of Sr/Ba and MgO/Al_2O_3*100; (**b**) correlation diagram of Rb/K and Ca/(Ca + Fe).

5.1.3. Redox Condition

The redox condition of water refers to the oxygen content and its variation in sedimentary water during the geological history. According to the difference in oxygen content, the sedimentary environment can be divided into an oxic environment, reducing environment, euxinic environment (sulfidic anoxic environment), and suboxic environment [2]. The redox condition of water is essential for OM preservation, and a more reducing environment is conducive to OM preservation [35]. Trace elements such as V, Ni, Cu, and Zn are common redox sensitive elements. They are easily dissolved in water under an oxidizing environment, but easily deposited in an reducing environment. After deposition, it is often difficult for these elements to migrate, and thus, the content of some element ratios can reflect the original redox condition of the sedimentary water. To enhance accuracy, this study selected both V/(V + Ni) and Cu/Zn as the discriminant parameters of redox conditions. Previous studies have demonstrated that when V/(V + Ni) < 0.46, the sedimentary water is in an oxidizing environment; when the V/(V + Ni) ratio is between 0.46 and 0.54, the water condition is in a transitional state between oxidizing and reducing environments; when V/(V + Ni) > 0.54, the sedimentary water is in a reducing environment [36]. In addition, V/(V + Ni) can also reflect the degree of water stratification. When 0.54 < V/(V + Ni) < 0.84, water stratification begins to occur. When V/(V + Ni) > 0.84, the water is strongly stratified, forming a sulfidic anoxic water environment [37]. Compared to V/(V + Ni), Cu/Zn has a more detailed classification standard. It is generally accepted that Cu/Zn > 0.63 indicates an oxygen-rich environment. Cu/Zn within 0.50~0.63 indicates a weak oxidation environment. When Cu/Zn ranges from 0.38 to 0.50, it indicates a weak reducing-oxidizing environment, and when Cu/Zn ranges from 0.21 to 0.38, it indicates a weak reducing environment. Cu/Zn < 0.21 denotes an anaerobic environment [38].

In this study, we conducted redox condition analysis on the mudstone samples from the Ying 4 Member. The results show that the V/(V + Ni) values range from 0.62 to 0.90, with an average value of 0.79. It is obvious that the values of all samples in the study area are greater than 0.54, indicative of a reducing environment. Meanwhile, the Cu/Zn values are between 0.06 and 1.38, with an average of 0.15. There are 66 samples with a Cu/Zn value less than 0.21, accounting for 95.65% of the total, indicating a reducing environment. Two samples show a Cu/Zn value between 0.21 and 0.38, accounting for 2.90% of the total, indicating a weak reducing environment. Overall, 98.55% of the data points fall within the reduction area (Figure 8), indicating a dominant reducing environment.

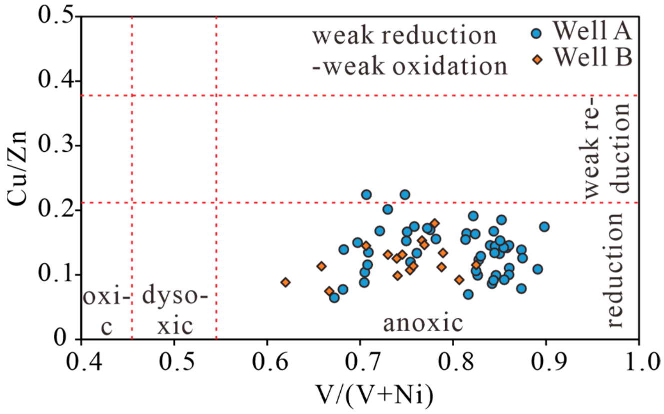

Figure 8. Correlation diagram of V/(V + Ni) and Cu/Zn.

5.1.4. Paleoproductivity

Productivity refers to the ability of organisms to produce organic matter by absorbing external substances and energy, that is, the organic matter produced per unit time and per unit area [39]. To avoid the errors caused by single index evaluation, the contents of P, Ni, Cu, and Zn were mainly selected as indexes when qualitatively analyzing the paleoproductivity of the Ying 4 Member. On this basis, the obtained contents were corrected by the content of Ti (mainly comes from terrigenous debris), and the X/Ti ratio (X represents P, Ni, Cu, and Zn) was used as an index reflecting paleoproductivity. The larger the X/Ti ratio, the higher the paleoproductivity of the area.

As trace nutrients, Ni, Cu, and Zn are primarily present in sediments in the form of organic–metal ligands. They are released by OM decomposition and can react with pyrite in a sulfurized environment to be retained in the sediments. If they cannot be absorbed, Ni, Cu, and Zn will not be substantially enriched in sediments despite the rapid formation of a reducing environment. Therefore, high heavy metal (Ni, Cu, and Zn) element content not only indicates strong reducibility, but also reflects high organic productivity. P is an essential nutrient element in organisms, and has a direct impact on the growth and development of organisms. In the absence of other factors, the increase in the concentration of P in water can promote the growth of organisms. P is mainly enriched in organisms through organic metabolism, and then buried in sediments after the death of organisms [40]. Thus, P content is regarded as an important index for measuring paleoproductivity and has been pervasively used in the evaluation of modern and paleoproductivity.

Based on the geochemical data of the dark mudstone from the Ying 4 Member, we statistically analyzed the distribution range and average value of X/Ti (X is Ni, Cu, Zn, or P) for Well A and Well B. The results show that the distribution range of P/Ti is 0.034–0.161, and its mean value is 0.079; Ni/Ti ranges from 17.9×10^{-4}–83.3×10^{-4}, with an average of 41.0×10^{-4}; Cu/Ti has a range of 22.9×10^{-4}–111.4×10^{-4}, with an average of 61.4×10^{-4}; the distribution range of Zn/Ti is 33.8×10^{-4}–1106.4×10^{-4}, and its average value is 474.7×10^{-4}. The above results all indicate that the paleoproductivity of the lake basin water was at a medium level during the deposition of the Ying 4 Member.

5.2. OM Enrichment Mechanism

5.2.1. Main Controlling Factors of OM Enrichment

To decipher the main controlling factors of OM enrichment, the correlations of TOC against paleoclimate, paleosalinity, redox conditions, and paleoproductivity (Figure 9) are analyzed.

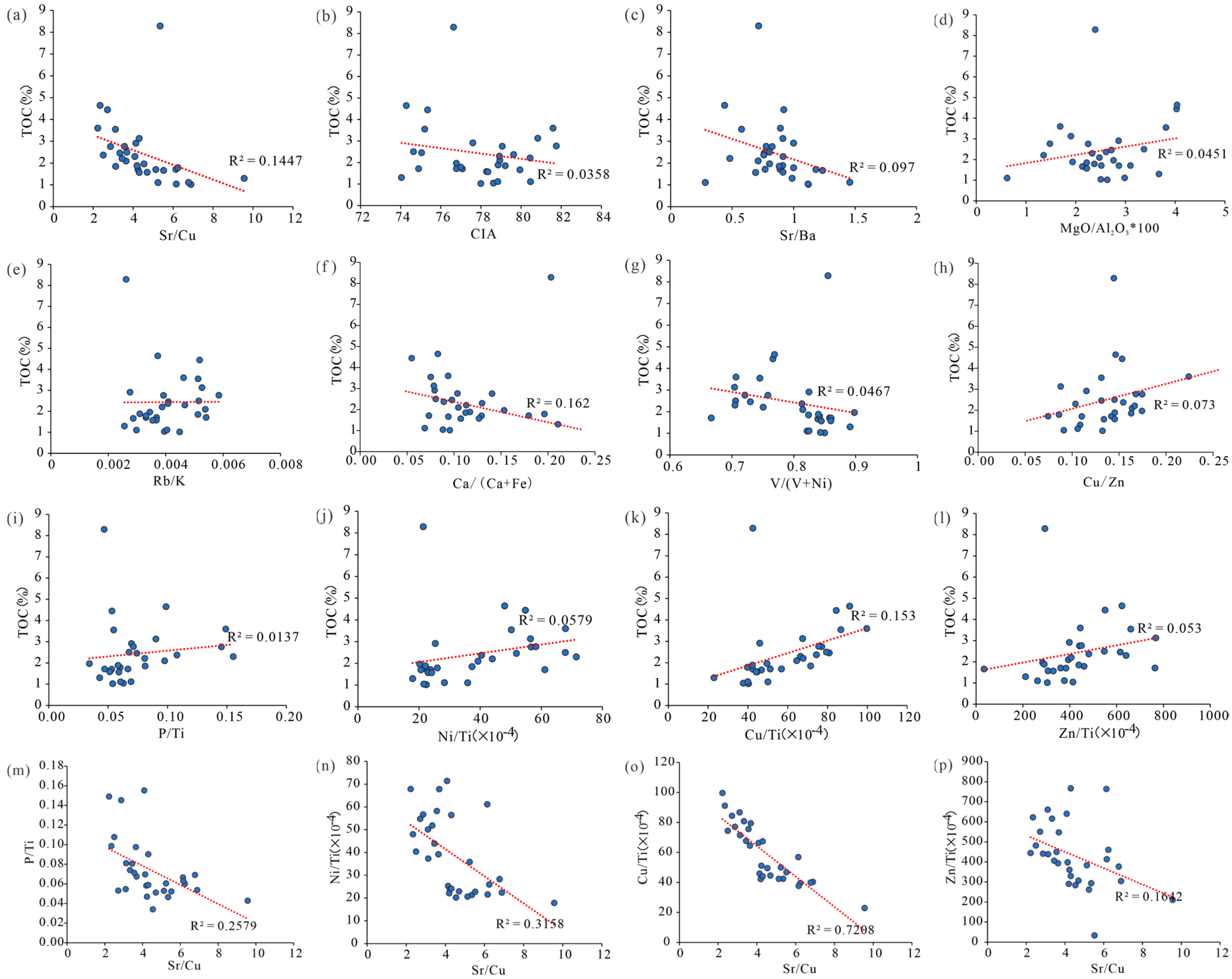

Figure 9. (**a**,**b**) Crossplot of TOC against paleoclimate proxies (Sr/Cu and CIA); (**c**–**f**) crossplot of TOC against paleosalinity proxies (Sr/Ba, MgO/Al_2O_3*100, Rb/K, and Ca/(Ca + Fe)); (**g**,**h**) crossplot of TOC against redox proxies (V/(V + Ni) and Cu/Zn); (**i**–**l**) crossplot of TOC against paleoproductivity proxies (P/Ti, Ni/Ti, Cu/Ti, and Zn/Ti); (**m**–**p**) crossplot of Sr/Cu against paleoproductivity proxies (P/Ti, Ni/Ti, Cu/Ti, and Zn/Ti).

The paleoclimate indicators CIA and Sr/Cu in the study area show a certain negative correlation with the TOC content (Figure 9a,b), indicating that the organic matter enrichment of the Ying 4 Member is controlled by the paleoclimate. This is because a warm and humid climate environment favors the reproduction of aquatic organisms, thereby promoting organic matter enrichment to some extent. The paleosalinity indicator Sr/Ba in the study area shows a slight negative correlation with the TOC content, while the correlations between TOC and MgO/Al_2O_3*100, Rb/K, and Ca/(Ca + Fe) are not significant (Figure 9c–f), suggesting that water salinity has some impact on organic matter enrichment but is not a primary controlling factor. This is because as water salinity increases, the survival and reproduction of microorganisms in the lake are restricted, reducing primary productivity. Although preservation conditions improve, the total amount of organic matter in the water does not increase. The redox indicators V/(V + Ni) and Cu/Zn in the study area show no clear correlation with the TOC content (Figure 9g,h), indicating that organic matter enrichment in the Ying 4 Member mudstone is not controlled by water redox conditions. The paleoproductivity indicators Ni/Ti, Cu/Ti, Zn/Ti, and P/Ti in the study area all show varying degrees of positive correlation with the TOC content (Figure 9i–l), indicating that the organic matter enrichment in the Ying 4 Member is controlled by productivity. This is because high paleoproductivity provides a rich source of organic carbon, increasing organic matter content in sediments and promoting organic matter enrichment. Additionally, the paleoclimate indicator Sr/Cu shows a clear negative correlation with the paleoproductivity indicators Ni/Ti, Cu/Ti, Zn/Ti, and P/Ti (Figure 9m–p), indicating that the paleoproductivity level of the Ying 4 Member is largely influenced by warm and humid climate conditions. This is because when the climate becomes humid, rainfall increases, and these rains and rivers continuously feed into the lake, delivering large amounts of dissolved nutrients and terrestrial plant debris, thus enhancing the paleoproductivity of the lake basin.

5.2.2. OM Enrichment Models

The main controlling factors of OM enrichment include paleoclimate, redox condition, paleosalinity, paleoproductivity, and the input of clastic flow. At present, there are three common OM enrichment models: productivity model, preservational model, and the anoxic productivity model [41–43].

The OM enrichment in the source rocks of the study area is mainly affected by the paleoclimate and paleoproductivity (Figure 10). During the deposition of the Ying 4 Member, the southern Shuangcheng area was at the end of the transformation stage (between fault-depression and subsidence), which provided a relatively stable tectonic setting for the deposition of the lake basin. In addition, the paleoclimate during the deposition period was warm and humid. Such a climatic condition allowed continuous precipitation and rivers to bring abundant soluble nutrients and terrestrial plant debris into the lake, providing a favorable growth and reproduction condition for algae and plankton and hence increasing the paleoproductivity of the lake. At the same time, the continuously reducing environment and the increase in water salinity facilitated good OM preservation. The contemporaneous volcanic activity [20] produced volcanic ash and hydrothermal fluids, which brought rich nutrients into the lake basin. The rich nutrients caused the flourishing development of algae, further improving the primary productivity of the lake basin. As a result, organic matters were enriched and organic-rich source rocks were formed.

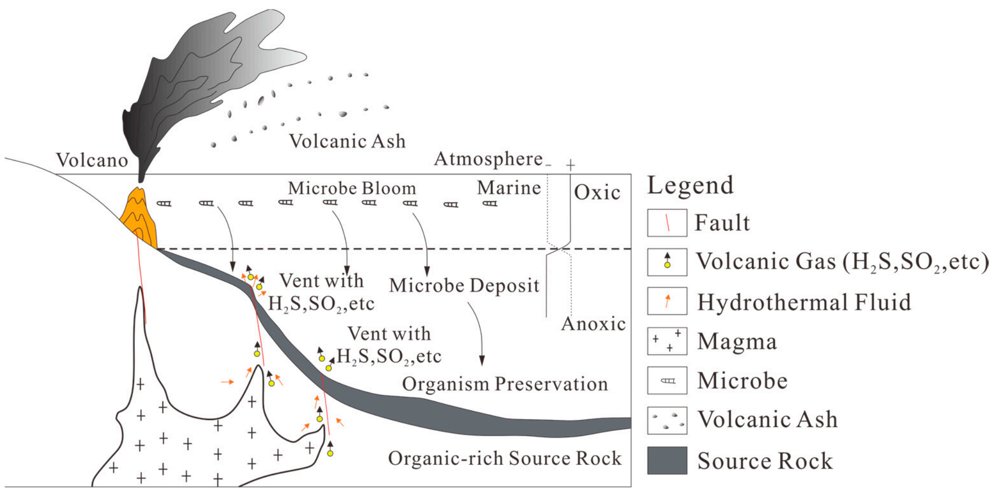

Figure 10. Diagram of OM enrichment in the Ying 4 Member (revised from [20]).

6. Conclusions

The Ying 4 Member hydrocarbon source rock has good abundance, with organic matter classified as type II_2, mainly derived from plankton and algae, followed by higher plants, and has reached the peak stage of hydrocarbon generation, indicating the study area has oil and gas exploration potential. During the Ying 4 Member sedimentary period, the paleoclimate was warm and humid, and the water body was brackish with low oxygen, under reducing conditions, with good primary productivity. Volcanic activity during this period transported large amounts of nutrients to the lake basin via volcanic ash and hydrothermal fluids, promoting algae blooms and forming a solid basis for hydrocarbon source rock formation. The organic matter enrichment in the study area is mainly controlled by paleoclimate and paleoclimate productivity. The warm and humid climate conditions enabled rivers to transport abundant soluble nutrients and terrestrial plant debris to the lake, providing favorable growth and reproduction conditions for algae and plankton, enhancing lake paleoproductivity and facilitating organic matter enrichment. High paleoproductivity provides a sufficient source of organic carbon, thereby controlling the enrichment of organic matter. This study offers valuable insights for reconstructing the depositional environment and studying organic matter enrichment in lacustrine hydrocarbon source rocks of the same period in the Songliao Basin.

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