Paleoenvironment Evolutionary Characteristics of Niutitang Shale in Western Hubei, Middle Yangtze, China

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ABSTRACT: The black shale developed in the first section of the Niutitang formation (ε1n1) is one of the most important shale gas reservoirs in western Hubei, and its geological characteristics have been sufficiently studied by many predecessors. However, there are still three aspects that need further research: the origin of silicon, the discrimination of the euxinic sulfitured and the anoxic ferruginous conditions, and the main controlling factors of organic matter enrichment. Based on geochemical data from well ZD1 located in the city of Yichang in western Hubei, first, the geochemical characteristics of ε1n1 are analyzed, then the provenance, depositional site, and paleoenvironment evolution are discussed, and finally, the main controlling factor of organic matter enrichment is revealed. The results show that ε1n1 can be divided into two units, organic-rich shales (ORS) and organic-lean shales (OLS), which have average total organic carbon contents of 4.21 and 0.84%, respectively. Additionally, the ORS is characterized by high contents of SiO2, U, V, Ni, Zn, and Cu and left-inclining types of rare earth element distribution curves. ε1n1 is located in a passive continental margin with a material source mainly from mixed felsic and mafic rocks. Compared with the OLS, the content of biological quartz is much greater, and the terrigenous input is less in the ORS. The paleoclimate is cold and humid with low salinity in the ORS, whereas it is hot and dry with high salinity in the OLS. ε1n1 is deposited in a semistagnant basin, and the ORS shows a relatively lower stagnant degree with euxinic to anoxic conditions and moderate to high paleoproductivity, while the OLS shows a high stagnant degree with suboxic to oxic conditions and lower paleoproductivity. The redox conditions are the main controlling factors affecting organic matter enrichment. The environmental evolution model with three stages shows that there is a good causal relationship between redox conditions, paleoproductivity, and sea level fluctuation. The black carbonaceous siliceous in the lower part of the ORS with a thickness of approximately 40 m is the most favorable layer, which will provide a theoretical basis for further shale gas exploration of ε1n1 in the western Hubei.

1. INTRODUCTION

The lower cambrian Niutitang formation (ε1n1) is one of the most promising marine shale gas reservoirs and has been widely developed in the Yangtze block.1–3 It is widely accepted that ε1n1 can be divided into two sections, and organic-rich shale (ORS) is mainly developed in the first section (ε1n1).4,5 Exploration practice has shown that the ORS of ε1n1 formed in a deep shelf with a high total organic carbon (TOC) value and a large shale thickness, and is the main shale gas exploration target layer.6,7

The method of inorganic geochemistry [major, trace, and rare earth elements (REE)] is generally used to study the paleoenvironment.8 For instance, some immobile elements, such as Th, Sc, La, Hf, and Zr, can be transferred from the provenance area and preserve the fingerprints of the source area, and the bivariate diagrams of Zr/Sc–Th/Sc, Hf–La/Th can be used to reflect the recycling, provenance of parent rock.9–11 The bivariate diagrams of Al2O3/(Al2O3 + Fe2O3)–Fe2O3/TiO2 and Al2O3/(Al2O3 + Fe2O3)–LaN/CeN (subscript N indicates PAAS standardization) are commonly used to judge the tectonic setting of parent rocks.12 The proxies of the chemical index of alteration (CIA), Sr/Cu and Rb/Sr, are usually used to evaluate the paleoclimatic10,13 and the proxy of the Sr/Ba ratio is widely used to evaluate seawater salinities.14–16 Some redox-sensitive elements such as V, Cr, Ni, Co, Th, U, and Mo in sedimentary rocks are usually used to indicate redox characteristics due to their differentiation under various conditions, and the ratios of U/Th, V/Cr, and Ni/Co are common proxies for judging paleoredox conditions.17–20 Furthermore, elements such as Ba, Cu, Ni, and Zn are nutrients of marine organisms that are absorbed by organisms and then preserved in sediments, and the
biogenic parts of the elements are common proxies for reflecting the paleoproductivity. The paleoenvironment characteristics of \( \epsilon_{1}n_{1} \) in the middle Yangtze block have been deeply studied. Previous studies have shown that the Niutitang shales in western Hunan were deposited under anoxic conditions with high primary productivity in a semirestricted deep basin setting, silica was derived primarily from biological origins, and the paleoclimate transformed from dry-cold to warm-wet conditions during deposition. The sedimentation of the Niutitang shale in the southeastern Sichuan Basin occurred in a weak hydrodynamic, deep water, and oxygen-deficient reducing environment.

From bottom to top, the climate of the Niutitang shales in western Hubei changed from cold and dry to hot and wet, the hydrodynamic conditions became stronger, the oxygen content of the bottom water gradually increased, and the paleoproductivity gradually decreased due to the depth of sea water gradually becoming shallow. According to the above research, two aspects need further research. First, previous studies have shown that silica was derived primarily from biological origins in deep-sea facies, whereas studies on the sources of silica in platform facies are insufficient. Second, the proxy of the iron component has been used for the discrimination of euxinic sulfuretted and anoxic ferruginous conditions in the \( \epsilon_{1}n_{1} \) of the...
lower Yangtze block,26 whereas it is poorly studied in the $\epsilon_{n}$ of western Hubei of the middle Yangtze block. Much research work has been conducted on the mechanism of organic matter enrichment for different areas and formations.9,24,25,27,28 The main factors controlling organic matter formation of $\epsilon_{n}$ in the upper Yangtze block shifted from oxygen deficiency to high productivity.28 Some studies indicated that the organic matter enrichment of the $\epsilon_{n}$ in western Hunan Province of the middle Yangtze block is mainly controlled by paleoredox conditions and paleoproductivity,24 whereas other scholars believe that it is controlled by the coupling of multiple factors.25 The enrichment of organic matter of the $\epsilon_{n}$ in western Hubei Province of the middle Yangtze block is influenced also by both paleoredox conditions and paleoproductivity, whereas organic matter accumulation during sea level lowstand is mainly controlled by paleoredox conditions because paleoproductivity remained persistently low in shallow water.27 It seems that the main controlling factors of organic matter enrichment are different in the different strata and regions, and the main controlling factors of organic matter accumulation of the $\epsilon_{n}$ in western Hubei Province need to be further clarified. Therefore, the typical well ZD1 was chosen for sample collection. The well ZD1 was drilled in 2014, and the shale gas was found for the first time in the $\epsilon_{n}$ (bottom buried depth of 358 m) and Sinian Doushantu formation (bottom buried depth of 854 m) in Yichang city in western Hubei with the average total gas content of 0.59 and 0.95 m$^{3}$/t, respectively. It should be mentioned that one of the oldest shale gas reservoirs was first found in the Sinian Doushantu formation in Yichang city in China. The concentrations of TOC, major, trace, and REEs, and iron components were tested, and the geochemical characteristics of the $\epsilon_{n}$ were further analyzed. Then, the provenance, depositional site, and paleoenvironment evolution were discussed. Furthermore, the main controlling factor of organic matter enrichment was revealed. In addition, the evolution mode for the $\epsilon_{n}$ in western Hubei was established. Overall, the study provides a theoretical basis for further shale gas exploration and development of the $\epsilon_{n}$ in western Hubei. Moreover, the study can provide a better understanding of the paleoenvironment evolutionary characteristics of Niutitang shale in the middle Yangtze of southern China during the Early Cambrian.

## 2. GEOLOGICAL SETTING

During the Early Cambrian, the South China Craton was located in the Southern Hemisphere along northern East Gondwana,29 and it formed through the collision of the Yangtze and Cathaysia Blocks during the early Neoproterozoic. The Nanhua Basin is located between the Cathaysia and Yangtze Blocks during the early Neoproterozoic. The Nanhua Basin is in the Southern Hemisphere along northern East Gondwana, and is close to the Sichuan Basin of upper Yangtze in the west, the oldland in the east, the Qinling Ocean in the north bounded by the Xiangguang fault, and the Nanhua Ocean in the south (Figure 1a,b).29 The sedimentary facies from west to the east of $\epsilon_{n}$ developed successively from shallow shelf, deep shelf, shallow shelf, and oldland in central Hubei, and the black shale of $\epsilon_{n}$ is mainly deposited in the deep shelf east of Chongqing and west of Yichang city (Figure 1b).3

Since 2015, shale gas was first discovered of $\epsilon_{n}$ in the city of Yichang in western Hubei Province in the middle Yangtze Block; the survey drilling wells ZD1 and YD2 are typical wells with high gas contents located in a deep shelf close to the shallow shelf in western Yichang city (Figure 1b).3,5 Vertically, the $\epsilon_{n}$ was overlain by the Cambrian Yanjiahe formation ($\epsilon_{y}$) with the lithology of limestone interbedded with shale and the Sinian Dengying formation ($Z_{d}$) with the lithology of dolomite and was overlain by the Cambrian Shipai formation ($\epsilon_{s}$) with the lithology of silty mudstone (Figure 1c). Generally, the $\epsilon_{n}$ can be vertically divided into two sections: the first section ($\epsilon_{1}$) with the main lithology of black shale and the second section ($\epsilon_{2}$) with the main lithology of grayish limestone, and $\epsilon_{n}$ is the main shale gas reservoir, which is also the target layer in the study (Figure 1c).

By carefully observing drilling cores, $\epsilon_{1}$ can be clearly divided into two subsections according to the color and lithology of the core: the ORS subsection with the main lithology of black or gray-black shale and the organic-lean shales (OLS) subsection with the main lithology of dark-gray limestone interbedded with shale. In addition, the OLS can be divided into the lower part (black carbonaceous siliceous shale) and upper part (gray-black carbonaceous calcareous silty shale) (Figures 1c and 2).

## 3. SAMPLES AND METHODS

### 3.1. Samples and Analytical Method

A total of 10 samples of $\epsilon_{n}$ were collected from well ZD1, and the samples are remarkably representative, of which four samples (Z7–Z10) with the lithology of black siliceous carbonaceous shale were collected from the lower part of the ORS, two samples (Z5 and Z6) with the lithology of gray-black carbonaceous calcareous silty shale were from the upper part of the ORS, four samples with the lithology of dark-gray carbonaceous calcareous silty shales (Z1 and Z3), and dark-gray carbonaceous silty limestones (Z2 and Z4) were collected from the OLS (Figure 2). All shale samples were fresh without weathering and were placed in paper bags immediately after recovery. Fresh samples were ground in an agate mortar to a particle size of less than 200 mesh and then divided into several parts for the content of TOC, major and trace element, and iron speciation geochemical analyses. All the samples were tested in the State Key Laboratory of Biogeology and Environmental Geology of China University of Geosciences (Wuhan). The TOC was tested by a Leco CS230 carbon–sulfur tester. Major elements (SiO$_{2}$, Al$_{2}$O$_{3}$, Fe$_{2}$O$_{3}$, MgO, CaO, Na$_{2}$O, K$_{2}$O, MnO, TiO$_{2}$, and P$_{2}$O$_{5}$) were analyzed using a ZSXPrimus II X-ray fluorescence spectrometer. Trace element (Sc, Hf, Zr, U, Th, V, Cr, Ni, Cu, Zn, Rb, and Sr) and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) concentrations were determined using an inductively coupled plasma source mass spectrometer. The total iron content (Fe$_{t}$) was determined by the sulfosalicylic acid spectrophotometric method. Highly reactive iron (Fe$_{HR}$) includes iron in pyrite (Fe$_{py}$), carbonate (Fe$_{carb}$), magnetite (Fe$_{mag}$), and ferric oxides (Fe$_{ox}$). The Fe$_{py}$ content was calculated from the concentration of pyrite sulfur (Fe$_{S_{py}}$) that was extracted using the CrCl$_{3}$ reduction method and
E_{xs} = E_{Sample} - Al_{Sample} \times (E/Al)_{PAAS} \tag{2}

(E/Al)_{PAAS} is the ratio of elements E to Al in the PAAS. The proxy of Si_{xs} was used to reflect the content of biogenic silicon, and the proxies of Cu_{xs}, Ni_{xs}, and Zn_{xs} were used to evaluate the paleoproductivity in e_{n}^{17}. The proxies of CIA before kalium metasomatism (CIA_{kal}) Sr/Cu, and Rb/Sr were used to evaluate the paleoclimates in e_{n}^{17}. The CIA was originally proposed by Nesbitt and Young (1982) to determine the chemical weathering intensity of the provenance of clastic rock and can be calculated using the formula below.\textsuperscript{36}

\[\text{CIA} = \frac{\text{molar} \left( \text{Al}_{2}O_{3}/\left[\left(\text{Al}_{2}O_{3} + \text{CaO}^{*} + \text{Na}_{2}O + \text{K}_{2}O\right) \times 100\right]\right)_{PAAS}}{\text{molar} \left(\text{CaO}^{*}\right)_{PAAS}}\] \tag{3}

All major element concentrations are calculated in mole fractions. CaO* refers to CaO in silicate. Mclennan (1993) proposed the method of indirect calculation of the value of CaO* as follows: CaO_{remain} = (CaO−P_{2}O_{5} \times 10/3), if molar (CaO_{remain}) < molar (Na_{2}O), then molar (CaO*) = molar (CaO_{remain}); if molar (CaO_{remain}) > molar (Na_{2}O), molar (CaO*) = molar (Na_{2}O).\textsuperscript{38} Generally, CIA values change greatly in different paleoclimates, and CIA values range from 50 to 70, 70 to 80, and 80 to 100, indicating low, moderate, and high degrees of chemical weathering, respectively.\textsuperscript{39} In general, weak weathering is associated with cold and/or arid climates, whereas intense weathering is associated with warm and/or humid climates.\textsuperscript{9} New kalium elements were introduced by kalium metasomatism during diagenesis, resulting in low CIA values. Therefore, it was necessary to be corrected. Generally, CIA_{kal} can be corrected by Al_{2}O_{3}/−CaO* + Na_{2}O−K_{2}O ternary diagrams.\textsuperscript{39} In general, Sr/Cu ratios between 1 and 10 and greater than 10 indicate cold and arid climates, respectively, whereas high and low values of Rb/Sr indicate humid and arid climates, respectively.\textsuperscript{14} The proxy of the Sr/Ba ratio is widely used to reconstruct sea water salinities in e_{n}.\textsuperscript{16,40} Generally, Sr/Ba less than 0.5, between 0.5 and 1.0, and greater than 1 indicate low, medium, and high salinity, respectively.\textsuperscript{14} The proxies of V/Cr, U/Th, Ni/Co, Sc/Ca, Fe_{mag}/Fe_{tot}, Mo/TOC covariant models were used to evaluate the paleoredox conditions in e_{n}.\textsuperscript{12} The V, Cr, Th, U, Ni, and Co elements in sedimentary rocks are often used to indicate the redox characteristics of bottom water due to their differentiation under different redox conditions.\textsuperscript{13} For instance, the element V existed in the form of V^{5+} in soluble vanadates under oxic conditions, and it is reduced to V^{4+} or V^{3+} when the environment is anoxic, forming precipitation of insoluble complexes such as VO(OH) \textsubscript{2} and VO(OH)\textsubscript{3}. The elements Cr, Th, U, Ni, and Co have similar characteristics to V under different redox conditions. It is well known that the proxies of V/Cr, U/Th, and Ni/Co are usually considered effective proxies for distinguishing the redox conditions of seawater to eliminate the limitation of utilizing a single trace element.\textsuperscript{10,41} In general, V/ Cr < 2, Ni/Co < 5, and U/Th < 0.75 indicate suboxic conditions; 2 < V/ Cr < 4.25, 5 < Ni/Co < 7, and 0.75 < U/Th < 1.25 indicate anoxic conditions; and V/ Cr > 4.25, Ni/Co > 7, and U/Th > 1.25 indicate euxinic conditions. In addition, the cerium anomaly (δCe) is a common redox indicator reflecting redox conditions and ancient sea level changes. The value of δCe is determined using the following formulas.\textsuperscript{42}

| Stratum       | System     | Formation     | Section   | Depth (m) | Lithology Column | Samples location | TOC (%) | Lithology description |
|--------------|------------|---------------|-----------|-----------|------------------|------------------|---------|-----------------------|
| Cambrian     | Lower      | Niutian       | Z1        | 240       | -                | 4                | 2       |                       |
|              |            |               | Z2        | 240       | -                | 4                | 2       | Organic-rich shale (IRS) |
|              |            |               | Z3        | 280       | -                | 4                | 2       | Upper part             |
|              |            |               | Z4        | 310       | -                | 4                | 2       | Organic-lean shales (OLS) |
|              |            |               | Z5        | 340       | -                | 4                | 2       | Lower part             |
|              |            |               | Z6        | 370       | -                | 4                | 2       |                       |
|              |            |               | Z7        | 370       | -                | 4                | 2       |                       |
|              |            |               | Z8        | 370       | -                | 4                | 2       |                       |
|              |            |               | Z9        | 370       | -                | 4                | 2       |                       |
|              |            |               | Z10       | 370       | -                | 4                | 2       |                       |
| Vanjiabao    | Limestone  | -             | -         | -         | -                | 4                | 2       |                       |
|              | Dark-grey carbonaceous calcareous silty shale | - | - | - | - | 4 | 2 |                       |
|              | Dark-grey carbonaceous calcareous silty shale | - | - | - | - | 4 | 2 |                       |
|              | Cretaearose argillicous silty limestone | - | - | - | - | 4 | 2 |                       |
|              | Calcareous argillicous silty limestone | - | - | - | - | 4 | 2 |                       |
|              | Black carbonaceous calcareous silty shale | - | - | - | - | 4 | 2 |                       |

**Figure 2.** Vertical distribution of the lithology and the TOC values in e_{n}^{1} of well ZD1, and the samples are numbered according to burial depth.

precipitated as Ag_{2}S in silver nitrate traps.\textsuperscript{31} The Fe_{mag} and Fe_{ox} fractions were extracted by the sequential procedure described in Poulton and Canfield (2005) and measured by atomic absorption spectroscopy (AAS).\textsuperscript{32}
\[ \delta Ce = \frac{Ce_N}{(La_N \times Pr_N)^{1/2}} \] 

In the formulas above, N represents PAAS normalized. Generally, positive \( \delta Ce \) with the value greater than 1 indicates suboxic conditions, whereas negative \( \delta Ce \) with the value less than 0.95 indicates euxinic conditions.\(^{42} \)

Iron speciation proxies \( Fe_{hr}/Fe_r \) and \( Fe_{py}/Fe_{hr} \) were used to evaluate the bottom water redox conditions in ancient oceans.\(^{43} \) In general, \( Fe_{hr}/Fe_r \) values less than 0.38 and greater than 0.38 were indicative of oxic and anoxic bottom water conditions, respectively. For anoxic bottom water conditions, \( Fe_{py}/Fe_{hr} \) less than 0.7–0.8 and greater than 0.7–0.8 show euxinic sulfiretted and ferruginous conditions, respectively.\(^{36} \) Iron speciation was initially applied only to fine clastic sedimentary rocks (e.g., mudstone and shale). Later, it was found that when \( Fe_r \) was greater than 0.5%, iron speciation can also be an effective indicator of the carbonate sedimentary environment.\(^{44} \)

The Mo–TOC model is commonly used to judge the retention degree of water in basins. The degree of stagnation can be classified into three types: a strong stagnant environment \( (Mo/TOC < 15 \times 10^{-4}) \), a semistagnant environment \( (15 \times 10^{-4} < Mo/TOC < 35 \times 10^{-4}) \), and a weak stagnant environment \( (Mo/TOC > 35 \times 10^{-4}) \).\(^{9} \)

The proxies of TOC, Ni/Al, and \( Ca_{21}Na + Zn_{34} \) were used to reflect the paleoproductivity in \( \epsilon_{n1}^{\mu} \), and the proxy of \( La_{n}/Yb_n \) (\( n \) represents chondrite normalization) can be used to indicate the deposition rate in \( \epsilon_{n1}^{\mu} \), and a lower value of \( La_{n}/Yb_n \) indicates a relatively high sedimentary rate.\(^{15,46} \)

### 4. RESULTS

#### 4.1. TOC Concentration.

The TOC values for \( \epsilon_{n1}^{\mu} \) of well ZD1 are presented in Table 1 and Figure 2. The test results show that the TOC values ranged from 0.49 to 8.77% (avg. 2.81%). The ORS exhibits high TOC values varying from 1.85 to 8.77% (avg. 4.12%) and can be divided into two parts. The lower part (Z10–Z7) has TOC values ranging from 3.24 to 8.77% (avg. 5.19%), and the upper part (Z6–Z5) has TOC values ranging from 1.85 to 2.12% (avg. 1.99%). The TOC values of the OLS (Z1–Z4) show distinctly lower values varying from 0.49 to 1.53% (avg. 0.84%).

#### 4.2. Major Elements.

The results of the major element analyses are presented in Table 1. Marine shale can be regarded as an admixture of three endmember oxides: \( SiO_2 \) (detrital quartz and/or biogenic silica), \( Al_2O_3 \) (clay fraction), and \( CaO \) (carbonate content).\(^{39} \) For the ORS and OLS samples, \( SiO_2 \) content (avg. 52.75 and 36.38%, respectively) is the most abundant oxide, followed by \( CaO \) (avg. 10.18 and 23.11%, respectively) and \( Al_2O_3 \) (avg. 9.42 and 8.60%, respectively) (Table 1). Obviously, compared with the OLS, the ORS has a greater \( SiO_2 \) content and a lower \( CaO \) content. In addition, the lower part of the ORS (Z10–Z7) has the greatest \( SiO_2 \) content and the lowest \( CaO \) content. In the upper part of the ORS (Z5–Z6), the \( CaO \) content markedly increased. In the OLS, the \( CaO \) and \( Al_2O_3 \) contents are markedly the greatest in limestone (Z2 and Z4) and shale (Z1 and Z3) samples, respectively (Figure 3).

The statistics show that \( Ca \) was significantly enriched (EF > 3), Na, P, K, Mg, Fe, and Si were moderately enriched (1 ≤ EF ≤ 3), and Ti was slightly depleted (EF < 1) in both the ORS and OLS. Compared with the OLS, the EF values of Ca and P were relatively depleted, and Si was relatively enriched in the ORS (Figure 4a).

#### 4.3. Trace Elements.

The results of the trace element analyses are presented in Table 2. The EF values show that Sr,
Ba, and U are significantly enriched (EF > 3), and Zr is relatively depleted (EF < 1) in both the ORS and OLS. By comparison, the contents of V, U, Ni, Cu, and Zn are much greater, and that of Sr is relatively lower in the ORS (Table 2 and Figure 4b). The results of the REE analyses are presented in Table 3. The total contents of REEs (ΣREE) for the ORS vary from 98.42 to 164.89 ppm (avg. 118.46 ppm) (Table 3). The ΣREE for the OLS fluctuate greatly due to the different lithologies, and the average ΣREE abundances are 69.94 and 157.8 ppm for the limestone and shale samples. The ratios of ΣLREE/ΣHREE and LaN/YbN can evaluate the differentiation degree of the REE; the greater the values of these two parameters are, the more enriched the light REE (LREE) contents are. The ratios of ΣLREE/ΣHREE of the ORS and OLS range from 6.03 to 8.46 (avg. 7.47) and 8.07 to 8.95 (avg. 8.58), respectively, and the ratios of LaN/YbN of the ORS and OLS range from 0.82 to 1.05 (avg. 0.92) and 0.97 to 1.12 (avg. 1.07), respectively. Both the ratios of ΣLREE/ΣHREE and LaN/YbN indicate that the LREE contents are much greater in the OLS. The PAAS-normalized curves of the ORS and OLS show different REE distribution curves (Figure 5). The REE distribution curves of the ORS were characterized by a marked left-inclining type (Figure 5a).

4.4. Iron Component. The results of iron component analyses are presented in Table 4. The contents of FePy, highly reactive iron (FeHR), and FeT in the ORS ranged from 1.01 to 2.05% (avg. 1.55%), 1.98 to 2.63% (avg. 2.21%), and 1.91 to 3.28% (avg. 2.43%), respectively, and the values of FePy/FeHR and FeHR/FeT ranged from 0.50 to 0.79 (avg. 0.69) and 0.60 to 1.14 (avg. 0.94), respectively. The contents of FePy, FeHR, and FeT in the OLS ranged from 0.33 to 1.22% (avg. 0.77%), 1.22 to 2.02% (avg. 1.61%), and 1.44 to 3.49% (avg. 2.49%), respectively, and the values of FePy/FeHR and FeHR/FeT ranged from 0.25 to 0.60 (avg. 0.45) and 0.58 to 0.92 (avg. 0.69), respectively. The shale samples had higher contents of FePy, FeHR, and FeT than the limestone samples. Generally, from bottom to
top, the contents of Fe$_{pp}$ and Fe$_{Hr}$ gradually decreased, while Fe$_{c}$ gradually increased.

5. DISCUSSION

5.1. Recycling, Provenance, and Tectonic Setting.

Some immobile elements, such as Th, Sc, La, Hf and Zr, can be transferred from the provenance area and preserve the fingerprints of the source area. In addition, the element Zr is easily enriched after sedimentary recycling in clastic rocks, and the bivariate diagrams of Zr/Sc have been used to indicate the degrees of sedimentary recycling of parent rock.

The results showed that the composition of $e_1n_1$ shale is controlled by the composition of felsic parent rock, and all the samples are almost unaffected by sedimentary recycling (Figure 6a). This result is consistent with the $e_1n_1$ shale in the southeastern South China Basin of the middle Yangtze.

5.2. Paleoenvironment.

5.2.1. Paleoclimate and Paleo-salinity.

The results show that the CIA$_{corr}$ of the shale samples ranged from 62.60 to 71.90 (avg. 67.64) (Figure 7), indicating a low to moderate degree of chemical weathering in $e_1n_1$. Vertically, the CIA$_{corr}$ value in the lower part of the ORS (Z7–Z10) ranged from 62.6 to 69.3 (avg. 65.6), indicating a low to moderate degree of chemical weathering, which implies cold weather. The CIA$_{corr}$ value of the upper part of the ORS (Z5–Z6) ranged from 70.0 to 70.5 (avg. 70.25), indicating a moderate degree of chemical weathering, which implies relatively hot weather. The CIA$_{corr}$ value of the OLS (Z1 and Z3) ranges from 66.4 to 71.9 (avg. 69.7), which indicates that the climate was close to moderate chemical weathering, which also implies relatively hot weather (Table 1 and Figure 8). Although the values of CIA$_{corr}$ are slightly lower than those of the $e_1n_1$ shale of the city of Enshi in western Hubei, the variation trend is generally similar, with the values of CIA$_{corr}$ gradually increasing from the lower to the upper part of the $e_1n_1$ shale.

The Sr/Cu and Rb/Sr ratios ranged from 4.53 to 13.97 (avg. 8.65) and 0.16 to 0.30 (avg. 0.22) in the lower part of the ORS (Z7–Z10), indicating a relatively cold and humid climate; they ranged from 20.05 to 53.86 (avg. 36.96) and 0.05 to 0.13 (avg. 0.09) in the upper part of the ORS (Z5–Z6), indicating a moderate hot and dry climate; and they ranged from 30.55 to 524.51 (avg. 247.62) and 0.01 to 0.11 (avg. 0.05) in the OLS (Z1–Z4), indicating a much hotter and drier climate. The trends in climate change with cold and humid weather in the lower part of $e_1n_1$ to hot and dry weather in the upper part of $e_1n_1$ are consistent with a previous study on the $e_1n_1$ shale in the city of Enshi in western Hubei. In particular, the average values of Sr/Fe and Cu show a consistent increase from the lower to the upper part of the $e_1n_1$ shale.
Cu and Rb/Sr ratios of shale samples Z1 and Z3 are 45.64 and 0.09, respectively, and the average values of limestone samples Z2 and Z4 are 449.6 and 0.01, respectively. This result indicates a much hotter and drier climate in limestone (Figure 8). The climate change of $\epsilon_{\text{Si}}^n$ is closely related to the falling sea level (Figure 8). The boundary between $\epsilon_{\text{Si}}^n$ and $\epsilon_{\text{H}}$, $\delta^{13}$C shows a negative deviation, reflecting the rapid decline in sea level; then, the sea level starts to increase and reaches its highest point at the bottom of the ORS in $\epsilon_{\text{Si}}^n$. Afterward, the sea level begins to fall until the top of $\epsilon_{\text{Si}}^n$, thus the climate shifts from cold and wet to hot and dry with increased salinity (Figure 8). The results show that the Sr/Ba ratio increases from bottom to top, indicating an increase in water salinity. The Sr/Ba ratio ranged from 0.24 to 0.35 (avg. 0.29) in the lower part of the ORS Z7–Z10, indicating a low salinity; the Sr/Ba ratio ranged from 0.65 to 0.94 (avg. 0.80) in the upper part of the ORS Z5–Z6, indicating a medium salinity; and the Sr/Ba ratio ranged from 0.98 to 11.82 (avg. 4.63) in the OLS, indicating most samples of high salinity. In particular, the Sr/Ba ratios of the shale (Z1 and Z3) and limestone (Z2 and Z4) samples range from 0.98 to 1.67 (avg. 1.32) and 4.06 to 11.82 (average 7.94), respectively, which indicates a higher salinity in limestone (Figure 8). The sea water salinity of $\epsilon_{\text{Si}}^n$ in the study area located in the platform is clearly much saltier than that of western Hunan, which is located on the margin shelf (Figure 1) with a Sr/Ba ratio much less than 0.5, indicating that the low salinity seawater in margin shelf has a relatively unrestricted marine environment and much colder weather with less water evaporation than the seawater in the platform.

5.2.2. Origin of Silicon and Terrigenous Input. Previous studies have shown that there are three main sources of silicon in sedimentary rocks: siliceous organisms, hydrothermal fluids, and silica-rich rock debris, such as terrigenous clastics and pyroclastic rocks. The ternary diagram of Al–Fe–Mn can distinguish hydrothermal and nonhydrothermal siliceous rocks. The results show that silicon had a nonhydrothermal origin in both the ORS and the OLS (Figure 9a). In addition, the REE ratios, such as Eu/Sm, Sm/Yb, and Y/Ho, are also used to judge hydrothermal activity. The results show that the samples in $\epsilon_{\text{Si}}^n$ are close to seawater and hydrogenetic Fe–Mn crusts, indicating that the proportion of seafloor hydrothermal activity is less than 0.1% (Figure 9b,c). Therefore, the siliceous rocks in the $\epsilon_{\text{Si}}^n$ shale have a nonhydrothermal origin, which is consistent with previous work in $\epsilon_{\text{Si}}^n$ of western Hubel. There is a positive correlation between the contents of SiO$_2$ and Al$_2$O$_3$ for the OLS, indicating that the silicon mainly comes from terrigenous clastics, and there is no obvious correlation between the contents of SiO$_2$ and Al$_2$O$_3$ for the ORS, indicating the presence of nonterrigenous silicon (Figure 9d). Because all the samples were nonhydrothermal, the silicon in the ORS should be partly derived from siliceous organisms. According to Formula 2 above, the content of biogenic silicon (Si$_{\text{ba}}$) in the ORS is clearly much greater than that of the OLS (Figure 9). The content of Si$_{\text{ba}}$ suddenly decreased from 13.62% of sample Z7 to 1.04% of sample Z6, and Sr/Cu and Sr/Ba suddenly increased from 4.53 to 53.86 and 0.29 to 1.94, respectively, which implies that the Si$_{\text{ba}}$ content is influenced by the paleoclimatic and paleosalinity. From bottom to top, the combination of the falling sea level with a hotter and drier climate and increased salinity of seawater would result in greater water mass restriction and weaker nutrient upwelling on the
conditions, and the value of Fe\(^0.70\) in the lower part of the ORS, indicating euxinic sulfuretted which ranged from 0.76 to 0.79 (avg. 0.78) with a value greater than Fe\(^{−}\) which led to the content of Si\(^{−}\) greatly decreasing.

The elements Al, Ti, Th, and Zr are widely used in the study of terrigenous input shows that, first, the terrigenous input of shale samples was higher than that of limestone samples; the average contents of Al and Ti of eight shale samples were 5.35 and 0.30%, respectively, and two limestone samples were 2.66 and 0.14%, respectively. Second, the contents of Al and Ti in shale samples gradually increased from bottom to top, with average contents of Al and Ti for the ORS and OLS of 4.99 and 0.28%, and 6.45 and 0.53%, respectively. Third, the contents of Al and Ti in shale samples increased slightly, whereas the content of Si\(^{−}\) decreased greatly (Figure 8), which indicated that the increasing Al and Ti contents were not the main factor that resulted in a sudden decrease in the Si\(^{−}\) content.

5.2.3. Paleoredox Conditions. The common proxies of Fe\(^{Py}/Fe^{HR}\), U/Th, Ni/Co, V/Cr, and δCe mentioned above have been used to study the paleoredox conditions in ε\(_n\)\(^{−}\). The results show that the value of Fe\(^{HR}/Fe^{T}\) ranged from 0.58 to 1.14 (avg. 0.84), greater than 0.38, indicating that both the ORS and OLS formed under anoxic conditions. The value of Fe\(^{Py}/Fe^{HR}\) ranged from 0.76 to 0.79 (avg. 0.78) with a value greater than 0.70 in the lower part of the ORS, indicating euxinic sulfuretted conditions, and the value of Fe\(^{Py}/Fe^{HR}\) ranged from 0.50 to 0.54 (avg. 0.52) and 0.25 to 0.60 (avg. 0.45) in the upper part of the ORS and OLS, respectively, with values much less than 0.70, indicating anoxic ferruginous conditions (Figures 10 and 11). Therefore, the value of Fe\(^{Py}/Fe^{HR}\) can be applied to distinguish euxinic sulfuretted and anoxic ferruginous conditions.

Further research showed that the value of Fe\(^{Py}/Fe^{HR}\) seemed to have a relationship with the lithology and TOC content. The siliceous shale with an average TOC value of 5.19% has the greatest Fe\(^{Py}/Fe^{HR}\) value, followed by the silty limestone with an average Fe\(^{Py}/Fe^{HR}\) value of 8.32, 9.38, and 7.08, respectively, indicating euxinic to suboxic to oxic conditions in the paleoocean (Figure 11). However, not all the lower parts of the ORS are in euxinic conditions, and suboxic to oxic conditions exist intermittently at certain times. Stage I is the lower part of the ORS (Z7−Z10), with average ratios of V/Cr, Ni/Co, U/Th, δCe, and Fe\(^{Py}/Fe^{HR}\) of 8.32, 9.38, 6.70, 0.88, and 0.78, respectively, indicating euxinic conditions in the paleoocean (Figure 11). Not all the lower parts of the ORS are in euxinic conditions, and suboxic to oxic conditions exist intermittently at certain times. Stage II is the upper part of the ORS (Z5−Z6), with average ratios of V/Cr, Ni/Co, U/Th, δCe, and Fe\(^{Py}/Fe^{HR}\) of 1.96, 4.15, 0.55, 0.93, and 0.52, respectively, indicating suboxic to anoxic conditions in the paleoocean. Stage III was the OLS (Z1−Z4), with average ratios of V/Cr, Ni/Co, U/Th, δCe, and Fe\(^{Py}/Fe^{HR}\) of 1.79, 3.36, 0.76, 0.96, and 0.46, respectively, indicating suboxic to oxic conditions in the paleoocean. In conclusion, from the bottom to the top, ε\(_n\) underwent a transition from euxinic sulfuretted (Z10−Z7) to anoxic ferruginous conditions (Z6−Z5) to suboxic to oxic conditions (Z4−Z1). The results of the study are consistent with
Figure 6. (a) Cross-plots of Zr/Sc vs. Th/Sc for the ORS and OLS in $\epsilon_{1n1}$. (b) Cross-plots of Hf vs. La/Th for the ORS and OLS in $\epsilon_{1n1}$. (c) Cross-plots of $\text{Al}_2\text{O}_3/\left(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3\right)$ vs. $\text{Fe}_2\text{O}_3/\text{TiO}_2$ for the ORS and OLS in $\epsilon_{1n1}$. (d) Cross-plots of $\text{Al}_2\text{O}_3/\left(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3\right)$ vs. $\text{La}_\text{N}/\text{Ce}_\text{N}$ for the ORS and OLS in $\epsilon_{1n1}$.

Figure 7. A−CN−K ternary diagrams exhibiting weathering degree for the ORS and OLS in $\epsilon_{1n1}$ in well ZD1 (all in mole percentages). A—$\text{Al}_2\text{O}_3$; CN—CaO* + Na$_2$O; K—K$_2$O; Ka—kaolinite; Chl—chlorite; Gi—gibbsite; Sm—smectite; Mu—muscovite; II—illite; Pl—plagioclase; and Kfs—feldspar.
the results of the other drilling wells, such as well YD2 in the city of Yichang, with euxinic and anoxic conditions at the bottom in ϵ₁n₁ (ORS) and then gradually changed to suboxic and oxic conditions at the top in ϵ₁n₁ (OLS). The trace element Mo tends to be enriched in a confined hydrostatic environment containing H₂S. The Mo/EF–U/EF covariant model is usually used to infer the paleoenvironment and water cycle conditions of sedimentary water bodies. According to the research results of well YD2, most samples of the ORS are deposited under euxinic conditions, and all the samples of the OLS are deposited under suboxic to oxic conditions, which is consistent with the ϵ₁n₁ shale in the upper Yangtze Platform. With the increase of the U/EF and Mo/EF value, the ratios of Mo/EF/ U/EF did not increase or decrease and were stable at approximately 1−3 times the sea water value, indicating that the paleoocean was semiclosed and semistagnant (Figure 12). The Mo/TOC ratios of the ORS in well YD2 range from 6.36×10⁻⁴ to 56.36×10⁻⁴ (avg. 20.41×10⁻⁴), implying that the ORS mainly formed in a semistagnant to strong stagnant environment, and the Mo/TOC ratios of the OLS range from 3.96×10⁻⁴ to 17.39×10⁻⁴ (avg. 12.17×10⁻⁴), implying that the OLS also mainly formed in a semistagnant to strong stagnant environment (Figure 13). It is noteworthy that the stagnation degree of the OLS is slightly greater than that of the ORS.

The conclusion of the study is consistent with previous results that ϵ₁n₁ shale in western Hubei is in a strongly restricted environment. A further study shows that the Mo/TOC ratios of the ORS and OLS almost between the modern Framvaren Fjord and Cariaco basin, but not as low as that of the strongly restricted Black Sea basin, which indicated that western Hubei was more or less connected with the open ocean, and that this environment is good for the upwelling of nutrients. 5.2.4. Paleoproductivity. As described in the Introduction, elements such as Ba, P, Cu, Zn, and Ni are common indicator elements of marine primary productivity. However, the elements Ba and P are readily released into the water column under strongly anoxic conditions and have a high retention under oxic conditions. In addition, TOC is the surface productivity of the ocean reflected in the sediment, and it has been regarded as the most direct indicator of primary productivity. Therefore, the proxies of TOC, Ni/Al, and Ni_XS + Cu_XS + Zn_XS were selected to analyze the paleoproductivity.

The results show that the TOC increases with burial depth, indicating that the paleoproductivity of ORS is obviously greater than that of OLS. The Ni/Al ratios of the ORS and OLS ranged from 7.41 to 51.16 (avg. 22.70) and 8.51 to 8.75 (avg. 8.63), respectively, and the Ni_XS + Cu_XS + Zn_XS values of the ORS and OLS ranged from 40.14 to 472.51 (avg. 184.93) and 29.79 to 68.88 (41.80), respectively. The values of Ni/Al and Ni_XS + Cu_XS
of the ORS are greater than those of the OLS, also indicating that the ORS had higher primary productivity, which reflected the growth and reproduction of organisms in the ancient oceans in the Early Cambrian. Previous studies have shown that the organisms in black siliceous shales of the Early Cambrian in South China were mainly derived from algae, bacteria, and radiolarians, which resulted in the high content of Si\(_{xs}\) in the lower part of the ORS (Figure 8).

There were two periods of rapid decline of paleoproductivity in the ORS: the first decline was the period of samples Z10 to Z9, and the second decline was the period of samples Z7 to Z6. A declining trend also existed in well YD2 of the city of Yichang. These two declines in paleoproductivity were accompanied by changes in TOC, major elements and redox conditions. From sample Z10 to Z9 at the stage of the first decline, TOC decreased from 8.72 to 3.92%, the contents of MgO and CaO increased slightly, and the values of V/Cr and Ni/Co decreased from 14.73 and 14.84 to 1.73 and 3.31, respectively, implying a rapid environmental change from euxinic to suboxic conditions. From samples Z7 to Z6 at the stage of the second decline, TOC decreased from 3.24 to 2.12%, and the change in major elements was much more significant than the first decline; for example, the content of SiO\(_2\) decreased from 61.41 to 33.92%, and the content of CaO increased significantly from 5.32 to 21.28%. The values of V/Cr and Ni/Co decreased from 12.42 and 10.43 to 1.68 and 2.91, respectively, reflecting the rapid change from

**Figure 9.** (a) Al−Fe−Mn ternary diagram to determine the hydrothermal origin for the ORS and the OLS in \(\epsilon_{n1}\). (b) Cross-plots of Eu/Sm vs Sm/Yb to determine the hydrothermal origin for the ORS and the OLS in \(\epsilon_{n1}\). (c) Cross-plots of Eu/Sm vs Y/Ho to determine the hydrothermal origin for the ORS and the OLS in \(\epsilon_{n1}\). (d) Correlation between the contents of Al\(_2\)O\(_3\) and SiO\(_2\) for the ORS and OLS in \(\epsilon_{n1}\).

**Figure 10.** Fe\(_{py}\)/Fe\(_{H}^1\) vs Fe\(_{H}^1\)/Fe\(_{T}\) plots for the ORS and OLS of \(\epsilon_{n1}\) in well ZD1.

+ Z\(_nxs\) of the ORS are greater than those of the OLS, also indicating that the ORS had higher primary productivity, which reflected the growth and reproduction of organisms in the ancient oceans in the Early Cambrian. Previous studies have shown that the organisms in black siliceous shales of the Early Cambrian in South China were mainly derived from algae, bacteria, and radiolarians, which resulted in the high content of Si\(_{xs}\) in the lower part of the ORS (Figure 8).
euxinic to suboxic conditions. The analysis shows that the two
decreases in paleoproductivity were related to sea level decline.
The fall of the sea level led to a change in the redox conditions
from euxinic to suboxic, which is not conducive to the
deposition of the sulfides Cu, Zn, and Ni and results in the
decline of paleoproductivity.

5.3. Factors Influencing Organic Matter Accumulation. In general, the enrichment of organic matter occurred for
three reasons: organic matter input (paleoproductivity), organic
matter preservation (redox conditions and deposition rates),
and organic matter dilution (terrigenous detrital input).

Considering that the contents of Al and Ti are significantly
different in shale and limestone samples, the shale samples were
selected only to eliminate the influence of the lithofacies on
organic matter enrichment.

Figure 11. Stratigraphic distributions of redox conditions (V/Cr, Ni/Co, U/Th, Fe_p/Fe_TiO, and δCe) and paleoproductivity (Ni/Al and Ni_ox + Cu_ox + Zn_ox) proxies in ε_r^1 of well ZD1.

Figure 12. Mo_EF vs. U_EF for samples in ε_r^1 of well YD2. The solid line shows the seawater Mo/U ratios (1 × SW), and dashed lines show multiples of the seawater Mo/U ratios (0.1 × SW, 0.3 × SW, 3 × SW).

Figure 13. TOC vs. Mo_EF scatter plots for samples in ε_r^1 of well YD2. Mo/TOC can reflect different degrees of stagnation. Most Mo/TOC values of the shale samples lie between 15 and 35 × 10^−4, suggesting a semistagnant environment.
were used to study the influencing factors for organic matter enrichment in the wells of ZD1 and YD2. The results show that TOC had a good positive correlation with terrigenous detrital input proxy Al (Figure 14a), whereas a relatively poor correlation with Ti (Figure 14b).

Figure 14. (a) Relationship between TOC and the concentration of element Al. (b) Relationship between TOC and the concentration of element Ti. (c) Relationship between TOC and V/Cr. (d) Relationship between TOC and U/Th. (e) Relationship between TOC and Ni/Co. (f) Relationship between TOC and $\delta$Ce. (g) Relationship between TOC and $Fe_{py}/Fe_{HR}$. (h) Relationship between TOC and Ni/Al. (i) Relationship between TOC and Ni$^{\text{xs}}$ + Cu$^{\text{xs}}$. (j) Relationship between TOC and La$^{\text{nn}}$/Yb$^{\text{nn}}$. TOC had good positive correlations with redox proxies V/Cr (Figure 14c), U/Th (Figure 14d), Ni/Co (Figure 14e), $\delta$Ce (Figure 14f), and $Fe_{py}/Fe_{HR}$ (Figure 14g), and U/Th had the best correlation with TOC, followed by $\delta$Ce, Ni/Co, V/Cr, and $Fe_{py}/Fe_{HR}$. TOC also had good positive correlation with the
paleoproductivity proxies Ni/Al (Figure 14h) and NiXS + CuXS (Figure 14i), and deposition rate proxy La\textsubscript{n}/Yb\textsubscript{n} (Figure 14j). Comprehensive studies show that organic matter enrichment is influenced by terrigenous detrital input, redox conditions, paleoproductivity, and deposition rates, and the main controlling factor affecting organic matter enrichment is paleoredox conditions, which is consistent with the previous study\textsuperscript{24,27} followed by paleoproductivity and deposition rates, and the terrigenous detrital input has a relatively weak influence on organic matter enrichment. In addition, the organic matter enrichment is influenced by the lithology (Figure 3). The siliceous shale is the most enriched in organic matter (avg. TOC = 5.19%), followed by calciferous silty shale (avg. TOC = 1.50%), whereas silty limestone (avg. TOC = 0.67%) is not enriched in organic matter.

5.4. Developmental Model of the $\epsilon^1n^1$ Shale. Based on the results of multiple geochemical proxies, an organic matter enrichment model of $\epsilon^1n^1$ is established for western Hubei (Figure 15). Stage I is the lower part of the ORS in early $\epsilon^1n^1$ with a relatively rising sea level (Figures 8 and 15a). The paleoenvironment is characterized by a cold and humid climate, euxinic conditions that include the free gas H\textsubscript{2}S, low salinity
seawater and terrigenous detrital input, and relatively high paleoproductivity, deposition rate, and Si\textsubscript{xs} content, which indicates marine microorganism propagation and preservation very well,\textsuperscript{69} which are conducive to organic matter enrichment, with a TOC average value of 5.19%.

Stage II is the upper part of the ORS in middle \(\epsilon_1,n^1\) with the sea level relatively falling (Figures 8 and 15b). The paleoenvironment is characterized by a moderate hotter and drier climate, anoxic conditions including ferrous ions, medium salinity seawater and paleoproductivity, high terrigenous detrital input, and low contents of Si\textsubscript{xw}. Generally, the high terrigenous detrital input would lead to the dilution of organic matter, which is not conducive to organic matter enrichment,\textsuperscript{69} with a TOC average value of 1.99%.

Stage III is the OLS in late \(\epsilon_1,n^1\), with the sea level continuing to fall (Figures 8 and 15c). Compared with stage II, the paleoclimate became much hotter and drier, and the salinity of sea water was higher. Although the terrigenous detrital input decreased, the bottom water was in suboxic conditions due to the continuous decline in the sea level, which was not conducive to organic matter enrichment, with a TOC average value of 0.84%.

Further research showed that there is a causal relationship between paleoproductivity, redox conditions, seawater salinity, the growth of microbes, and sea level fluctuations. At the stage of sea level rise, increasing seawater depth may also cause less-restricted water mass circulation and increased nutrient upwelling to the deep shelf, which may result in blooms of marine plankton and high surface primary productivity (Figure 15a).\textsuperscript{27,28} Meanwhile, increasing seawater depth could lead to euxinic water conditions and enhanced preservation of organic matter. At the stage of sea level fall, the shallowing water depth would lead to greater water mass restriction and weaker nutrient upwelling into the deep shelf, which were not conducive to the growth of microorganisms and the increase of surface primary productivity; meanwhile, the lowstand of the sea level would lead to suboxic andoxic conditions, which are not conducive to the preservation of microorganisms (Figure 15b,c). The evolution model has similarities and differences with previous studies,\textsuperscript{27,28} the similarity is that both models can be basically divided into two stages of sea level rise and sea level fall. The difference is that the stage of sea level fall was divided into two substages in the study (Figure 15b,c), which can better show the change in the sedimentary environment, such as the content of Si\textsubscript{xw}, terrigenous detrital input, paleoclimate, paleoredox conditions, and paleoproductivity.

In conclusion, the study has revealed the black carbonaceous siliceous shale in the lower part of the ORS with the thickness approximately 40 m and the average TOC value of 5.19%, which was deposited under euxinic conditions with high paleoproductivity. The analysis indicates that this black carbonaceous siliceous shale is the most favorable shale gas reservoir. The research results are helpful to identify the target layers of \(\epsilon_1,n^1\), and can further provide the geological basis for the commercial development of shale gas of the city of Yichang in western Hubei.

6. CONCLUSIONS

The \(\epsilon_1,n^1\) can be divided into ORS and OLS with average TOC contents of 4.21 and 0.84%, respectively. The ORS is characterized by high contents of SiO\textsubscript{2}, U, V, Ni, Zn, Cu, and left-inclining types of REE distribution curves.

The \(\epsilon_1,n^1\) was deposited in the continental margin with a provenance consisting of mixed felsic and mafic rocks. The biological silicon content is greater in the ORS. The paleoclimate is cold and humid with low salinity in the ORS and hot and arid with high salinity in the OLS. \(\epsilon_1,n^1\) was deposited in a semistagnant basin, and the ORS shows a relatively lower stagnant degree with euxinic sulferretted conditions and high paleoproductivity. Redox condition is the main factor affecting organic matter enrichment.

The organic matter enrichment of \(\epsilon_1,n^1\) can be divided into three stages: early \(\epsilon_1,n^1\) with a cold and humid climate, euxinic conditions, and high paleoproductivity; middle \(\epsilon_1,n^1\) with a relatively hot and dry climate, anoxic ferruginous conditions, and moderate paleoproductivity; and late \(\epsilon_1,n^1\) with a much hotter and drier climate, suboxic tooxic conditions, and relatively low paleoproductivity. The study revealed that the black carbonaceous siliceous shale in the lower part of the ORS with a thickness of approximately 40 m and the average TOC value of 5.19% is the most favorable layer for shale gas exploration.

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