Lithosphere

Research Article

Organic Matter Enrichment of Black Shale at the Turn of Ordovician-Silurian in the Paleosedimentary Center in Southern Sichuan Basin, Upper Yangtze Area

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Received 12 January 2022; Accepted 29 April 2022; Published 24 May 2022

Academic Editor: Min-Te Chen

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Herein, integrated vertical variation characteristic analysis was conducted by measuring total organic carbon (TOC), major and trace elements in Upper Ordovician-Lower Silurian (Wufeng-Longmaxi formations) black shale in Weiyuan, Luzhou, and Changning areas, southern Sichuan Basin to clarify the control of organic matter (OM) enrichment in different sublayers. According to the cycle boundary, it was divided into member 1 (submember 1 and submember 2) and member 2 from early to late Longmaxi formation, while it was divided into 4 sublayers from early to late during submember 1 depositional period. Under the warm and humid paleoclimate, high paleoproductivity, and gradually oxic paleoredox conditions, the TOC content (0.22-3.27 wt% in Luzhou area) in Wufeng formation increased gradually from early to late under the cocontrolling of tectonic framework and stagnant sea. After the glacial period, the warm and humid climate of Wufeng formation continued in Longmaxi formation, and TOC content reached the highest in sublayer 1 (2.02-4.02 wt%, 4.78 wt%, and 6.45 wt% in Weiyuan, Luzhou, and Changning areas, respectively), due to the high paleoproductivity and high sea level caused by melting glaciers, causing the extremely anoxic environment. The OM was preserved best. It remains higher in sublayer 2 (2.39 wt%, 3.69-4.18 wt%, and 3.5-3.86 wt% in three areas, respectively) because of the anoxic environment caused by deep water and the high paleoproductivity, but the temporary hot and dry environment has a certain negative impact on the OM preservation. Under the stable paleoproductivity, sublayer 3 has a character of water decreasing slowly, and the suboxic environment led to the decrease of TOC content (3.82-5.28 wt% and 3.77-4.13 wt% in Luzhou and Changning areas, respectively). Meanwhile, that in the yuan area became deeper and the TOC content became relatively higher (1.92-3.33 wt%). Under the open environment, sublayer 4 was controlled by lower sea level caused by regression, resulting in lower TOC content (1.31-4.57 wt%, 1.64-3.52 wt%, and 3.88-4.49 wt% in three areas, respectively). However, the global regression of the submember 2 period, high terrigenous debris dilution, and oxic environment lead to the no preservation of OM. Generally speaking, the enrichment of OM is not only affected by the changes of global sea level and paleoproductivity to some extent (Longmaxi shale) but also controlled by the tectonic framework in Sichuan Basin (Wufeng shale). The findings of this study can help for a better understanding of the OM enrichment mechanism and provide a theoretical basis for the evaluation of high-quality source rocks.

1. Introduction

The black shales developed in the Wufeng-Longmaxi formation respond favorably to the global marine environmental changes at the turn of Ordovician-Silurian (marine anoxic events, Late Ordovician biological extinction events, Hirnantian glacial events, etc.) [1–3]. In the Late Ordovician, the South China continental where the Yangtze Plate was located was far away from Gondwana. Global geological events (such as glacial activity, volcanic eruption, tectonic movement, and sea-level change) were different in this area [4–6]. Under the influence of the Guangxi movement, the Yangtze platform developed differential uplift, forming the Xuefeng, Chuanzhoong, and Qianzhong uplifts, and three deep-water paleosedimentary centers in the northern, eastern, and southern Sichuan Basin.

The black shale from Late Hirnantian to Early Rhuddanian is deposited more widely than that of Katian. The black shale in North Africa and Arab is called "HOT SHALES" due to its high U content and obvious change of logging curve, which was one of the most famous source rocks around the world [7]. Meanwhile, this black organic-rich shale with similar characteristics was also developed in Sichuan Basin during this period, with much more long term since Katian and more extensive development compared with the HOT SHALES, which has always been the focus of many scholars [5, 6, 8–10]. In addition, the hydrocarbon generation potential, reservoir space, adsorption capacity, and even the gas content of shales were influenced by the organic matter (OM) content [11–20].

It is generally believed that the transgression post glacial led to an anoxic marine environment, resulting in the black shale deposition during the Late Hirnantian and Early Rhuddanian [15, 21], although the deposition of black shale was also developed in the Katian period, which has obvious differences in distribution, mainly developed in equatorial tropical subtropical areas compared with that of Late Hirnantian and Early Rhuddanian [22]. The sedimentary environment of black shale in Katian is shallow water epicontinental sea environment (black shale of North American Central continent and Baltic continent [23], restricted offshore environment (black shale of Wufeng-Longmaxi formation in Yangtze Basin [24] and upwelling area at the edge of continental shelf (Moffatt shale in Scotland and YrAIIT shale in Wales Basin [25–27])).

For the development of organic-rich black shale in the Wufeng-Longmaxi formation in the Yangtze region, predecessors generally believe that it is the influence of anoxic environment, sea-level change, high productivity, and the comprehensive effect of the above [8–10, 28–32]. They have used paleontological methods to establish an isochronous stratigraphic framework, element, and isotope inversion of paleoenvironment to study the strata in different areas of the Yangtze Plate [6, 30, 33–35]. Preservation in anoxic environment [35], restricted deep-water shelf environment [33], sea-level changes [28, 31], and high paleoproductivity [32] are considered to be the main controlling factors of organic matter enrichment in this period in the Yangtze platform [29, 30]. It is generally believed that the transgression post glacial led to an anoxic marine environment, resulting in the black shale deposition during the Late Hirnantian and Early Rhuddanian [15, 21].

However, it has been turned to the sublayer 1, 2, 3, and 4 in submember 1 of the early Longmaxi formation as the target stratum currently. Moreover, the OM content of different sublayers, even the same sublayer in different areas, ranges variously, which means there is still a lack of cognition in discrepancy mechanism. Furthermore, most of them ignore the response of sea-level changes caused by glaciation at the turn of Ordovician and Silurian, the impact of regional tectonic movement on sedimentary model, and the impact of differences in deposition rate on shale [10, 30, 31, 34]. The OM enrichment of shale is jointly controlled by many factors, which will be affected by any event. Therefore, the further study of OM enrichment mechanism in different formations and sublayers shales is of great significance to supply a scientific basis for exploration and development. It has been reported that geochemical characteristics of major and trace elements in shale have been effectively used in the reconstruction of the paleoenvironment [36-38].

Therefore, this paper focuses on the differences of OM enrichment between different sublayers ignored in previous studies, and systematic vertical geochemical variation characterization of the newly drilled wells of Wufeng formation (O_3w) and early Longmaxi formation (S_1l_1) , divided into sublayer 1, 2, 3, and 4, located in the depositional center of southern Sichuan Basin was carried out. The effects of the total organic carbon (TOC), major, trace, and rare earth elements (REE) amounts, terrigenous detritus, paleoproductivity, paleoclimate, sea-level changes, paleoredox, and restriction of water column have been evaluated. Furthermore, the OM enrichment of O_3w and S_1l_1 located in the sedimentary center of southern Sichuan Basin combined with regional tectonic evolution from multiple perspectives has been reconstructed.

2. Geological Setting

The Yangtze Plate has experienced multistage tectonic movements since the Sinian period. The Late Ordovician (Wufeng formation)-Early Silurian (Longmaxi formation) is a period of strong compression in southern China. During the Late Ordovician, under the continuous subduction of the Paleo-Tethys Ocean, the west of the basin was tensioned to the west of Longmen Mountain, the South Qinling Ocean to the north of the basin subducted to the north, the Yangtze Craton was close to the North China Craton, the Cathaysian landmass to the east was further pushed northwestward, and the dew surface was raised in Central Guizhou. The scope of the Upper Yangtze Craton where the Sichuan Basin is located is further reduced, which makes the extensive sea in the Early-Middle Ordovician transform into a restricted sea surrounded by uplifts. The sedimentary basement is characterized by high in the southeast and low in the northwest, and the sea gradually deepens from southeast to north (Figure 1(a)) [6]. Sichuan Basin is located the northwest of the Upper Yangtze platform, which is one of the secondary structural units, and had the prototype of the basin during



FIGURE 1: The general sketch of the problem in studying OM enrichment.

the Indosinian period, and then, the current structural appearance through the Himalayan movement is formed (Figure 2(b)).

During the sedimentary period of Longmaxi formation, the further expansion of the Qianzhong Uplift was integrated with the Kangdian archicontinent in the west and the Xuefeng Uplift in the east. At the same time, the Leshan-Longnvsi underwater uplift in Central Sichuan Basin was further uplifted, making the southern Sichuan Basin dominated by restricted epicontinental sea sedimentation, including Weiyuan, Luzhou, and Changning area. Underwater low uplift is developed in some areas of Weiyuan [39], and a set of marine shale with OM enrichment was widely developed in Southern Sichuan Basin (Figure 2(a)) [40, 41].

The Wufeng and Longmaxi formation in Sichuan Basin is in integrated contact. During the deposition of Wufeng formation, the sea level rose, until the Hirnantian glacier occurred all over the world made and the sea level fell rapidly [5], while the sea level rose rapidly after the Hirnantian glacier epoch. The global sea level fluctuated frequently in this period. Affected by the Guangxi movement, the sealevel change in the Yangtze region was slightly different from that of the global [4-6, 21]. The internal strata of the Longmaxi formation are in an integrated contact relationship, which is a progradational sedimentary cycle in which the water column continues to become shallower [42]. There is a short-term slow decline to rapid rise stage in the cycle. According to the cycle boundary and graptolite biostratigraphy, it was divided into member 1 (submember 1 (LM 1-5) and submember 2 (LM 6-8)) and member 2 (LM 9) from early to late Longmaxi formation. Submember 1 is in integrated contact with the underlying Wufeng formation, which develops dark calcareous shale and siliceous shale, mixed with a small amount of silty mudstone [43]. The natural gamma logging curve shows the characteristics of "extremely high value" at the bottom of submember 1, rapidly decreases upward, then slowly increases, and rapidly decreases at the top. Silty mudstone, argillaceous siltstone, and calcareous siltstone are developed in submember 2, and the natural gamma value is less than that of submember 1 as a whole. However, submember 1 of the target layer is the main shale gas producing layer in Sichuan Basin. At present,

general stratification is difficult to meet the actual needs of shale gas benefit development. Therefore, according to the rock characteristics and paleontological and logging data, the key layer was finely divided into sublayers 1 (LM 1), 2 (LM 2-3), 3 (LM 4), and 4 (LM 5) from early to late (Figure 2(c)) [43].

3. Samples and Methods

3.1. Sample Section. Considering the comparative analysis of different stratus in three shale gas production areas in southern Sichuan Basin, 9 samples of O₃w were collected from new drilled well Y101, and 65 samples of S₁l₁ were collected from three new drilled wells W214, Y101, and N222 in Weiyuan, Luzhou, and Changning areas, respectively. Sample depths are ranged from 3520.3 m to 3575.6 m, 4102.8 m to 4159.1 m, and 4305.1 to 4332.6 m in well W214, Y101, and N222, respectively. 3 core samples in submember 2 were collected in well W214, and 2, 1, 2, and 12 core samples, 1, 6, 7, and 24 core samples, and 1, 2, 2, and 2 core samples in sublayer 1, sublayer 2, sublayer 3, and sublayer 4, respectively, were collected in well W214, Y101, and N222, respectively, among them (Figure 3). Massive graptolite black organic-rich shale is developed in S_1l_1 during sampling. The selected samples with fairly less weathering and diagenesis can provide decent indications for initial depositional environments.

3.2. Experimental Methods. Measurements of major, trace element, and REE concentrations of all shale samples were conducted at 14°C and relative humidity of 30% at the Radionuclide Lab, Beijing Institute of Geology, Nuclear Industry. All samples were pulverized into less than 200 mesh size in a clean environment for further analysis.

The most accurate melt sheet method and X-ray fluorescence spectrometry (XRF) were used for major element analysis. After baking in a muffle furnace at 1000°C for 3-5 hours, $0.7 g \pm 0.0003 g$ powder samples were mixed with $7.7 \text{ g} \pm 0.003 \text{ g}$ anhydrous $L_{i2}B_4O_7$ solvent, using the Analymate-V4D melting mechanism of Beijing Jingyuan Century Science and Technology Ltd. to form a melting sheet, and then measured with Epsilon3XLE type X-ray fluorescence spectrometer manufactured by Netherlands. The experiment was conducted based on the reference material GB/T 14506.28-2010 and GB/T14506.14-2010, with analysis error of less than 5%. Inductively coupled plasma mass spectrometry (ICP-MS) was used for trace elements and REE analysis. The samples were dissolved using a mixed acid closed digestion method. The volume ratio of hydrochloric acid, nitric acid, hydrofluoric acid, and perchloric acid was 4:3.5:2:6.5, and the dilution factor was 500 (diluted 0.1 g to a constant volume of 50 ml). The principle is that the ICP uses a high-frequency RF signal of powerful power applied on the inductor coil to form a high-temperature plasma inside the coil (that is, ionizes an electron to form a monovalent positive ion) and promotes the plasma continuous balance and ionization by pushing the gas, while mass spectrometry is a mass screening and analyzer that measures the intensity of an ion by selecting ions of different mass-to-



FIGURE 2: (a) Lithofacies palaeogeographic map of the Yangtze block during the Late Ordovician to Early Silurian after literature [6]; (b) geological map of South Sichuan Basin and the location of selected samples; and (c) graptolite biostratigraphy and stratigraphic division [42, 43], the change of global sea level after literature [21], and the sea level and sedimentary cycle of Yangtze after literature [5].

nuclear ratios (m/z) to calculate the intensity of an element. The experiment was conducted based on the reference material GB/T14506.30-2010 and GB/T14506.11-2010, with an analysis error of less than 5%.

The TOC content was tested by Eltre CS580A type carbon-sulfur analyzer produced by Germany. The powder sample is dissolved with 5% dilute hydrochloric acid for many times until no bubbles can be generated, soaked for 24 hours and dried, so as to remove inorganic carbon. Then, open the analyzer and the oxygen valve, the samples were burned in pure oxygen at 1400°C for about 2 minutes, and the signals were detected when CO_2 was generated. The accuracy of analysis is greater than 0.5%.

3.3. Data Analysis. The trace elements usually come from autogenic and detrital components, whereas only the former can indicate the depositional features under paleoenvironments. Furthermore, due to the compositional variability of rock samples, errors can be introduced into the analysis if solely relying on the comparison between trace elemental concentration and average shale. To minimize the impact from detrital components, the concentrations of trace elements need to be normalized to aluminum content that stabilized during diagenesis. This value will be compared to that of the Post Achaean Australian Shale (PAAS) to determine the enrichment or depletion of this trace element, often referred to as the enrichment factor (EF) [44]. Its calculation formula is as follows:

$$EF_X = \frac{(X/Al)_{Sample}}{(X/Al)_{PAAS}},$$
(1)

where *X* is the content of one specific element or its oxide, %, and EF_X is the concentration of this element or its oxide, dimensionless. Values of $EF_X > 1$ indicate element or its

oxide enrichment relative to the PAAS [45], conversely, depletion relative to it [37].

The chemical alteration index (CIA) can quantitatively reflect the chemical weathering degree of sedimentary rocks and furthermore reconstruct the paleoclimate conditions change in the source area. Its calculation formula is as follows:

$$CIA = (Al_2O_3/(Al_2O_3 + CaO * + Na_2O + K_2O)) \times 100, \quad (2)$$

where each oxide is measured in moles and CaO* refers to CaO in silicate minerals only. Because of the approximation between the proportion of Ca²⁺ and Na⁺ in the lattice of silicate minerals, if the CaO* value obtained after correction calculation is greater than Na₂O, the mole content of Na₂O can replace CaO; if conversely, CaO* is the mole content of CaO in silicate minerals [46].

In addition, K metasomatic reaction during the transformation between clay minerals in weathered sediments, especially the transformation of kaolinite into illite, results in the increase of foreign K content and the decrease of CIA value due to the influence of diagenesis in practical application [47]. Therefore, the metasomatism of K needs to be corrected [48]. Its calculation formula is as follows:

$$CIA_{c} = \frac{Al_{2}O_{3}}{Al_{2}O_{3} + CaO * + Na_{2}O + K_{2}O_{c}} \times 100, \qquad (3)$$

$$K_{2}O_{c} = \frac{(m \times Al_{2}O_{3} + m \times (CaO * + Na_{2}O))}{(1 - m)},$$

$$m = \frac{K_{2}O}{Al_{2}O_{3} + CaO * + Na_{2}O + K_{2}O},$$
(4)

where $K_2 O_c$ is the corrected $K_2 O$ content.



FIGURE 3: Graptolite biostratigraphy and stratigraphic correlation section, gamma-ray logging, location of samples, and relative sea level of O_3w and S_1l_1 .

There are various sources of Ba in sediments, such as terrigenous clastic Ba, biological Ba, submarine hydrothermal Ba, and some compounds of benthic heterotrophic biosynthesis Ba, where only biological Ba can be used as an indicator of paleoproductivity [37, 49]. Its calculation formula is as follows:

$$Ba_{bio} = Ba_{Sample} - Al_{Sample} \times (Ba/Al)_{PAAS},$$
(5)

where Ba_{Sample} and Al_{Sample} are the total contents of Ba and Al in the measured rock samples, respectively.

The calculation formula of Si_{excess} is as follows [50]:

$$Si_{excess} = Si_{Sample} - Al_{Sample} \times (Si/Al)_{PAAS},$$
 (6)

where Si_{Sample} is the total contents of Si in the measured rock samples.

4. Results

4.1. Major Element. The testing results of major elements are shown in Table 1, in which all elements are represented by their corresponding oxides. SiO₂, Al₂O₃, and CaO were commonly considered to be the largest proportion in the marine shale [50]. Among these, SiO₂ displays the greatest contribution, ranging from 38.11 wt% to 72.97 wt% (avg. 53.09 wt%) in the samples of O₃w in well Y101 and from 38.12 wt% to 72.82 wt%, 43.83 wt% to 71.36 wt%, and 52.28 wt% to 63.89 wt% in the samples of S_1l_1 in well W214, Y101, and N222, with the average of 54.42 wt%, 59.29 wt%, and 58.67 wt%, respectively. Al₂O₃, the second highest content of oxide, has the content varying from 9.46 wt% to 14.84 wt% (avg. 13.05 wt%) in the samples of O_3w in well Y101 and from 5.66 wt% to 18.65 wt%, 3.83 wt% to 18.86 wt%, and 5.62 wt% to 15.85 wt% in the samples of S₁l₁ in well W214, Y101, and N222, with the average of 14.66 wt%, 12.24 wt%, and 10.87 wt%, respectively. CaO has the third highest major elemental concentration, ranging from 1.18 wt% to 14.92 wt% (avg. 7.99 wt%) in the

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Sample	Depth (m)	Formation	Member	TOC (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	MnO (%)	TiO ₂ (%)	P ₂ O ₅ (%)	FeO (%)	Si _{excess} (%)	CIA
W1	3520.3	S ₁ I ₁		0.24	57.82	18.65	7.03	2.76	1.07	0.83	4.57	0.10	0.65	0.11	4.38	-1.94	71.9
W2	3523.3	$S_1 l_1$	Submember 2	0.19	61.19	17.83	6.72	2.48	0.38	1.03	4.19	0.05	0.71	0.12	4.25	0.91	73.0
W3	3529.3	$S_1 l_1$		0.57	59.07	17.61	7.16	2.64	1.13	0.91	4.22	0.07	0.63	0.11	3.97	0.26	71.3
W4	3535.2	$S_1 l_1$	Sublayer 4	1.31	57.25	16.20	7.93	2.45	1.97	0.84	4.05	0.06	0.55	0.10	3.64	1.60	70.7
W5	3538.0	$S_1 l_1$	Sublayer 4	1.68	53.17	16.24	6.21	2.60	5.21	1.00	3.91	0.09	0.55	0.10	3.5	-0.37	69.8
W6	3538.6	$S_1 l_1$	Sublayer 4	1.65	54.93	16.26	8.33	2.55	2.78	0.85	4.04	0.06	0.55	0.09	3.5	0.42	70.7
W7	3540.0	$S_1 l_1$	Sublayer 4	1.92	54.17	15.82	5.70	2.68	5.20	0.91	3.87	0.10	0.56	0.10	2.96	0.75	70.1
W8	3541.0	$S_1 l_1$	Sublayer 4	1.89	55.16	15.49	5.38	2.60	4.75	0.95	3.77	0.08	0.56	0.09	3.23	1.72	69.8
6M	3543.1	$S_1 l_1$	Sublayer 4	1.69	53.67	15.45	6.13	3.13	4.86	0.91	3.73	0.12	0.55	0.10	3.72	1.09	70.1
W10	3547.6	$S_1 l_1$	Sublayer 4	2.77	57.36	15.41	4.79	2.45	3.64	0.85	3.89	0.05	0.65	0.19	2.21	2.87	70.1
W11	3553.6	$S_1 l_1$	Sublayer 4	3.35	38.12	10.38	4.16	2.86	16.51	0.63	2.60	0.07	0.44	0.16	1.72	1.69	69.0
W12	3558.5	$S_1 l_1$	Sublayer 4	2.97	48.63	10.92	4.26	2.91	11.52	0.69	2.65	0.05	0.52	0.17	1.15	5.76	69.3
W13	3560.1	$S_1 l_1$	Sublayer 4	3.83	54.42	9.97	3.57	2.89	9.59	0.63	2.43	0.05	0.47	0.23	0.95	9.94	69.3
W14	3563.7	$S_1 l_1$	Sublayer 4	2.42	41.67	10.17	3.40	3.13	16.07	0.52	2.61	0.09	0.44	0.12	2.01	3.68	70.0
W15	3566.1	$S_1 l_1$	Sublayer 4	4.57	53.15	13.42	6.00	2.72	5.36	0.78	3.33	0.03	0.56	0.17	1.65	3.99	69.8
W16	3568.0	$S_1 l_1$	Sublayer 3	3.33	53.92	15.44	9.77	2.64	2.04	0.88	3.79	0.02	0.67	0.14	2.29	1.22	70.2
W17	3569.6	$S_1 l_1$	Sublayer 3	1.92	55.73	18.51	5.47	2.35	1.66	1.17	4.37	0.03	0.49	0.11	2.03	-2.70	69.3
W18	3572.0	$S_1 l_1$	Sublayer 2	2.39	52.66	15.84	5.20	2.72	5.27	1.24	3.73	0.05	0.61	0.10	1.7	0.01	67.8
W19	3572.7	$S_1 l_1$	Sublayer 1	2.02	53.49	17.90	4.24	2.59	3.92	1.17	4.33	0.05	0.53	0.10	1.62	-2.79	69.2
W20	3575.6	$S_1 l_1$	Sublayer 1	4.02	72.82	5.66	4.12	1.29	3.52	0.38	1.37	0.03	0.26	0.09	0.85	25.21	69.1
Y1	4102.8	S_1l_1	Sublayer 4	2.56	52.42	14.85	5.03	2.68	6.45	1.09	3.60	0.04	0.67	0.13	3.59	1.44	68.1
Y2	4105.0	$S_1 l_1$	Sublayer 4	1.64	43.83	15.45	4.14	3.82	10.63	0.83	4.06	0.07	0.58	0.12	3.59	-3.50	69.5
Y3	4107.5	$S_1 l_1$	Sublayer 4	3.01	48.52	14.34	11.39	2.41	3.38	0.87	3.69	0.03	0.63	0.12	2.96	0.41	69.1
Y4	4109.0	$S_1 l_1$	Sublayer 4	2.21	52.25	18.86	4.54	2.95	3.67	0.77	4.83	0.02	0.61	0.10	2.52	-4.86	71.9
Y5	4111.5	$S_1 l_1$	Sublayer 4	3.52	54.55	16.82	6.26	2.53	2.38	0.96	4.16	0.02	0.69	0.13	2.78	-0.63	70.1
Y6	4113.4	$S_1 l_1$	Sublayer 4	2.24	50.33	15.21	10.54	2.89	2.96	0.78	3.94	0.03	0.66	0.10	2.46	-0.10	70.3
Y7	4115.2	$S_1 l_1$	Sublayer 4	2.52	54.96	14.82	5.25	2.71	5.04	0.81	3.65	0.04	0.62	0.11	2.87	2.67	70.4
Y8	4117.2	$S_1 l_1$	Sublayer 4	1.97	57.80	14.83	7.45	2.09	2.38	0.64	3.69	0.03	0.50	0.08	2.22	3.98	72.0
Y9	4119.1	$S_1 l_1$	Sublayer 4	2.07	58.16	14.23	4.89	2.99	4.17	0.74	3.48	0.05	0.55	0.09	3.10	5.08	71.0
Y10	4120.2	$S_1 l_1$	Sublayer 4	2.67	61.00	14.80	5.17	2.38	2.17	0.74	3.62	0.02	0.60	0.11	2.51	5.52	71.3
Y11	4122.4	$S_1 l_1$	Sublayer 4	2.26	59.76	14.40	6.92	2.34	2.09	0.71	3.57	0.02	0.56	0.10	3.05	5.56	71.2
Y12	4125.9	$S_1 l_1$	Sublayer 4	1.83	55.19	15.84	7.11	2.85	3.25	1.01	3.90	0.04	0.65	0.12	3.17	1.19	69.3
Y13	4128.8	$S_1 l_1$	Sublayer 4	2.54	60.70	14.48	4.72	2.25	2.75	1.10	3.44	0.03	0.61	0.10	2.67	5.87	68.2

TABLE 1: Maior elemental composition of black shales in S.I. of well W214 and N222, S.I. and O.w of well Y101.

$\label{eq:TABLE 1: Continued.} TABLE 1: Continued. \\ th (m) Formation Member TOC SiO_2 Al_2O_3 Fe_2O_3 MgO \\ (\%) (\%) (\%) (\%) (\%) (\%) (\%) (\%) \\ 31.4 S_1l_1 Sublayer 4 2.15 58.93 13.70 4.07 2.60 \\ \end{array}$	$\begin{tabular}{ c c c c c c c } TOL & SiO_2 & Al_2O_3 & Fe_2O_3 & MgO \\ \hline Formation & Member & (\%) & (\%) & (\%) & (\%) & (\%) \\ S_1l_1 & Sublayer 4 & 2.15 & 58.93 & 13.70 & 4.07 & 2.60 \\ \hline \end{tabular}$	TABLE I: Continued. Member TOC SiO2 Al2O3 Fe2O3 MgO Noblayer 4 2.15 58.93 13.70 4.07 2.60	TABLE I: Continued. TOC SiO2 Al2O3 Fe2O3 MgO (%) (%) (%) (%) (%) 2.15 58.93 13.70 4.07 2.60	TABLE I: Continued. SiO2 Al2O3 Fe2O3 MgO (%) (%) (%) (%) 58.93 13.70 4.07 2.60	TABLE I: Continued. Al ₂ O ₃ Fe ₂ O ₃ MgO (%) (%) (%) 13.70 4.07 2.60	LE 1: Continued. Fe2O3 MgO (%) (%) 4.07 2.60	tinued. MgO (%) 2.60		CaO (%) 4.50	Na ₂ O (%) 1.26	K ₂ O (%) 3.23	MnO (%) 0.04	TiO ₂ (%) 0.60	P ₂ O ₅ (%) 0.11	FeO (%) 2.26	Si _{excess} (%) 6.26	CIA 66.2
133.2 S ₁ l ₁ Sublayer 4 2.30 57	S ₁ l ₁ Sublayer 4 2.30 57.	Sublayer 4 2.30 57	2.30 57.	57.	. [9]	13.26	5.53	2.67	4.87	1.18	3.10	0.04	0.62	0.11	3.02	0.22 6.32	
[34.8 S ₁ l ₁ Sublayer 4 2.88 58	S ₁ I ₁ Sublayer 4 2.88 58	Sublayer 4 2.88 58	2.88 58	58	3.86	11.60	6.84	2.12	4.01	1.04	2.82	0.03	0.55	0.10	1.80	9.48 8.77	66.
.35.9 S.I. Sublaver 4 2.36 55	S.I. Sublayer 4 2.36 55 59	Sublayer 4 2.36 59	2.36 55	5 6	1.01 .92	12.63	4.70 4.70	2.34	4.72	1.11 1.31	2.86 2.86	0.04	دد.ں 19.0	0.11	2.80	0.73 8.38	65.2
$(36.2 ext{ S}_{1})_{1}$ Sublayer 4 2.18 5	S ₁ l ₁ Sublayer 4 2.18 5	Sublayer 4 2.18 5	2.18 5	5	9.30	13.33	4.25	2.41	4.76	1.28	3.07	0.04	0.59	0.10	2.52	7.00	66.0
136.8 S ₁ l ₁ Sublayer 4 2.48 6	S ₁ l ₁ Sublayer 4 2.48 6	Sublayer 4 2.48 6	2.48 6	U	60.54	12.52	4.45	2.41	4.66	1.12	2.91	0.04	0.59	0.10	2.66	8.84	66.7
(37.5 S ₁ l ₁ Sublayer 4 2.68 €	S ₁ l ₁ Sublayer 4 2.68 6	Sublayer 4 2.68 6	2.68 6	Ð	60.18	12.89	4.78	2.41	4.46	1.21	2.96	0.04	0.63	0.11	3.16	8.10	66.3
(38.1 S ₁ l ₁ Sublayer 4 2.64 ($S_1 l_1$ Sublayer 4 2.64 (Sublayer 4 2.64 (2.64 (~	51.21	12.63	4.99	2.34	4.52	1.17	2.96	0.03	0.60	0.10	2.43	8.98	66.2
140.5 S ₁ l ₁ Sublayer 4 2.61 (S ₁ l ₁ Sublayer 4 2.61 (Sublayer 4 2.61 (2.61 (0	52.08	13.97	4.58	2.14	2.48	1.02	3.37	0.03	0.56	0.10	2.28	7.31	68.4
$[40.8 S_1 l_1 Sublayer 4 2.77 ext{ } ext{ }$	$S_1 l_1$ Sublayer 4 2.77 ϵ	Sublayer 4 2.77 6	2.77 6		53.13	12.94	5.19	1.93	2.20	0.95	3.05	0.02	0.53	0.09	2.18	9.40	68.6
$(42.8 S_1 l_1 Sublayer 3 4.34 6$	S ₁ l ₁ Sublayer 3 4.34 6	Sublayer 3 4.34 6	4.34 6	Q	5.84	11.33	4.44	1.70	1.89	0.82	2.77	0.02	0.50	0.10	2.05	13.16	68.3
(43.2 S ₁ l ₁ Sublayer 3 4.15 6	S ₁ I ₁ Sublayer 3 4.15 6	Sublayer 3 4.15 6	4.15 6	9	1.00	14.37	4.34	2.09	1.92	0.87	3.62	0.02	0.58	0.09	2.87	6.18	69.4
(45.1 S ₁ l ₁ Sublayer 3 4.97 58	S ₁ l ₁ Sublayer 3 4.97 58	Sublayer 3 4.97 58	4.97 58	58	.86	8.05	4.64	3.18	6.39	0.58	2.03	0.11	0.36	0.11	1.93	14.99	67.9
(45.9 S ₁ l ₁ Sublayer 3 5.09 6(S ₁ I ₁ Sublayer 3 5.09 60	Sublayer 3 5.09 60	5.09 6(90	0.03	13.40	4.25	2.17	3.28	0.74	3.49	0.02	0.50	0.11	1.91	7.24	69.7
146.3 S ₁ l ₁ Sublayer 3 3.82 66	S ₁ l ₁ Sublayer 3 3.82 66	Sublayer 3 3.82 66	3.82 66	66	.53	10.75	5.67	1.46	2.14	0.69	2.77	0.02	0.40	0.08	2.01	14.38	68.7
146.8 S ₁ l ₁ Sublayer 3 5.28 64	S ₁ l ₁ Sublayer 3 5.28 64	Sublayer 3 5.28 64	5.28 64	64	.02	7.97	3.29	2.27	5.43	0.56	2.04	0.03	0.37	0.10	0.64	17.52	68.0
147.3 S ₁ l ₁ Sublayer 3 4.71 63	S ₁ l ₁ Sublayer 3 4.71 63	Sublayer 3 4.71 63	4.71 63	63	.49	7.16	2.67	2.26	6.98	0.46	1.84	0.03	0.29	0.10	0.71	18.53	68.7
148.6 S ₁ l ₁ Sublayer 2 3.98 64	S ₁ l ₁ Sublayer 2 3.98 64	Sublayer 2 3.98 64	3.98 64	64	60.1	8.87	3.56	1.69	5.36	0.68	2.24	0.02	0.44	0.08	0.56	16.15	67.3
(49.0 S ₁ l ₁ Sublayer 2 4.00 7	S ₁ l ₁ Sublayer 2 4.00 7	Sublayer 2 4.00 7	4.00 7		1.36	5.67	2.80	1.64	4.62	0.39	1.46	0.02	0.23	0.09	0.70	24.51	68.1
$(49.2 ext{ S}_{1}l_{1} ext{ Sublayer } 2 ext{ 3.71 } 5$	S ₁ I ₁ Sublayer 2 3.71 5	Sublayer 2 3.71 5	3.71 5		54.31	14.12	4.88	2.61	4.99	0.94	3.64	0.02	0.55	0.18	0.60	3.45	68.3
(49.6 S ₁ l ₁ Sublayer 2 3.69 5	S ₁ l ₁ Sublayer 2 3.69 5	Sublayer 2 3.69 5	3.69 5	Ŋ	9.45	6.60	5.81	2.49	7.68	0.56	1.71	0.03	0.33	0.07	0.59	17.51	65.8
150.9 S ₁ l ₁ Sublayer 2 4.18 68	S ₁ l ₁ Sublayer 2 4.18 68	Sublayer 2 4.18 68	4.18 68	6	3.29	4.31	3.88	2.17	6.59	0.40	1.08	0.03	0.21	0.06	0.40	25.19	65.3
151.4 S ₁ l ₁ Sublayer 2 4.15 69	S ₁ l ₁ Sublayer 2 4.15 69	Sublayer 2 4.15 69	4.15 69	ő	9.33	3.83	1.46	2.44	7.33	0.38	0.95	0.04	0.18	0.06	0.65	26.42	64.8
152.8 S ₁ l ₁ Sublayer 1 4.78 55	S ₁ I ₁ Sublayer 1 4.78 55	Sublayer 1 4.78 55	4.78 55	5	60.9	7.69	2.73	3.20	10.01	0.56	1.99	0.06	0.37	0.08	1.05	13.78	67.3
155.2 O ₃ w 3.27 6	O ₃ w 3.27 6	3.27 6	3.27 6	9	0.12	11.14	2.60	2.35	6.64	0.56	2.96	0.05	0.45	0.13	1.09	10.78	70.1
155.7 O ₃ w 2.46 77	O ₃ w 2.46 7.	2.46 7.	2.46 7.	2	2.97	10.57	3.04	1.61	1.18	0.62	2.68	0.03	0.41	0.09	2.24	17.66	69.7
156.3 O ₃ w 0.63 51	O ₃ w 0.63 51	0.63 51	0.63 51	51	.75	14.45	4.56	3.07	8.24	0.85	3.54	0.12	0.69	0.07	3.56	1.74	69.69
157.2 O ₃ w 0.51 30	O ₃ w 0.51 36	0.51 38	0.51 38	3	8.11	9.46	5.40	6.25	14.92	0.42	2.35	0.34	0.43	0.05	3.67	3.12	71.4
157.8 O ₃ w 0.58 4	O ₃ w 0.58 4	0.58 4	0.58 4	4	9.67	13.78	5.77	3.03	8.80	0.87	3.37	0.13	0.69	0.10	2.85	1.81	69.3
158.3 O ₃ w 0.22 E	O ₃ w 0.22 5	0.22	0.22		50.31	14.74	5.19	3.36	8.09	0.93	3.54	0.14	0.74	0.06	3.89	0.62	69.69
158.4 O ₃ w 0.22 4	O ₃ w 0.22 4	0.22	0.22	1.	ł9.12	13.70	4.91	3.27	9.85	0.83	3.32	0.19	0.69	0.06	3.32	1.68	69.8
158.7 O ₃ w 0.54 5	O ₃ w 0.54 5	0.54 5	0.54 5	Ŋ	3.02	14.84	4.93	3.06	6.90	0.81	3.67	0.11	0.71	0.07	3.29	1.73	70.4
159.1 O ₃ w 0.47 52	O ₃ w 0.47 52	0.47 52	0.47 52	5	2.73	14.78	4.86	3.09	7.30	0.82	3.65	0.12	0.70	0.07	3.27	1.69	70.3

CIA	67.5	67.8	67.5	63.5	62.9	62.6	69.0
Si _{excess} (%)	3.89	1.28	8.23	18.02	15.68	16.52	9.97
FeO (%)	2.12	2.26	1.64	0.96	1.01	0.7	1.5
P ₂ O ₅ (%)	0.12	0.12	0.11	0.08	0.10	0.08	0.11
TiO ₂ (%)	0.65	0.68	0.55	0.31	0.27	0.31	0.51
MnO (%)	0.02	0.03	0.02	0.03	0.04	0.04	0.03
K ₂ O (%)	3.97	4.31	3.67	1.81	1.48	1.69	3.61
Na ₂ O (%)	1.06	1.02	0.85	0.76	0.60	0.75	0.67
CaO (%)	3.17	3.09	3.05	8.17	14.18	10.83	2.12
MgO (%)	2.56	3.12	2.07	2.40	2.22	2.73	2.58
$\operatorname{Fe_2O_3}_{(\%)}$	5.17	5.51	4.46	2.35	3.71	2.43	2.53
Al ₂ O ₃ (%)	15.02	15.85	13.12	7.11	5.62	6.60	12.80
SiO ₂ (%)	58.25	55.42	61.24	62.25	52.28	57.34	63.89
TOC (%)	3.88	4.49	3.77	4.13	3.50	3.86	6.45
Member	Sublayer 4	Sublayer 4	Sublayer 3	Sublayer 3	Sublayer 2	Sublayer 2	Sublayer 1
Formation	$S_1 l_1$	$S_1 l_1$	$S_1 l_1$	$S_1 l_1$	S_1l_1	$S_1 l_1$	$S_1 l_1$
Depth (m)	4306.6	4309.3	4311.3	4317.9	4325.6	4328.4	4334.1
Sample	N1	N2	N3	N4	N5	N6	N7

TABLE 1: Continued.

samples of O_3 w in well Y101, and that of S_1l_1 in well W214, Y101, and N222 averages 5.32 wt%, 4.53 wt%, and 6.37 wt%, variable from 0.38 wt% to 16.51 wt%, 1.89 wt% to 10.63 wt%, and 2.12 wt% to 14.18 wt%, respectively. In addition, the contents of Fe₂O₃, MgO, and K₂O in three wells have average values of 5.06 wt%, 2.58 wt%, and 3.18 wt%, respectively. While the value of Na₂O in three wells fluctuates up and down at 1 wt%, the remaining three major element oxides contents (MnO, TiO₂, and P₂O₅) are below 1 wt%. Overall, the distribution of major element oxides in different samples of the three wells is relatively consistent.

4.2. Trace and Rare Earth Elements. The results and analysis of trace element concentrations of samples are shown in Table 2, which contains significant paleoenvironmental information that would be discussed later in this paper [37]. The Ba element has the highest concentration of all, ranging from 1293 ppm to 2202 ppm in well Y101, with an average of 1894 ppm in O3w, and from 726 ppm to 1942 ppm in well W214, 967 ppm to 4964 ppm in well Y101, and 804 ppm to 2242 ppm in well N222, with the average of 1345 ppm, 2667 ppm, and 1531 ppm in S₁l₁, respectively, which is slight to moderately enriched relative to PAAS, same as Th, V, and Ni in S_1l_1 , Sc and Co are neither enriched nor depleted compared with PAAS in S₁l₁, and U and Mo generally exhibit moderate to high enrichment comparing to PAAS in S_1l_1 , while those of O_3w all are neither enriched nor depleted compared to PAAS in O₃w. The enrichment of these trace elements showed a similar trend in S_1l_1 within 3 wells (Figure 4).

The rare earth element (REE) concentrations and their corresponding chondrite and Post Archean Australian Shale (PAAS) compositions are shown in Table 3. The total REE concentrations (\sum REE) for O₃w samples in well Y101 range from 163.61 ppm to 341.52 ppm with an average of 231.24 ppm, for S_1l_1 samples in well W214, Y101, and N222 range from 111.57 ppm to 234.82 ppm, 67.83 ppm to 289.32 ppm, and 88.57 ppm to 201.14 ppm, with the average of 173.15 ppm, 168.13 ppm, and 146.08 ppm, respectively. The ratios of light REEs (LREEs, La-Eu) to heavy REEs (HREEs, Gd-Lu) (\sum LREE/ \sum HREE) of O₃w samples in well Y101 are 6.55-10.36 (avg. 8.89), and those of S_1l_1 samples in three wells (W214, Y101, and N222) are 6.71-10.28 (avg.8.50), 6.86-9.61 (avg.8.58), and 7.49-9.66 (avg.8.18), respectively, indicating that the amount of shale in well Y101 is slightly higher than that of W214, followed by N222. After being normalized against the Chondrite [51], the REE distribution patterns of the shale samples all show sloping LREE trends towards the right and flat HREE trends with negative Eu abnormal (Figures 5(a), 5(c), 5(e), and 5(g)). While the PAAS normalization of REE distribution pattern [52], all demonstrate a similar variation in three wells with slightly Ce abnormal and obviously negative Eu abnormal (Figures 5(b), 5(d), 5(f) and 5(h)). The similar distribution circumstance of chondrite-normalized REE in three wells and PAAS-normalized of that indicates the consistency of REE sources in marine shale samples and the relatively stable supplying of terrigenous clastic material [53, 54].

4.3. TOC. TOC is an important index for evaluating the OM abundance, which can also indicate the OM preservation in source rocks intuitively. Samples in O₃w from well Y101 has a TOC content ranging from 0.22 wt% to 3.27 wt% with the average of 0.99 wt%; the submember 1 of S_1l_1 from well W214, Y101, and N222 has a TOC content ranging from 1.31 wt% to 4.57 wt%, 1.64 wt% to 5.28 wt%, and 3.50 wt% to 6.45 wt%, with the average of 2.57 wt%, 3.14 wt%, and 4.30 wt%, respectively, while that of samples in submember 2 of S₁l₁ from well W214 ranges from 0.19 wt% to 0.57 wt% (avg.0.33 wt%) (Table 1). Vertically, TOC content has a gradual rising trend from early to late O₃w and is higher during the early S_1l_1 depositions and gradually decreasing upwards throughout the late S_1l_1 depositions. Moreover, TOC content in late S_1l_1 is much lower than that of the early S_1l_1 . The TOC contents of most samples in the three wells are relatively high (more than 2 wt%), while the values in the well N222 are the highest, followed by that of Y101 and W214, orderly.

4.4. Correlation Coefficient. The correlation coefficient results of geochemical parameters of O₃w and S₁l₁ of three wells are shown in Figure 6. To reflect the possibility of an event occurrence, the author calculated the p value according to the significance test method using statistical theory. Generally, it is considered that $p(\alpha) < 0.05$ is significant and $p(\alpha) < 0.01$ is very significant, which means that the probability of the difference between samples caused by sampling error is less than 0.05 or 0.01. Ti has high positive correlation coefficient with Al in O₃w of well Y101 (0.97, with $p(\alpha) < 0.01$, n = 9) and in S₁l₁ of well W214, Y101, and N222 (0.78, 0.92, and 0.99, with all $p(\alpha) < 0.01$, n = 20, 38, and 7, respectively). It is commonly considered to be a great representative of terrigenous materials, which indicates that Ti was dominated by detrital inputs according to the result. Though Si_{excess} has a strong negative correlation with Al, the $p(\alpha)$ only in well W214 less than 0.01, and greater than 0.05 in the others, means no significance of them. REE and LREE/HREE covary positively with each other in O_3 w of well Y101 (0.77, with $p(\alpha) < 0.01$, n = 9) and in $S_1 l_1$ of well W214, Y101, and N222 (0.63, 0.65, and 0.75, with all $p(\alpha) < 0.01$, n = 20, 38, and 7, respectively). Moreover, EF_U, EF_{Mo}, U/Th, Ni/Co, and V/Sc exhibit an excellent positive correlation in O₃w of well Y101 and in S₁l₁ of well W214, Y101, and N222, with all $p(\alpha) < 0.01$. Ba_{bio} has a great positive correlation with CIA in S₁l₁ of well Y101 and N222 (0.73 and 0.94, both $p(\alpha) < 0.01$, n = 38 and 7, respectively) while having a negative correlation with that of W214 and in O₃w of well Y101 (-0.37 and -0.7, with both $p(\alpha) <$ 0.01, *n* = 20 and 9, respectively).

5. Discussion

5.1. Sedimentary Environment Analysis

5.1.1. Terrestrial Detrital Influx. Organic-rich shales are normally considered high concentration of silicon, which has three sources—biogenic, hydrothermal, and terrigenous detrital sources [55, 56]. Al-Mn-Fe ternary diagram confirms

V Co Ni	Sc Sc
(mdd) (mqq) (mqq)
49.9	151 19.2
41.1	109 17.5
49.1	140 17.5
55.9	147 17.8
60.5	114 14.5
95.3	190 20.1
58.4	114 13.4
62.1	216 13.4
63.4	170 16.1
82.8	354 12.8
39.5	67 111.0
87.0	266 15.1
61.8	179 13.5
70.3	175 11.8
125.0	298 24.6
197.0	272 39.8
52.7	103 13.3
77.9	243 12.7
41.8	97 10.8
118.0	192 16.2
87.9	143 15.9
47.4	121 7.0
148.0	183 21.3
69.1	130 13.5
76.5	136 23.5
68.2	155 19.3
85.8	132 16.4
65.1	125 15.6
59.4	136 11.6
76.5	189 14.9
59.6	94 16.2
63.6	106 17.8
65.0	103 13.0

TABLE 2: Selected trace elemental composition of black shales in S,l, of well W214 and N222, S,l,, and O₃w of well Y101.

						TABLI	E 2: Contir	ned.								
Sample	Depth (m)	Formation	Member	Sc (ppm)	(mqq)	Co (ppm)	Ni (ppm)	Cu (ppm)	Sr (ppm)	(mqq)	Mo (ppm)	Ba (ppm)	Th (ppm)	U U	EF_{U}	EF _{Mo}
Y14	4131.4	S ₁ l ₁	Sublayer 4	12.4	92	10.8	56.2	30.9	164	23.1	13.6	2604	16.0	7.6	3.4	18.8
Y15	4133.2	$S_1 l_1$	Sublayer 4	11.9	179	14.8	61.5	39.3	165	25.4	14.6	2558	15.7	7.5	3.5	20.8
Y16	4134.8	$S_1 l_1$	Sublayer 4	11.3	89	15.8	55.0	48.8	152	22.4	29.3	2496	15.5	8.9	4.7	47.8
Y17	4135.1	$S_1 l_1$	Sublayer 4	10.8	66	12.8	69.5	39.8	164	24.6	17.6	2156	14.6	7.7	3.8	26.8
Y18	4135.9	$S_1 l_1$	Sublayer 4	11.4	84	13.4	62.9	40.7	159	22.3	19.6	2281	14.8	7.8	3.8	29.3
Y19	4136.2	$S_1 l_1$	Sublayer 4	11.1	96	10.1	56.9	33.5	163	22.3	15.7	2494	13.9	7.2	3.3	22.3
Y20	4136.8	$S_1 l_1$	Sublayer 4	10.6	157	13.0	67.9	40.5	150	23.2	18.3	2419	15.5	8.9	4.3	27.6
Y21	4137.5	$S_1 l_1$	Sublayer 4	11.8	96	14.8	73.7	45.0	156	25.6	21.1	2344	15.9	10.2	4.8	31.0
Y22	4138.1	$S_1 l_1$	Sublayer 4	10.9	117	13.4	79.7	46.5	161	24.0	23.1	2414	15.9	9.2	4.4	34.6
Y23	4140.5	$S_1 l_1$	Sublayer 4	12.5	148	14.4	76.7	47.8	149	23.5	19.0	2897	19.1	9.0	3.9	25.7
Y24	4140.8	$S_1 l_1$	Sublayer 4	10.7	138	13.6	81.9	55.8	132	20.6	27.9	2637	19.2	7.9	3.7	40.8
Y25	4142.8	$S_1 l_1$	Sublayer 3	10.5	117	16.8	62.2	66.5	116	24.9	27.7	2361	13.6	12.3	6.6	46.2
Y26	4143.2	$S_1 l_1$	Sublayer 3	13.2	135	14.4	88.7	63.0	130	28.1	24.1	2841	18.0	13.3	5.6	31.7
Y27	4145.1	$S_1 l_1$	Sublayer 3	7.1	111	12.5	65.4	57.1	148	24.9	46.2	1733	9.1	16.3	12.3	108.5
Y28	4145.9	$S_1 l_1$	Sublayer 3	12.1	194	13.4	127.0	76.0	146	38.7	46.7	3366	18.1	24.0	10.9	62.9
Y29	4146.3	$S_1 l_1$	Sublayer 3	9.3	187	15.1	134.0	70.3	115	20.8	55.5	2550	13.3	16.0	9.1	97.6
Y30	4146.8	$S_1 l_1$	Sublayer 3	7.4	154	12.0	111.0	66.4	149	25.1	58.6	1717	9.8	20.0	15.3	139.0
Y31	4147.3	$S_1 l_1$	Sublayer 3	6.0	190	8.1	94.9	45.2	173	22.0	45.8	1842	10.4	14.7	12.5	120.9
Y32	4148.6	S_1l_1	Sublayer 2	7.4	124	12.2	91.2	65.6	188	20.8	61.4	1951	11.1	14.3	9.8	130.9
Y33	4149.0	$S_1 l_1$	Sublayer 2	4.7	119	6.5	79.9	38.8	131	16.7	40.3	1601	6.8	13.3	14.3	134.4
Y34	4149.2	$S_1 l_1$	Sublayer 2	13.3	242	11.7	161.0	78.7	195	36.9	94.4	2759	18.4	18.6	8.0	126.4
Y35	4149.6	$S_1 l_1$	Sublayer 2	6.4	214	9.8	138.0	52.7	183	21.5	75.9	1426	8.9	17.9	16.5	217.4
Y36	4150.9	$S_1 l_1$	Sublayer 2	3.7	144	6.1	104.0	35.9	149	15.3	52.4	1054	5.5	16.7	23.6	229.9
Y37	4151.4	$S_1 l_1$	Sublayer 2	3.4	130	5.0	85.7	24.1	148	15.1	58.6	967	4.3	15.0	23.9	289.3
Y38	4152.8	$S_1 l_1$	Sublayer 1	7.6	270	8.9	142.0	51.1	188	25.5	75.8	1544	8.9	53.5	42.4	186.4
Y39	4155.2	$O_3 W$		11.5	179	6.8	76.6	104.0	181	41.3	3.1	1801	13.7	8.3	4.6	5.2
Y40	4155.7	O_3W		8.8	92	8.5	47.3	94.1	78	40.0	3.0	1600	11.4	4.4	2.6	5.3
Y41	4156.3	$O_{3}W$		14.6	127	15.5	52.0	68.2	245	29.5	1.5	1939	18.8	2.6	1.1	2.0
Y42	4157.2	$O_{3}W$		8.9	70	9.1	36.7	36.8	310	30.5	0.7	1293	10.6	2.0	1.3	1.4
Y43	4157.8	$O_3 W$		15.0	100	20.6	61.3	98.0	282	29.9	1.3	2058	18.9	3.0	1.3	1.8
Y44	4158.3	$O_{3}W$		16.4	107	16.8	53.1	72.1	242	32.3	1.0	2202	21.7	3.3	1.4	1.3
Y45	4158.4	$O_3 W$		14.4	97	16.8	47.9	50.5	258	35.6	1.4	2034	17.9	2.6	1.1	2.0
Y46	4158.7	O_3W		14.7	136	22.2	55.4	87.3	216	26.2	1.5	1994	18.0	3.0	1.2	1.9
Y47	4159.1	$O_{3}W$		16.1	120	20.0	53.2	82.0	235	29.9	1.5	2122	20.0	2.9	1.2	1.9

$\mathrm{EF}_{\mathrm{Mo}}$	30.7	35.5	34.2	117.8	130.5	134.9	25.6	
EF_{U}	4.0	4.2	4.3	9.3	12.5	14.8	8.1	
U (mqq)	9.6	10.9	9.2	10.9	11.5	16.0	17.1	
Th (ppm)	16.8	19.7	15.0	8.1	7.2	8.5	19.1	
Ba (ppm)	1949	2242	1869	1060	804	960	1834	
Mo (ppm)	24.4	29.8	23.7	44.3	38.8	47.1	17.3	
Y (ppm)	31.8	24.4	24.5	20.2	19.6	20.9	27.0	
Sr (ppm)	100	91	86	160	228	197	66	
Cu (ppm)	57.4	66.1	59.7	29.8	30.5	28.2	79.4	
Ni (ppm)	56.6	77.3	59.0	81.3	96.7	89.0	100.0	
Co (ppm)	17.8	19.1	15.4	7.8	8.1	7.6	9.3	
V (mqq)	113	163	190	102	103	155	455	
Sc (ppm)	13.9	16.1	11.9	5.8	5.6	5.9	12.5	
Member	Sublayer 4	Sublayer 4	Sublayer 3	Sublayer 3	Sublayer 2	Sublayer 2	Sublayer 1	
Formation	S ₁ l ₁	$S_1 l_1$	$S_1 l_1$	$S_1 l_1$	S_1l_1	$S_1 l_1$	$S_1 l_1$	
Depth (m)	4306.6	4309.3	4311.3	4317.9	4325.6	4328.4	4334.1	
Sample	IN	N2	N3	N4	N5	N6	N7	

TABLE 2: Continued.

Lithosphere



FIGURE 4: Enrichment of trace elements compared with PAAS in (a) well W214 in S_1l_1 , (b) well Y101 in S_1l_1 , (c) well Y101 in O_3w , and (d) well N222 in S_1l_1 .

no signal of hydrothermal influence during the deposition of the three areas in O_3w and S_1l_1 (Figure 7). REE can also indicate hydrothermal activities during sedimentation [57]. For hydrothermal-influenced siliceous rocks, after normalized by PAAS, LREEs show less concentration than HREEs, where (La/Yb)n < 1 [57–59]. From our samples in O_3w and S_1l_1 of well W214, Y101, and N222 (Table 4), there are no spikes in LREE or HREE concentration, while (La/Yb)n is almost larger than 1 $(O_3w: 0.84-1.43, avg. 1.20; S_1l_1: 0.90-1.50, avg. 1.29; 0.81-1.62, avg. 1.18; and 0.93-1.58, avg. 1.24, respectively), providing the evidence of no hydrothermal influence during the <math>O_3w$ and S_1l_1 deposition of three areas.

Al and Ti, the very stable chemical properties with nearly no affected on weathering and diagenesis, are always considered as indicators of terrestrial detrital influx [49]. The strong positive correlation between Al and Ti ($p(\alpha) < 0.01$) (Figure 6) indicates that both have great feasibility for terrestrial detrital influx index. The strength of terrigenous input is mainly controlled by the change of relative sea level. Its sedimentary center will retrograde to the continental margin during transgression and prograde to the inner edge of the basin during regression [34]. And terrigenous detrital influx will decrease, when sea level rises. Fluctuations of the two parameters (Al and Ti) indicate sea-level changes indirectly [57]. The relatively high values of Al and Ti in O_3w of well Y101 indicate a certain degree of terrigenous debris during this period. The increasing concentrations of Al and Ti from sublayer 1 to 4 suggest a reflection of incremental detrital influx contemporaneous during this sedimentation stage. And the value of W214 is higher than that of Y101 and N222, indicating that Weiyuan was more affected by terrigenous debris than that of Luzhou and Changning. Meanwhile, REE has a strong positive correlation with Ti and Al in S_1l_1 of three wells (0.81 and 0.58 in W214, 0.75 and 0.82 in Y101, and 0.99 and 0.99 in N222, respectively), suggesting that REE was sourced principally from the lithogenous fraction, while REE has no correlation with Ti and Al in O₃w of well Y101. Furthermore, the negative correlation between TOC and these indexes indicates that it is affected by terrigenous debris to a certain extent.

As REEs are normally stable and less soluble in seawater, their concentrations, coupled with the Y/Ho ratio, can be used to indicate terrigenous detrital input [61, 62]. If the \sum REE in sedimentary rocks is far less than that of the PAAS (184.8 ppm), and the Y/Ho ratio is higher than that of the

PAAS (27) and close to that of modern seawater (44), it is likely to have very less terrigenous detrital input [61–63]. In our analysis shown in Table 4, \sum REE and Y/Ho of our samples in O₃w of well Y101 are 163.6-341.5 ppm (avg.231.2 ppm) and 26.2-34.2 (avg.28.5) and in S₁l₁ of well W214, Y101H2-7, and N222 are 111.6-234.8 ppm (avg.173.2 ppm) and 26.8-35.6 (avg.30.3), 67.8-289.3 ppm (avg.168.1 ppm) and 25.2-36.9 (avg.29.4), and 88.6-201.1 ppm (avg.146.1 ppm) and 28.6-35.0 (avg.31.4), respectively. The values all close to those of the PAAS, which confirms the terrigenous detrital input exit in siliceous components but contribute a little.

Furthermore, the correlation coefficient between Si_{excess} and TOC in O_3w of well Y101 is 0.88 and in S_1l_1 of well W214, Y101, and N222 is 0.58, 0.66, and -0.18, respectively, of which only the well Y101 in S_1l_1 is very significant ($p(\alpha) < 0.01$), indicating that the enrichment of biosilica was not mainly controlled by bioproductivity, like planktons in well W214 and N222, while conversely in that of well Y101.

5.1.2. Paleoclimate. CIA, the proxy of paleoclimate, can be used to distinguish the tropical climate (85-100), mild and humid climate (65-85), and cold and dry climate (50-65) [64-66], while the ratio of Sr/Cu can also be used for indicating paleoclimate: warm humid climate (1.3-5.0) and dry hot climate (>5.0) [60, 67]. As shown in Table 1 and Figures 8-10, the CIA varies from 69.3 to 71.4 (avg.70.0) in O_3 w of well Y101 and from 67.8 to 73.0 (avg. 70.0), 64.8 to 72.0 (avg. 68.2), and 62.6 to 69.0 (avg. 65.8), respectively, in S_1l_1 of well W214, Y101, and N222, while the Sr/Cu ratio of those ranges from 0.83 to 8.42 (avg. 3.47) in O₃w of well Y101 and from 1.4 to 6.4 (avg. 3.2), 1.6 to 10.3 (avg. 3.5), and 0.8 to 7.5 (avg. 3.6) in S_1l_1 of well W214, Y101, and N222, respectively (Table 4). Vertically, it was an overall warm and humid paleoclimate during the depositional period in O₃w and S_1l_1 of the three areas, which aligns well with the previous study (Figures 8-10) [57, 68, 69]. However, a temporarily slightly tropical climate happened in Luzhou and Changning areas during the sublayer 2 period after a comprehensive analysis of the two parameters (CIA and Sr/Cu); however, there is no significant reduction of the TOC value (Figures 9 and 10). The temporary dry and hot climate may be due to the greenhouse gas CO₂ brought by volcanic activity [68], which can raise the temperature for a period of time.

Formation Member (Member ()	La		Ce	Pr	PN (mmr)	Sm	Eu (mm)	Gd	Tb	Dy	Ho (mun)	Er (mmm)	Tm	Yb	Lu
S ₁ I ₁			(ppm) 135.5	(ppm) 87.5	(ppm) 77.3	(ppm) 54.7	(ppm) 31.2	(ppm) 15.7	(ppm) 19.6	(ppm) 16.7	(ppm) 15.9	(ppm) 14.7	(ppm) 14.7	(ppm) 16.9	(ppm) 16.1	(ppm) 15.9
$S_1 l_1$		Submember 2	131.3	84.6	70.3	55.8	28.9	16.3	21.1	18.1	17.0	15.1	14.2	18.2	17.2	18.4
$S_1 l_1$			136.1	88.3	72.3	55.5	29.1	16.3	18.4	16.7	15.7	12.3	13.4	17.8	14.5	16.1
S_1l_1		Sublayer 4	126.1	82.2	68.5	50.2	27.4	13.5	16.6	15.5	12.5	11.5	11.3	14.0	13.3	13.3
S_1l_1		Sublayer 4	118.1	78.9	63.2	52.7	31.4	17.7	19.1	19.8	18.0	15.3	19.2	22.6	18.5	18.2
S_1l_1		Sublayer 4	130.0	85.3	66.8	48.8	26.0	14.6	16.3	15.4	14.1	11.8	12.4	14.0	12.5	13.5
$S_1 l_1$		Sublayer 4	132.9	84.6	69.2	58.0	29.0	16.1	21.0	17.3	15.5	12.7	12.9	16.6	14.5	13.6
$S_1 l_1$		Sublayer 4	136.8	87.8	70.9	57.2	28.9	15.1	18.9	16.3	17.2	13.5	14.5	18.0	15.6	15.1
S_1l_1		Sublayer 4	119.4	80.2	68.2	56.8	32.8	15.7	20.8	17.8	15.6	13.1	14.1	16.3	13.1	15.0
$S_1 l_1$		Sublayer 4	161.6	102.7	86.7	66.7	34.9	19.0	22.1	20.0	16.1	13.6	15.0	16.2	14.5	13.8
S_1l_1		Sublayer 4	116.1	76.7	61.1	49.0	28.2	16.1	18.7	15.9	15.6	13.1	14.3	17.7	14.9	17.3
S_1l_1		Sublayer 4	117.4	72.2	68.0	49.2	27.3	14.6	19.2	16.4	15.7	11.7	11.6	12.6	11.7	13.4
$S_1 l_1$		Sublayer 4	112.3	9.77	66.2	55.8	31.8	18.3	19.8	17.9	15.1	12.7	11.5	14.1	11.2	12.5
$S_1 l_1$		Sublayer 4	109.4	71.5	57.4	45.8	26.5	14.3	17.6	16.3	12.9	10.5	12.2	13.1	11.0	11.9
$S_1 l_1$		Sublayer 4	134.8	92.1	78.3	59.8	30.0	16.3	22.2	16.6	14.4	12.6	11.6	13.1	11.7	12.4
$S_1 l_1$		Sublayer 3	169.4	114.1	101.7	78.8	41.4	19.0	25.4	21.4	17.6	12.6	14.2	15.2	13.2	13.8
$S_1 l_1$		Sublayer 3	119.4	81.2	65.1	45.8	29.3	10.6	18.7	16.9	14.2	12.1	13.0	16.6	14.3	15.2
$S_1 l_1$		Sublayer 2	123.2	81.9	65.8	46.2	27.5	12.2	17.1	15.8	13.5	11.3	11.9	15.0	12.2	14.0
$S_1 l_1$		Sublayer 1	132.9	93.3	72.0	55.3	29.2	13.5	18.5	16.0	15.4	13.9	15.3	20.5	18.7	20.3
$S_1 l_1$		Sublayer 2	76.5	52.1	45.8	36.5	20.6	12.3	14.4	13.9	11.7	9.4	9.6	10.9	8.9	8.5
S_1l_1		Sublayer 4	47.1	80.0	10.3	37.8	7.2	0.97	5.90	1.06	5.28	0.95	3.01	0.44	2.86	0.41
$S_1 l_1$		Sublayer 4	62.7	108.0	14.6	60.1	11.4	1.64	8.86	1.59	8.98	1.47	4.66	0.77	3.93	0.62
S_1l_1		Sublayer 4	42.2	71.9	9.3	34.5	5.9	0.73	5.16	0.92	5.35	0.89	2.78	0.44	2.44	0.38
S_1I_1		Sublayer 4	50.2	84.1	10.8	40.4	9.9	0.63	5.98	0.95	5.38	1.00	3.32	0.51	2.98	0.45
$S_1 l_1$		Sublayer 4	47.2	79.4	10.2	36.2	6.5	0.92	5.66	0.93	5.10	0.94	2.76	0.47	2.72	0.38
$S_1 l_1$		Sublayer 4	46.1	75.5	9.2	35.1	5.9	0.83	5.15	0.91	5.05	0.89	2.69	0.40	2.63	0.37
$S_1 l_1$		Sublayer 4	44.3	62.9	8.7	32.2	5.9	0.89	5.20	0.93	5.03	0.83	2.74	0.41	2.72	0.36
$S_1 l_1$		Sublayer 4	43.6	79.8	10.5	36.5	6.2	0.68	5.18	1.00	5.59	1.11	3.51	0.65	3.54	0.54
$S_1 l_1$		Sublayer 4	39.5	64.3	8.1	30.0	5.7	0.79	5.00	0.83	5.19	0.87	3.05	0.49	2.87	0.45
$S_1 l_1$		Sublayer 4	45.0	72.1	9.4	34.5	5.6	0.81	5.30	0.88	4.46	0.83	2.59	0.40	2.59	0.38
$S_1 l_1$		Sublayer 4	42.7	72.1	8.7	32.4	5.7	0.88	5.00	0.86	4.79	0.80	2.76	0.41	2.67	0.42
$S_1 l_1$		Sublayer 4	37.0	63.0	8.1	29.2	5.3	0.67	4.58	0.85	4.25	0.74	2.32	0.37	2.40	0.39
$S_1 l_1$	I	Sublayer 4	41.8	70.4	8.5	32.8	5.7	0.96	5.11	0.86	4.78	0.89	2.77	0.47	2.67	0.39

TABLE 3: Rare earth elemental composition of black shales in S,l, of well W214 and N222, S,l., and O₃w of well Y101.

							TABLE 3: (Continue	q.								
Sample	Depth (m)	Formation	Member	La (ppm)	Ce (ppm)	Pr (ppm)	(mqq) bN	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	(mqq)	Lu (ppm)
Y14	4131.4	S ₁ l ₁	Sublayer 4	40.3	70.2	8.4	32.6	5.4	1.05	5.17	06.0	4.73	0.86	2.59	0.42	2.63	0.38
Y15	4133.2	$S_1 l_1$	Sublayer 4	41.2	73.6	9.0	35.9	6.5	1.08	5.37	1.01	4.82	0.92	2.87	0.46	2.90	0.41
Y16	4134.8	$S_1 l_1$	Sublayer 4	38.4	66.7	8.3	34.2	6.0	1.08	5.17	0.83	4.72	0.83	2.65	0.38	2.30	0.37
Y17	4135.1	$S_1 l_1$	Sublayer 4	34.7	66.3	8.3	31.8	6.3	1.06	4.82	0.85	4.99	0.85	2.60	0.41	2.49	0.41
Y18	4135.9	$S_1 l_1$	Sublayer 4	36.4	65.6	8.3	30.8	5.6	0.85	4.89	0.86	4.39	0.76	2.48	0.41	2.32	0.37
Y19	4136.2	$S_1 l_1$	Sublayer 4	38.1	65.4	8.0	30.9	5.6	0.94	4.88	0.85	4.11	0.82	2.33	0.35	2.43	0.35
Y20	4136.8	$S_1 l_1$	Sublayer 4	40.9	65.6	8.2	33.9	6.0	0.74	5.25	0.88	4.75	0.85	2.61	0.41	2.48	0.39
Y21	4137.5	$S_1 l_1$	Sublayer 4	40.8	73.9	8.8	33.2	6.2	1.14	5.18	0.92	4.59	0.79	2.68	0.46	2.59	0.40
Y22	4138.1	$S_1 l_1$	Sublayer 4	40.1	71.6	9.1	33.8	5.7	1.01	5.58	0.96	5.07	0.85	2.52	0.44	2.66	0.36
Y23	4140.5	$S_1 l_1$	Sublayer 4	42.3	9.99	8.7	33.2	6.1	1.04	4.91	0.82	4.94	0.84	2.61	0.45	2.51	0.40
Y24	4140.8	$S_1 l_1$	Sublayer 4	34.2	57.2	6.6	27.4	4.5	0.70	4.09	0.71	3.81	0.67	2.08	0.39	2.15	0.32
Y25	4142.8	$S_1 l_1$	Sublayer 3	37.7	59.3	8.1	31.9	5.5	0.78	4.87	0.83	4.29	0.83	2.42	0.38	2.19	0.32
Y26	4143.2	$S_1 l_1$	Sublayer 3	47.3	72.8	9.2	37.3	6.2	1.06	5.81	0.95	5.32	1.01	2.93	0.55	3.37	0.46
Y27	4145.1	$S_1 l_1$	Sublayer 3	31.8	48.6	6.3	27.6	5.0	0.93	4.45	0.70	3.98	0.83	2.42	0.39	2.35	0.35
Y28	4145.9	$S_1 l_1$	Sublayer 3	54.9	95.0	12.5	51.6	9.4	1.03	7.52	1.26	7.37	1.34	3.96	0.77	4.45	0.59
Y29	4146.3	$S_1 l_1$	Sublayer 3	34.0	54.3	6.1	24.7	4.8	0.44	3.91	0.67	3.99	0.74	2.31	0.36	2.18	0.34
Y30	4146.8	$S_1 l_1$	Sublayer 3	29.7	50.0	7.0	28.4	4.8	0.89	4.37	0.73	4.06	0.73	2.21	0.41	2.23	0.34
Y31	4147.3	$S_1 l_1$	Sublayer 3	23.1	40.7	5.5	22.2	4.4	0.61	3.87	0.69	3.51	0.66	2.00	0.33	2.04	0.29
Y32	4148.6	$S_1 l_1$	Sublayer 2	35.5	51.3	6.3	25.6	4.0	0.78	4.44	0.69	4.01	0.74	1.94	0.37	2.29	0.36
Y33	4149.0	$S_1 l_1$	Sublayer 2	19.2	31.2	4.1	16.7	3.0	0.57	2.76	0.58	2.96	0.55	1.82	0.30	1.43	0.24
Y34	4149.2	$S_1 l_1$	Sublayer 2	59.7	92.6	12.9	50.5	8.8	1.55	7.16	1.20	6.62	1.12	3.60	0.59	3.44	0.54
Y35	4149.6	$S_1 l_1$	Sublayer 2	26.7	38.9	5.0	21.5	3.8	0.73	3.56	0.61	3.30	0.63	1.75	0.33	1.68	0.30
Y36	4150.9	$S_1 l_1$	Sublayer 2	17.6	26.7	3.8	16.0	2.6	0.62	2.92	0.43	2.69	0.51	1.41	0.26	1.35	0.19
Y37	4151.4	S_1l_1	Sublayer 2	14.4	24.5	3.2	14.1	2.5	0.53	2.28	0.44	2.39	0.41	1.35	0.23	1.37	0.16
Y38	4152.8	$S_1 l_1$	Sublayer 1	29.5	45.4	6.5	23.1	5.0	0.83	4.25	0.75	4.52	0.78	2.49	0.38	2.53	0.39
Y39	4155.2	$O_{3}W$		43.5	64.6	9.8	37.9	7.2	1.42	6.55	1.06	6.66	1.33	3.93	0.71	4.24	0.64
Y40	4155.7	$O_{3}W$		67.0	128.0	18.4	82.6	13.4	2.07	9.28	1.56	8.04	1.41	4.46	0.72	4.01	0.58
Y41	4156.3	$O_{3}W$		47.1	90.1	9.5	40.9	6.9	1.29	6.25	0.95	6.02	1.08	2.82	0.57	3.18	0.45
Y42	4157.2	$O_{3}W$		32.1	67.7	7.0	29.6	5.9	1.13	5.09	0.97	5.75	1.06	3.04	0.53	3.27	0.46
Y43	4157.8	O_{3W}		50.7	98.5	10.8	42.2	7.8	1.33	6.86	1.11	5.96	1.08	3.42	0.63	3.68	0.52
Y44	4158.3	$O_{3}W$		57.9	111.0	11.8	45.4	8.5	1.48	7.38	1.17	6.29	1.20	3.71	0.53	3.71	0.58
Y45	4158.4	$O_{3}W$		49.3	97.3	10.6	40.4	8.0	1.23	6.33	1.13	6.25	1.04	3.37	0.59	3.37	0.49
Y46	4158.7	$O_{3}W$		46.5	6.68	10.0	35.8	7.0	1.19	5.56	0.92	5.47	0.99	2.91	0.50	2.99	0.43
Y47	4159.1	$O_{3}W$		48.7	103.0	10.6	40.9	7.5	1.24	7.00	1.18	5.82	1.14	3.25	0.58	3.24	0.50

Lithosphere

Counto	Depth	Downotion	Mombae	La	Ce	Pr	рŊ	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
oampic	(m)	FUI IIIAUUII	INICITAL	(mdd)	(mqq)	(mdd)	(mqq)	(mqq)									
NI	4306.6	$S_1 l_1$	Sublayer 4	150.0	96.8	76.9	62.2	36.2	17.0	23.0	20.6	17.5	15.7	15.9	19.6	15.0	16.5
N2	4309.3	$S_1 l_1$	Sublayer 4	146.1	91.6	81.2	61.7	34.1	15.9	21.1	18.4	15.2	11.9	12.9	14.5	11.7	11.9
N3	4311.3	$S_1 l_1$	Sublayer 3	133.2	81.2	72.9	51.3	30.1	14.7	19.2	18.1	14.8	12.2	13.5	13.3	12.1	12.7
N4	4317.9	$S_1 l_1$	Sublayer 3	77.7	48.5	42.4	34.2	18.9	10.1	12.8	12.1	10.7	8.4	9.4	9.5	8.4	9.2
N5	4325.6	$S_1 l_1$	Sublayer 2	68.4	39.8	36.8	27.3	17.0	7.5	10.4	10.4	9.3	8.0	7.9	8.6	7.3	7.8
N6	4328.4	$S_1 l_1$	Sublayer 2	68.7	47.4	43.0	30.7	18.1	10.1	11.0	11.5	10.2	8.6	9.4	10.2	7.4	8.1
N7	4334.1	$S_1 l_1$	Sublayer 1	122.6	76.9	71.6	49.5	30.2	12.7	18.6	17.9	14.9	13.3	15.2	16.9	16.6	17.7
Chondrite				0.31	0.81	0.12	09.0	0.20	0.07	0.26	0.05	0.32	0.07	0.21	0.03	0.21	0.03
PAAS				41.0	83.0	10.1	38.0	7.5	1.61	6.35	1.23	5.49	1.34	3.75	0.63	3.51	0.61

TABLE 3: Continued.





FIGURE 5: REE concentrations normalized by chondrite of the (a) well W214 in S_1l_1 , (c) well Y101 in S_1l_1 , (e) well Y101 in O_3w , and (g) well N222 in S_1l_1 ; REE concentrations normalized by PAAS of the (b) well W214 in S_1l_1 , (d) well Y101 in S_1l_1 , (f) well Y101 in O_3w , and (h) well N222 in S_1l_1 . The chondrite data is cited from the literature [51], and the PAAS data is cited from the literature [52].

No good correlation between the TOC amount and the CIA values as well as the Sr/Cu ratios can be observed suggesting the paleoclimate is not the controlling factor for organic matter enrichment of the three areas.

5.1.3. Paleoredox Conditions. Mo, U, V, Ni, and Co are redox-sensitive elements, and their solubilities and existing status are strongly affected by the redox environment of

the water mass [36, 39, 70, 71]. Generally, elements either get oxidized into high-valent ions and dissolve in water, or get reduced into low-valent ions and dissolve in an anaerobic environment [71, 72]. However, only elements in marine and biogenic sediments can be used for redox analysis [73–76]. Based on previous analysis, there is limited hydrothermal and terrigenous detrital impact for this provenance. Moreover, the ratios of U/Th, Ni/Co, and V/Sr are used for



FIGURE 6: Correlation coefficient of geochemical parameters in (a) S_1l_1 of well W214 and N222 and (b) S_1l_1 and O_3w of well Y101. The red circle indicates a positive correlation, while the blue circle indicates a negative correlation. The darker the color and the larger the circle, the stronger the correlation.

redox analysis as well. There is some debate over the impact of diagenesis on these indicators, but the overall reliability of these ratios is widely accepted. The ratios of U/Th above 1.25 and Ni/Co above 7 indicate the anoxic or euxinic environment with the concentration of O_2 in bottom water being less than 0.2 mlO₂/lH₂O, and the ratios of U/Th between 0.75 and 1.25, Ni/Co between 5 and 7, and V/Sr above 9.1 indicate the suboxic environment with that of the bottom water ranging from 0.2mlO₂/lH₂O to 2mlO₂/lH₂O, and the rest of them indicate the oxic environment with that of the bottom water being over than 2mlO₂/lH₂O [77, 78].

The U/Th, Ni/Co, and V/Sr ratios in well W214 located in Weiyuan area of submember 2 are 0.18–0.22, 2.35–2.81, and 6.26–8.53, with the averages of 0.19, 2.58, and 7.23, respectively; that of sublayer 4 is 0.42–0.98, 3.14–6.47, and 4.78–25.09, with the averages of 0.63, 4.70, and 14.50, respectively; that of sublayer 2 are 0.48–1.04, 3.96–4.95, and 8.05–24.73, with the averages of 0.76, 4.46, and 16.39, respectively; that of sublayer 3 is 0.50, 6.13, and 22.71, respectively; and that of sublayer 1 are 0.35–2.50, 3.87– 7.28, and 7.21–29.54, with the averages of 1.42, 5.58, and 18.37, respectively.

The U/Th, Ni/Co, and V/Sr ratios in well Y101 located in Luzhou area of sublayer 4 are 0.26–1.05, 3.26–6.95, and 6.63–15.04, with the averages of 0.59, 4.97, and 10.20, respectively; that of sublayer 3 are 0.74–2.05, 3.70–11.72, and 10.23–31.67, with the averages of 1.35, 7.77, and 17.95, respectively; that of sublayer 2 are 1.01–3.46, 7.48–17.02, and 16.87–39.13, with the averages of 2.13, 13.60, and

28.53, respectively; that of sublayer 1 are 6.01, 15.88, and 35.48, respectively; and that of O_{3W} are 0.14-0.61, 2.50-11.23, and 6.53-15.57, with the average of 0.23, 4.26, and 8.80, respectively.

The U/Th, Ni/Co, and V/Sr ratios in well N222 located in Changning area of sublayer 4 are 0.55–0.59, 3.18–4.05, and 8.13–10.12, with the averages of 0.57, 3.61, and 9.13, respectively; that of sublayer 3 are 0.62–1.35, 3.83–10.49, and 15.97–17.68, with the averages of 0.98, 7.16, and 16.82, respectively; that of sublayer 2 are 1.59–1.88, 11.70–11.95, and 18.53–26.14, with the averages of 1.73, 11.82, and 22.33, respectively; and that of sublayer 1 are 0.90, 10.71, and 36.40, respectively.

The above redox indicators and vertical changes indicate oxic bottom water column first then suboxic bottom water column as time goes during the O₃w depositional period; an anoxic-euxinic bottom water column in sublayer 1, 2, and early sublayer 3 depositional period; a suboxic bottom water column in late sublayer 3 depositional period; and an oxic-suboxic bottom water column in sublayer 4 depositional period in Luzhou and Changning areas, while the oxygen content of bottom water column seems different slightly in Weiyuan area. The bottom water column changed from anoxic and euxinic to oxic environment during the deposition of sublayer 1, and this oxic environment was sustained in the deposition of sublayer 2 and early sublayer 3, then it became a suboxic-oxic environment until later sublayer 3 depositional period, and finally, it became an oxic environment in the middle and late deposition of sublayer 4 and



FIGURE 7: Al-Mn-Fe ternary diagram after by literature [60]. W214-L2 stands for samples of the submember 2 of Longmaxi formation; W214-1, 2, 3, and 4 stand for the sublayer 1, 2, 3, and 4, respectively, the same with the Y101-1, 2, 3, and 4 and N222-1, 2, 3, and 4; Y101-W stands for the samples of Wufeng formation.

continued as time goes. Generally speaking, Weiyuan area was in an anoxic environment until the late sublayer 1 depositional period; it became and continued an oxic environment.

However, when predecessors interpreted the deposition of O₃w in Sichuan Basin, they interpreted it as that the sedimentary environment of O₃w was anoxic first and then oxic as global regression [57]. The difference of this study and previous is due to the differential uplift of the Upper Yangtze Plate caused by Guangxi movement. The paleogeomorphology of each region has certain differences. The low sea level of early O₃w [24] caused a different response of depositional environment to each area. The southern Sichuan Basin sedimentary area shows oxic characteristics in early O₃w. And at the end of the glacial period, large-scale transgression makes it difficult for the microvolt structure to become the main factor affecting the sedimentary environment. The difference between Weiyuan and Luzhou-Changning areas in sublayers 2, 3, and 4 seems to have a relatively plausible explanation, which is well W214 was located along the southern margin of the Chuanzhong Uplift, with the continuously uplifting of southern basin due to the northern extension of Qianzhong Uplift, was beginning with an anoxic environment, and then became an oxic environment due to the gradually shallower water in Weiyuan area [79].

5.1.4. Paleoproductivity. The warm and humid paleoclimate during O_3w and S_1l_1 period promoted the growth and

reproduction of marine organism. This served as a foundation for OM enrichment as a warmer, and more nutritious environment indicates more organism activities and higher paleoproductivity. As paleoproductivity is not easily measurable, the Ba and P are used as indicators of paleoproductivity [80–83].

Among all four Ba sources in sedimentary rocks (biogenic, terrigenous detrital, hydrothermal, and generated by benthonic life), only biogenic Ba (Ba_{bio}) can be used for primary paleoproductivity. Some exceptions may be made when in anaerobic environment; the BaSO₄ that is easily generated from sulfate reduction reactions can affect Ba concentration measurements, thus underestimating paleoproductivity [80, 81]. The results show that the productivity in O₃w of Y101 is (Ba_{bio}: 967–1695 ppm, avg. 1445 ppm) and in S₁l₁ of Y101 (Ba_{bio}: 835 - 4315 ppm, avg. 2245 ppm) overall experienced high paleoproductivity than that of N222 (Ba_{bio}: 611-1697 ppm, avg. 1157 ppm), followed by W214 (Babio: 531-1326 ppm, avg. 840 ppm) (Table 4). The value of Babio remains at a high level in sublayer 2 and 3, while it is slightly lower and changes relatively gently in other sublayers in Weiyuan area (Figure 8). And that of Luzhou area is increasing as time goes during the O_3w and S_1l_1 , while in Changning area, it decreases firstly and then increases from sublayer 1 to sublayer 4 (Figures 9 and 10). The Babio content of high productivity water near the equator of the modern Pacific Ocean is generally more than 1000 ppm [84], and that of ancient organic-rich sediments is generally more than 500 ppm [85]. Previous studies have found that the Ba_{bio} content of shale in Wufeng and Longmaxi formations in South China is generally higher than 500 ppm [31], indicating the high productivity of surface water during marine sedimentation.

P takes participation in biological metabolism, as well as in organism skeletons, therefore can be buried and preserved after organism dies [82, 83]. In P evaluations, the P/Al ratio is introduced to counteract detrital influence and achieve an accurate productivity analysis. The results show completely different from those of Ba_{bio} , where the value of P/Al in O_3w of Y101 is from 35×10^{-4} to 98×10^{-4} (avg. 52×10^{-4}) and in S_1l_1 of N222 is the highest among them (range from 63×10^{-4} to 139×10^{-4} , avg. 87×10^{-4}), followed by that of W214 (range from 45×10^{-4} to 189×10^{-4} , avg. 78×10^{-4}), then by Y101 (range from 43×10^{-4} to 131×10^{-4} , avg. 74 $\times 10^{-4}$) (Table 4). However, unlike the evaluations from Ba_{bio}, the ratio of P/Al in S₁l₁ presents an appearance of first decreasing during the sublayer 1 and 2 deposition, then increasing, and then decreasing as time goes during the deposition of sublayer 3 and 4 in Weiyuan area, and that of Luzhou area demonstrates stronger productivity in early S_1l_1 (sublayer 1, 2, and 3) than later on, followed by O_3w , while that of Changning area shows a tendency of increasing first and then increasing from sublayer 1 to 4 (Figures 8, 9, and 10).

The difference of trend of indicator between Ba_{bio} and P/ Al is likely due to $BaSO_4$ generation in an anaerobic environment, meaning that the trend of P/Al seems more reasonable. That is, the paleoproductivity was rapidly increasing until late O_3w and was higher in sublayer 1 and early

Mo/TOC	4.08	5.39	3.66	6.78	5.55	9.94	4.14	3.98	3.53	2.65	6.81	4.85	3.19	6.24	6.24	20.63	10.78	10.67	8.86	10.67	8.83	7.20	9.63	6.29	9.38	5.94	6.90	7.46	4.93	4.94	6.68	8.25	69.9
(La/Yb)n	0.91	0.82	1.02	1.02	0.69	1.13	0.99	0.95	0.99	1.20	0.84	1.09	1.08	1.08	1.25	1.38	06.0	1.09	0.77	0.93	1.21	1.17	1.27	1.24	1.27	1.29	1.19	06.0	1.01	1.27	1.17	1.13	1.15
y/Ho	26.8	29.9	30.9	27.4	33.9	28.8	30.0	30.6	29.3	31.0	30.4	30.0	31.6	35.6	29.3	31.0	27.3	30.1	29.4	32.8	29.2	30.3	28.7	30.0	26.7	26.5	29.1	25.2	29.1	28.7	30.0	27.4	26.0
LREE/HREE	8.32	7.68	8.85	9.47	6.71	9.33	8.49	8.37	8.05	9.63	7.56	8.02	8.47	8.35	9.51	10.28	8.14	8.99	8.32	7.39	9.21	8.37	8.96	9.37	9.52	9.55	8.67	8.39	7.91	9.61	9.18	9.01	8.93
REE (ppm)	181.8	178.6	181.0	166.3	169.1	169.3	178.5	182.6	170.8	211.9	160.3	156.4	164.3	148.4	186.6	234.8	162.5	162.7	185.3	111.6	203.3	289.3	182.9	213.3	199.4	190.7	176.2	198.4	167.0	184.8	180.2	159.2	178.2
EF _{Co} ×EF _{Mn}	0.77	0.40	0.57	0.57	0.71	0.67	0.73	0.65	1.11	0.35	1.07	0.97	0.86	1.45	0.64	0.57	0.18	0.35	0.23	2.36	0.43	0.28	0.37	0.11	0.23	0.37	0.38	0.28	0.38	0.23	0.26	0.41	0.25
Co×Mn	1.47	0.70	0.98	0.83	1.02	0.97	1.00	0.85	1.46	0.46	0.63	0.63	0.47	0.82	0.63	0.74	0.34	0.48	0.40	0.41	0.52	0.37	0.41	0.22	0.36	0.46	0.46	0.34	0.42	0.28	0.30	0.57	0.28
Sr/Cu	3.18	1.84	2.93	2.46	4.13	1.68	3.44	3.67	3.07	2.79	6.34	3.92	3.41	6.41	1.72	1.37	3.02	3.25	4.04	1.58	4.06	10.26	2.81	4.93	2.17	2.40	3.84	3.33	3.89	2.40	2.53	3.20	3.35
P/AI (10 ⁻⁴)	50	57	53	49	49	45	54	49	51	102	123	128	189	100	106	75	49	54	45	128	74	63	67	43	62	55	60	44	53	60	56	62	57
${\operatorname{Ba}}_{\operatorname{bio}}(10^{-6})$	813	644	686	758	790	757	727	932	772	918	808	712	690	714	838	1083	1238	1072	1326	531	2726	3220	4261	4315	3100	3209	2646	2867	2762	2743	2603	2721	2298
V/Sc	8.53	6.26	6.90	9.42	7.76	11.52	7.97	14.21	10.69	22.26	7.48	25.09	18.55	17.64	21.44	24.73	8.05	22.71	7.21	29.54	10.92	9.53	13.17	9.85	8.66	11.07	10.23	10.87	11.43	13.22	6.63	7.68	7.63
Ni/Co	2.60	2.35	2.81	3.14	4.17	4.74	4.36	4.63	3.94	6.47	3.59	5.76	4.58	5.96	5.08	4.95	3.96	6.13	3.87	7.28	5.53	6.81	6.95	5.12	3.26	3.53	5.23	4.17	5.12	5.13	3.68	3.57	5.00
U/Th	0.18	0.18	0.22	0.42	0.60	0.54	0.58	0.65	0.49	0.53	0.62	0.59	0.89	0.71	0.98	1.04	0.48	0.50	0.35	2.50	0.72	0.72	1.05	0.63	0.96	0.53	0.56	0.46	0.50	0.66	0.63	0.26	0.61
Member		Submember 2		Sublayer 4	Sublayer 3	Sublayer 3	Sublayer 2	Sublayer 1	Sublayer 2	Sublayer 4																							
Formation	S ₁ l ₁	S_1l_1	S_1l_1	$S_1 l_1$	S_1l_1	$S_1 l_1$	$S_1 l_1$	S_1l_1	$S_1 l_1$	$S_1 l_1$	S_1l_1	$S_1 l_1$	S_1l_1	S_1l_1	$S_1 l_1$	S_1l_1	S_1l_1	S_1l_1	$S_1 l_1$	S_1l_1	S_1l_1	S_1l_1	S_1l_1	$S_1 l_1$									
Depth (m)	3520.3	3523.3	3529.3	3535.2	3538.0	3538.6	3540.0	3541.0	3543.1	3547.6	3553.6	3558.5	3560.1	3563.7	3566.1	3568.0	3569.6	3572.0	3572.7	3575.6	4102.8	4105.0	4107.5	4109.0	4111.5	4113.4	4115.2	4117.2	4119.1	4120.2	4122.4	4125.9	4128.8
Sample	W1	W2	W3	W4	W5	W6	W7	W8	6M	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	49	Y10	Y11	Y12	Y13

TABLE 4: Geochemical parameters of black shales in S₁1, of well W214 and N222, S₁1, and O₃w of well Y101.

							TAI	3le 4: Co	ntinued.							
Sample	Depth (m)	Formation	Member	U/Th	Ni/Co	V/Sc	${ m Ba}_{ m bio} \ (10^{-6})$	P/AI (10 ⁻⁴)	Sr/Cu	Co×Mn	$\rm EF_{Co} \times \rm EF_{Mn}$	REE (ppm)	LREE/HREE	Y/Ho	(La/Yb) <i>n</i>	Mo/TOC
Y14	4131.4	$S_1 l_1$	Sublayer 4	0.47	5.20	7.38	2133	69	5.31	0.31	0.30	175.7	8.94	27.0	1.12	6.33
Y15	4133.2	$S_1 l_1$	Sublayer 4	0.48	4.16	15.04	2102	69	4.20	0.46	0.48	186.0	8.92	27.7	1.04	6.35
Y16	4134.8	$S_1 l_1$	Sublayer 4	0.58	3.48	7.88	2097	70	3.11	0.34	0.46	171.9	8.97	27.0	1.22	10.17
Y17	4135.1	$S_1 l_1$	Sublayer 4	0.53	5.43	9.18	1729	72	4.12	0.35	0.41	165.9	8.52	28.9	1.02	7.49
Y18	4135.9	$S_1 l_1$	Sublayer 4	0.53	4.69	7.33	1846	72	3.91	0.36	0.42	164.1	8.95	29.3	1.15	8.31
Y19	4136.2	$S_1 l_1$	Sublayer 4	0.52	5.63	8.67	2035	62	4.87	0.27	0.28	165.0	9.24	27.3	1.15	7.20
Y20	4136.8	$S_1 l_1$	Sublayer 4	0.57	5.22	14.81	1988	67	3.70	0.38	0.44	173.0	8.82	27.4	1.21	7.38
Y21	4137.5	$S_1 l_1$	Sublayer 4	0.64	4.98	8.15	1900	70	3.47	0.41	0.45	181.6	9.32	32.3	1.16	7.87
Y22	4138.1	$S_1 l_1$	Sublayer 4	0.58	5.95	10.73	1979	66	3.46	0.35	0.40	179.7	8.75	28.2	1.11	8.75
Y23	4140.5	$S_1 l_1$	Sublayer 4	0.47	5.33	11.84	2416	61	3.12	0.29	0.27	175.4	9.04	28.0	1.24	7.28
Y24	4140.8	$S_1 l_1$	Sublayer 4	0.41	6.02	12.90	2192	58	2.37	0.23	0.25	144.8	9.18	30.6	1.17	10.07
Y25	4142.8	$S_1 l_1$	Sublayer 3	06.0	3.70	11.14	1971	72	1.74	0.25	0.35	159.4	8.88	29.9	1.26	6.38
Y26	4143.2	$S_1 l_1$	Sublayer 3	0.74	6.16	10.23	2347	53	2.06	0.20	0.18	194.3	8.52	27.8	1.03	5.81
Y27	4145.1	$S_1 l_1$	Sublayer 3	1.79	5.23	15.57	1456	115	2.59	1.02	2.86	135.7	7.76	29.9	0.99	9.30
Y28	4145.9	$S_1 l_1$	Sublayer 3	1.33	9.48	16.03	2905	70	1.92	0.23	0.23	251.7	8.24	28.9	06.0	9.17
Y29	4146.3	$S_1 l_1$	Sublayer 3	1.20	8.87	20.13	2180	59	1.64	0.22	0.35	138.9	8.58	28.1	1.14	14.53
Y30	4146.8	$S_1 l_1$	Sublayer 3	2.05	9.25	20.90	1443	101	2.24	0.25	0.72	135.9	8.01	34.4	0.98	11.10
Y31	4147.3	$S_1 l_1$	Sublayer 3	1.41	11.72	31.67	1596	116	3.83	0.19	0.69	110.0	7.21	33.2	0.83	9.72
Y32	4148.6	$S_1 l_1$	Sublayer 2	1.29	7.48	16.87	1646	77	2.87	0.20	0.46	138.4	8.32	28.1	1.14	15.43
Y33	4149.0	$S_1 l_1$	Sublayer 2	1.95	12.22	25.21	1406	124	3.38	0.12	0.66	85.5	7.04	30.4	0.98	10.08
Y34	4149.2	$S_1 l_1$	Sublayer 2	1.01	13.76	18.20	2273	103	2.48	0.22	0.20	253.3	9.44	32.9	1.27	25.44
Y35	4149.6	$S_1 l_1$	Sublayer 2	2.00	14.10	33.44	1199	92	3.47	0.23	0.95	108.8	7.95	34.0	1.17	20.57
Y36	4150.9	$S_1 l_1$	Sublayer 2	3.05	17.02	39.13	906	115	4.15	0.14	1.35	77.1	6.90	30.2	0.96	12.54
Y37	4151.4	$S_1 l_1$	Sublayer 2	3.46	17.00	38.35	835	131	6.14	0.14	1.70	67.8	6.86	36.9	0.77	14.12
Y38	4152.8	$S_1 l_1$	Sublayer 1	6.01	15.88	35.48	1279	90	3.68	0.39	1.20	126.4	6.86	32.7	0.86	15.86
Y40	4155.2	$O_3 W$		0.61	11.23	15.57	1418	98	1.74	0.26	0.39	189.5	6.55	31.1	0.75	0.93
Y41	4155.7	$O_3 W$		0.39	5.56	10.47	1236	70	0.83	0.18	0.30	341.5	10.36	28.4	1.23	1.20
Y42	4156.3	$O_3 W$		0.14	3.35	8.70	1442	40	3.59	1.45	1.27	217.1	9.18	27.3	1.09	2.44
Y43	4157.2	$O_{3}W$		0.19	4.05	7.88	967	45	8.42	2.37	4.82	163.6	7.11	28.8	0.72	1.42
Y44	4157.8	$O_{3}W$		0.16	2.98	6.67	1584	62	2.88	1.99	1.91	234.6	9.09	27.7	1.01	2.30
Y45	4158.3	$O_3 W$		0.15	3.16	6.52	1695	35	3.36	1.87	1.57	260.7	9.61	26.9	1.14	4.42
Y46	4158.4	$O_3 W$		0.14	2.85	6.72	1563	37	5.11	2.41	2.34	229.3	9.16	34.2	1.07	6.53
Y47	4158.7	$O_3 W$		0.16	2.50	9.25	1483	41	2.47	1.81	1.49	210.1	9.63	26.4	1.14	2.76
Y48	4159.1	$O_3 W$		0.14	2.66	7.45	1613	40	2.87	1.86	1.55	234.7	9.33	26.2	1.10	3.16

Lithosphere

Mo/TOC	6.29	6.64	6.29	10.73	11.09	12.20	2.68
(La/Yb)n	1.08	1.36	1.19	1.00	1.02	1.01	0.80
y/Ho	28.9	29.3	28.6	34.3	35.0	34.7	29.0
LREE/HREE	8.45	9.66	8.72	7.65	7.49	7.69	7.61
REE (ppm)	201.1	192.2	171.3	105.7	88.6	99.0	164.6
$\rm EF_{Co} \times \rm EF_{Mn}$	0.27	0.35	0.25	0.61	1.27	0.94	0.22
Co×Mn	0.33	0.49	0.24	0.17	0.22	0.22	0.20
Sr/Cu	1.74	1.38	1.43	5.37	7.48	6.99	0.83
P/AI (10 ⁻⁴)	1432	1697	1418	815	611	733	1394
$\substack{\text{Ba}_{\text{bio}}\\(10^{-6})}$	1432	1697	1418	815	611	733	1394
V/Sc	8.13	10.12	15.97	17.68	18.53	26.14	36.40
Ni/Co	3.18	4.05	3.83	10.49	11.95	11.70	10.71
U/Th	0.59	0.55	0.62	1.35	1.59	1.88	06.0
Member	Sublayer 4	Sublayer 4	Sublayer 3	Sublayer 3	Sublayer 2	Sublayer 2	Sublayer 1
Formation	S_1l_1	$S_1 l_1$	$S_1 l_1$	S_1l_1	S_1l_1	$S_1 l_1$	$S_1 l_1$
Depth (m)	4306.6	4309.3	4311.3	4317.9	4325.6	4328.4	4334.1
Sample	NI	N2	N3	N4	N5	N6	N7

TABLE 4: Continued.

Lithosphere

Graptolite biostrati-	Series & Fm. M		Member	Depth (m)	тос	C (%)	U	/Th	1	Ni/Co	V/Sc	Ba _{bio}	(10^{-6})	P/Al (10 ⁻⁴)		CIA	Sr/C	Cu
grapny					2	4	1	2	e	b 12	10 20 30	600	1800	50 100 150	65	5 70	2 4	6
LM 6-8			Sub-member 2	3520 - 3525 -			Ī		Ī		Į	ſ						
LM 5	Paleozoic	Silurian (Longmaxi formation)	Sublayer 4	3535 - 3540 - 3545 - 3550 - 3555 - 3560 - 3565 -														\rangle
LM 4			Sublayer 3			··· · ··			J		2			4		···•		
IM22			Sublayer 2	-3570-	· · · • •		· 🐔 -										· · · · • • · ·	
LIVI 2-3			Sublayer 2		🍖								A				····•	
LM 1			Sublayer 1	3575 -		>						•		~		•		

FIGURE 8: TOC, redox index (U/Th, Ni/Co, and V/Sr), paleoproductivity (Ba_{bio} and P/Al), and paleoclimate (CIA and Sr/Cu) vertical diagram in S_1I_1 of well W214.

sublayer 4 depositional period, compared with the others in Weiyuan area, while the paleoproductivity decreased gently as time goes in Luzhou area and Changning area. Luzhou area had the highest paleoproductivity during the S_1l_1 depositional period in the mass, followed by Weiyuan area, and then Changning area. This analysis aligns well with the TOC trends of these area, but not exactly well in Changning, suggesting paleoproductivity is only one of the controlling factors for OM enrichment in S_1l_1 .

5.2. The Degree of Restriction in Bottom Water Column

5.2.1. Upwelling. In previous studies of five global stagnant water column and four upwelling oceanic zones, the element Co and Mn were found to show similar distribution patterns, and their similarity suggests that their enrichment and consumption in sediments receive similar process controls. Al, being an element for tracing terrestrial detrital sources, can be coupled with Co, Mn, EF_{Co} , and EF_{Mn} to eliminate the contribution from terrestrial detrital minerals

and is used to discriminate between stagnant and openupwelling environments [86]. We collected the data from Black Sea and Cariaco Basin, which represent a strong and an inferior stagnant environment, respectively. The data of the Black Sea fall in a stagnant area, while that of Cariaco Basin fall in the upwelling current area; its positive correlation between Al and Co×Mn indicate the value of Co and Mo being influenced by terrigenous detrital minerals influx and seasonal upwelling. In addition, the weak stagnant environment meaning a certain connectivity with the open sea fits well with the actual geographical environment of Cariaco Basin [87].

From the Al–Co×Mn diagram, the shale samples of S_1l_1 deposited in Luzhou and Changning areas are located near the upwelling current boundary and the shale samples of S_1l_1 in Weiyuan area and that of O_3w fall in the stagnant region. The positive correlation between Co×Mn and Al of O_3w in well Y101 and of S_1l_1 in well W214 shows that its value is affected by terrigenous debris (Figure 11(a)), which aligns well with the previous study. In order to eliminate

Graptolite biostrati- graphy	Ser & F	ries ⁷ m.	Member	Depth (m)	TOC (%)	U/Th	Ni/Co	V/Sc	Ba _{bio} (10^{-6}) 2500	P/Al (10 ⁻⁴) 40, 80, 120	CIA 65 70	Sr/Cu
LM 5	Paleozoic	Silurian (Longmaxi formation)	Sublayer 4	4105 - 4110 - 4115 - 4120 - 4125 - 4130 - 4135 - 4140 -								
LM 4			Sublayer 3	4145 -			L.		2 m	s v	2	
LM 2-3			Sublayer 2	4150 -		(3.05) (3.46) (6.01)		×	*	×,	K	44
LM 1			Sublayer 1	4155 -								
WF 2-3		Ord (V for	dovician Vufeng mation)				ž	Ę	ž	5	ż	(8.42)

FIGURE 9: TOC, redox index (U/Th, Ni/Co, and V/Sr), paleoproductivity (Ba_{bio} and P/Al), and paleoclimate (CIA and Sr/Cu) vertical diagram in O_3w and S_1l_1 of well Y101.

the contribution and dilution of terrigenous debris, enrichment factor has been used for calculation; it is found that the samples of O_3w in Luzhou area are similar to those in Black Sea, basically plot in the stagnant area and of S_1l_1 in the three areas are similar to those in Cariaco Basin (Figure 11(b)), basic plot in the weak or unrestricted area. The sample plot in the grey region between 0.5 and 2 does not accurately distinguish the water environment (Figure 11(b)), which speculated that these samples may be affected by unstable seasonal upwelling currents. It is also found that at the turn of Ordovician and Silurian, the region close to the Qinling paleoocean and located in the passive continental margin of low latitude was the active area of upwelling currents [88].

5.2.2. Mo/TOC Cross Plot. Confined paleobasins are often subject to differences in trace element enrichment due to the impeded circulation of bottom water. The correlation between Mo and TOC has been proposed to determine the degree of water restriction in the basin [92, 93]. Mo, as a

Graptolite biostrati-	Baleozoic	ies m.	Member	Depth (m)	TOC (%)		U/Th		Ni/Co		V/Sc	$Ba_{bio} (10^{-6})$	P/Al (10 ⁻⁴)	CIA	Sr/Cu
graphy	<u> </u>			· ,	2	4	1	2	6	12	10 20 30	600 1200	50 100	65 70	246
LM 5			Sublayer 4	4305-		1	Ţ	Ì	Ţ		Į			Ţ	ļ
LM 4	Paleozoic	ı (Longmaxi formation)	Sublayer 3	4315-							•				
LM 2-3		Silurian	Sublayer 2	4325- 4330-	((6.45)									
LM 1			Sublayer 1				• •			•			•	•	•

FIGURE 10: TOC, redox index (U/Th, Ni/Co, and V/Sr), paleoproductivity (Ba_{bio} and P/Al), and paleoclimate (CIA and Sr/Cu) vertical diagram in S_1l_1 of well N222.



FIGURE 11: (a) Al-Co×Mn and (b) Al- $EF_{Co}×EF_{Mn}$ diagram of black shale after by literature [86], Black Sea data from literature [89, 90], and Cariaco Basin data from literature [91].

redox-sensitive element, is generally enriched under anoxic reduction conditions and susceptible to OM in the sediment. There is also a coupling correlation between Mo/TOC and Mo concentration in the seawater. In a well-circulated environment, seawater has sufficient Mo elements, and the corresponding Mo/TOC values into the sediments are high; while in a confined environment, the recharge of Mo elements is slow or even suspended, resulting in the reduction



FIGURE 12: Mo-TOC discrimination diagram of black shale in three wells. Mo-TOC regression line slopes for modern environments are given in literature [36].

of Mo concentration in the bottom water. In the anoxic reduction conditions, the rate of Mo elements enrichment by sediment uptake is greater than the recharge rate. With the low Mo concentration in the bottom water, the sediments in this environment can be "starved" for Mo due to insufficient supply and thus demonstrate a low value for Mo/TOC [36].

The values of Mo/TOC range from 3.66 to 5.39 (avg. 4.38) in submember 2 shale of W214; from 2.65 to 9.94, 4.93 to 10.17, and 6.29 to 6.64 (avg. 5.32, 7.51, and 6.46) in sublayer 4 shale of W214, Y101, and N222, respectively; from 10.78 to 20.63, 5.81 to 14.53, and 6.29 to 10.73 (avg. 15.71, 9.43, and 8.51) in sublayer 3 shale of W214, Y101, and N222, respectively; 10.67, from 10.08 to 25.44 (avg. 16.36), and 11.09 to 12.20 (avg. 11.64) in sublayer 2 shale of W214, Y101, and N222, respectively; from 8.86 to 10.67 (avg. 9.77), 15.86, and 2.68 in sublayer 1 shale of W214, Y101, and N222, respectively; and from 0.93 to 6.53 (avg. 2.80) in O_3 w shales of Y101 (Table 4).

From the Mo-TOC patterns (Figure 12), it can be concluded that the O₃w shale in Luzhou area was deposited in a more restricted water column. This phenomenon is similar to the modern Black Sea environment, indicating that the submarine uplift in the Late Ordovician Yangtze platform restricted water flow, resulting in strongly stagnant water mass in O_3w [89, 90]. Among the samples in S_1l_1 of Y101 and N222, except for the 4 samples may have a high ratio of Mo enrichment due to the reduction environment, and 1 sample of N222 may have a low ratio due to high TOC, the other samples of sublayer 1, 2, and 3 plot in the moderately restricted region, which is similar to the stratified anoxic basin of Norway Framvaren Bay [36]. The water column became shallower and more restricted during the sublayer 4 deposition period. The Chuanzhong Uplift developed in the west of Weiyuan area and the Neijiang-Zigong Uplift developed in the east sandwich Weiyuan area [94], making the ratio of Mo/TOC of some samples is relatively low and belongs to medium-strong restriction environment. And the water column limitation degree of these has a good agreement with that of previous studies [69].

5.2.3. EF_U - EF_{Mo} Covariation Pattern. Three covariation patterns of EF_{U} and $\mathrm{EF}_{\mathrm{Mo}}$ representing different degrees of restriction were built upon present-day sea to evaluate paleoredox of marine environments due to the relatively low abundance of Mo and U in the continental crust with the low impact of terrigenous debris on Mo and U in the ocean [92]. One is unrestricted marine environment. In this model, the enrichment of U in sediments takes precedence over that of Mo, making the ratio of Mo/U in sediments relatively low (only 0.1-0.3 times than that of modern seawater), representing a relatively suboxic and weak restricted environment. With the decreased oxygen concentration of seawater, the enrichment of Mo accelerates, and the ratio of Mo/U ratio increases significantly, reaching 1-3 times than that of normal open seawater, such as the unrestricted sedimentary environment in the East Pacific Ocean. The second one is weak restricted marine environment. In this model, Mo is easily absorbed by metal hydroxide particles which enter the sediments together as carriers, resulting in a high value of Mo, making the ratio of Mo/U be as high as 3-10 times than that of normal seawater, such as Cariaco Basin sedimentary environment. The last one is a strongly restricted environment. Due to the enhanced restriction of the water column, the circulation and intersection of seawater are blocked. When Mo and U are absorbed by the sediment, there is no resupply of Mo and U from the open sea, while the absorption and consumption rate of Mo in the anoxic-euxinic environment is greater than U, resulting in a significant decrease in the ratio of Mo/U in the sediment



FIGURE 13: The covariation patterns of EF_U and EF_{Mo} of black shale in well W214, Y101, and N222. The base plot was taken from literature [37]. Solid line shows the ratio equal to seawater value (1 × SW). Dashed lines indicate the ratios equal to fractions of seawater value (3 × SW and 0.3 × SW) [92, 95]. Gray field represents the "unrestricted marine" trend, characteristic of depositional systems with no limited trace metal renewal. Green field represents the "particulate shuttle" trend, characteristic of environment in which intense redox cycling of metals occurs within the water column [95].

(usually lower than 1 time of normal seawater), such as modern Black Sea sedimentary environment [92, 95].

In this study, well-defined EF_U - EF_{Mo} covariation characteristics are obtained for the shales of different strata. Samples of O₃w in well Y101 and of submember 2 in well W214 plot in the region between 0.3 × SW and 1 × SW, indicating a restricted marine environment (Figure 13). Most samples in sublayer 1, 2, 3, and 4 plot in the region between 1 × SW and 3 × SW, indicating an unrestricted marine environment (Figure 13). The EF_U ranges from 0.98 to 42.42 (avg. 6.64), and the EF_{Mo} ranges from 1.00 to 289.29 (avg. 48.62) (Table 2), showing different degrees of enrichment. The EF_{Mo} of sublayer 1, 2, and early 3 shale is higher than

that of the late sublayer 3, sublayer 4, and O_3w shales in well Y101 in general. Its values are 1.25-5.29 (avg. 2.53), 186.37, 126.42-289.29 (avg. 188.05), 31.71-139.02 (avg. 87.13), and 13.55-47.76 (avg. 25.24) in O_3w and sublayer 1, 2, 3, and 4, respectively, indicating that the bottom water in Luzhou area in O_3w was oxic and sunoxic environment, and during S_1l_1 began with a relatively euxinic-anoxic environment. In contrast to the above-mentioned well Y101, similar EF_{U} - EF_{Mo} covariation characteristics are observed in the shale from well N222, while the value of EF_U and EF_{Mo} in sublayer 1 (with only one sample) is lower than that of other sublayers. The similar trend with well Y101, meaning the

gradually increasing oxygen concentration from sublayer 1 to sublayer 4 in Changning area. While the EF_U - EF_{Mo} covariation characteristics seem a little different in well W214 compared with the above two. The value of EF_{Mo} is 18.91-143.31 (avg. 81.11), 30.44, 21.14-84.13 (avg. 52.64), 7.29-41.53 (avg. 19.43), and 1.00-2.23 (avg. 1.44) in sublayer 1, 2, 3, and 4 and submember 2, respectively, indicating a euxinic-anoxic environment at the beginning and then rapidly reverting a suboxic-oxic environment with intermittently anoxic-suboxic environment as time goes in Weiyuan area. This can be interpreted that well W214 was located in deep water with an anoxic environment along the southern margin of the Chuanzhong Uplift during the early S_1l_1 and then continuously uplifted southern basin due to the northern extension of Qianzhong Uplift, resulting in the gradually shallower water in Weiyuan area [79]. Along with the unstable seasonal upwelling current [96], the bottom water shows an intermittently anoxicsuboxic characteristic.

5.3. The Influence of Relative Sea Level to OM Enrichment and Its Model. The above discussions show that well Y101 located in Luzhou area was in relatively strong restricted depositional environment during Wufeng formation in Upper Ordovician, and the two wells (Y101 and N222) located in Luzhou and Changning areas were in relatively open and weakly restricted depositional environment and affected by seasonal and intermittent ocean currents during Longmaxi formation in Lower Silurian, which proves that the sedimentary environment of O₃w was controlled by the restriction of water column, while that of S₁l₁ was controlled by the depth of water column, that is, the change of relative sea level. The well W214 located in Weiyuan area, developed in the slope zone between the Chuanzhong Uplift and Neijiang-Zigong Submarine Uplift, was in a relatively restricted environment, but not as restricted as the O₃w.

Wang et al. [43] and Zhao et al. [42] used graptolite to determine the changes of relative sea level and determined the sedimentary cycle change according to argillaceous and silty particles. It is clear that Wufeng formation (WF 2-3) in the southern Sichuan Basin has a character with increasing water column and then rapidly decreased until Hirnantian glacier epoch and then rapidly increased after Hirnantian glacier epoch. So the sublayer 1 (LM 1) was a progradational reverse cycle with a slow decreasing water column, and the depth of sublayer 1 reached the maximum. Sublayer 2 (LM 2-3) was the marker layer of the whole region, and Changning and Luzhou areas were retrograde positive cycles with the slow increasing water column, Weiyuan area was a progradational reverse cycle with the high system tract water column rising rapidly first then slow decreasing. Sublayer 3 (LM 4) was the lime mud shed deposition with the water column slowly receding, and sublayer 4 (LM 5) was the reverse cycle with the water column slowly receding. The characteristics of shale thickness, OM content, and mineral composition of Longmaxi formation in southern Sichuan Basin have obvious regional changes, showing strong heterogeneity. The foremost reason is that different paleogeomorphic leads to sediment source, original sedimentary environment, rise and fall of sea level, and tectonic evolution [88, 94, 96].

During the Late Ordovician to Early Silurian, due to the northward extension of the Qainzhong Uplift, the southern basin continued to rise and the water column became shallow. After the Hirnantian glaciation, the Longmaxi formation inherited the previous paleogeographic pattern.

During the deposition of early to middle O_3 w, with the influence of Katian interglacial period, the global climate went through warm and humid, and the global sea level reached a high level due to the dissolution of glaciers. Due to the compression of the Upper Yangtze Craton basin by Guangxi movement and the structural pattern of sedimentary differentiation in Sichuan Basin, basement subsidence occurred in southern Sichuan Basin. However, the study area was not in the semi-deep-water suboxic environment like other areas during this period; the sea water was shallow and in a strong oxic environment with weak hydrodynamics, strong restriction, and high deposition rate. The structural differentiation leads to a sedimentary difference of the stagnant sea. The climate was warm and humid, which is suitable for a large number of plankton breeding, giving this period high primary productivity. However, the OM content of the shale deposited is extremely low, indicating that the high paleoproductivity is only the basis of OM enrichment, and its anoxic degree with high deposition rate is the key factor for its preservation. Due to the detrital input the OM was diluted in the sediments, and the water column was shallow in this area, the OM cannot be effectively preserved due to the oxidizing environment, which results in extremely low TOC content in early O₃w. Until the deposition of late O₃w, the relative sea-level began rising caused by global sea-level change. Coupled with the rising sea level and the restricted stagnant environment, the expansion of anoxic zone led to the gradual transition from a strongly oxic environment to a suboxic environment. Previously, it is discovered that the global upwelling led to the flow of nutrientrich and CO₂-rich oceanic currents from high latitudes to low latitudes along the deep continental slope during the Late Paleozoic [97]. This upwelling brought nutrients from the deep ocean to the continental shelf and slope to promote primary productivity. In contrast, during late O₃w in this region, with a warm and humid climate, the plankton proliferated, making the primary productivity higher. Given the presence of some seasonal upwelling, the primary productivity was slightly higher than that of the early O₃w. The development of organic-rich shale during this period is due to the reduced terrestrial detrital input, the high paleoproductivity, and the restricted stagnant suboxic depositional environment (Figure 14(a)).

During the deposition of sublayer 1, large-scale transgression occurred around the world due to the end of the Hirnantian glaciation. And the transgression direction mainly came from the east in the Sichuan Basin [96]. The relative sea level reached the highest and decreased slightly during sublayer 1. Since Luzhou and Changning areas were located in deep-water sedimentary areas, the slow reduction of sea level has no impact, contributing to an anoxic-euxinic



FIGURE 14: Enrichment of OM pattern in the southern Sichuan Basin during the O_3w and S_1l_1 , Southeast China.

environment, while Weiyuan area is located in the middle depression of Chuanzhong Uplift and Neijiang-Zigong Uplift, making well W214 located in a slope area deposited in an anoxic environment in the early stage due to the relative high sea level. And the water column became shallower in the later stage, resulting in a suboxic environment, relatively more uplift exposure, more input of terrigenous debris from the Chuanzhong uplift than in the early stage, dilution of OM to a certain extent, and poor preservation of TOC. The end of the glaciation makes extremely rich nutrients, and transera organisms began to multiply, resulting in the gradual flourish of organisms. Therefore, the paleoproductivity was at a high level. Just after the glaciation, the temperature of the surface seawater increased rapidly in a warm and humid environment, while the bottom seawater was still at a relatively low temperature, making the seawater stratification obvious and more conducive to the preservation of OM in this environment (Figure 14(b)).

Lithosphere

During the deposition of sublayer 2, the relative sea level rose first and then fell, but also at a high relative sea level. Primary producers became the most prosperous after a certain period of reproduction, and then, consumers began to appear. Therefore, an anoxic environment in deep-water depositional region was maintained followed by sublayer 1 of Luzhou and Changning areas, which paleoproductivity was relatively higher. However, Changning and Luzhou areas were in an unabiding hot and dry environment during the early sublayer 2, in which paleoproductivity level first became lower. This environment has a certain negative impact on the preservation of OM, resulting the TOC of the sublayer 2 being still lower than that of sublayer 1. Due to the special geographical pattern of Weiyuan area, the changes of relative sea level briefly affected the location of W214, making it in a suboxic-oxic environment and continuously receiving the dilution of terrigenous debris. Although it is in a warm environment, the OM is still not effectively preserved (Figure 14(c)).

During the deposition of sublayer 3, the water column declined slowly on the whole region, which response well to the redox indicators. It was changed from an anoxic to a suboxic environment in Luzhou and Changning areas. The prosperity of various organisms (including the increase of consumers) also led to a slight decline of paleoproductivity but remained at a relatively stable level, making the OM affected from enrichment to lower enrichment under the environment influence. Southern Sichuan Basin was affected by Guangxi movement and received compression from the southeast direction during the whole Longmaxi formation, which may make the basement subsidence rate in Weiyuan area greater than that of sea-level decline, resulting in the depth of sea column showing a trend of gradually deepens, that is, from oxic to suboxic environment. And the content of TOC changes from low to high in sublayer 3 in Weiyuan area (Figure 14(d)).

During deposition of sublayer 4, the structure rose slowly causing a certain extent sea-level fluctuation, and towards the northwest, the regression happened, making the sedimentary center move towards central and northern Sichuan Basin, and the water column of southern Sichuan Basin was relatively shallow [42]. Weiyuan, Luzhou, and Changning areas were in an oxic-suboxic environment during this period. The sedimentary environment of sublayer 3 continued in Weiyuan area, causing the water column to be deep in the suboxic environment in the early sublayer 4 and well W214 showing the characteristics of strong restriction. However, its restriction did not bring a continuous anoxic environment like that of Wufeng formation, and it was still in an oxic environment, receiving the dilution of terrigenous debris from the Chuanzhong Uplift, while Luzhou and Changning area were in an open environment, receiving the dilution of terrigenous debris from the Qianzhong Uplift [98, 99]. There was a brief increase in paleoproductivity in the early sublayer 4 deposition in Weiyuan area. However, these three areas were in an oxic-suboxic environment, which has a greater impact on OM enrichment, so that OM cannot be effectively preserved. TOC in Luzhou and Changning areas was relatively stable and at a relatively

low value. The transitory suboxic environment and high paleoproductivity in Weiyuan area show the trend of TOC first high and then low (Figure 14(e)).

During deposition of submember 2, the global regression happened [21], causing the rapid reduction of sea level and the extremely oxic environment, and the high input of terrigenous debris made the OM content unable to be enriched in the shale (Figure 14(f)).

6. Conclusion

Based on the characteristics of geochemical parameters of black shale in the southern Sichuan Basin, we analyze the paleoenvironmental changes and enrichment of OM of 3 wells in early S_1l_1 . The conclusions are as follows:

- (1) The TOC content is lower and gradually increases upwards throughout O_3w (0.22-3.27 wt% in Luzhou area) and reaches the highest in sublayer 1 (2.02-4.02 wt%, 4.78 wt%, and 6.45 wt% in Weiyuan, Luzhou, and Changning areas, respectively), followed by sublayer 2 (2.39 wt%, 3.69-4.18 wt%, and 3.5-3.86 wt% in Weiyuan, Luzhou, and Changning areas, respectively) and sublayer 3 (1.92-3.33 wt%, 3.82-5.28 wt%, and 3.77-4.13 wt% in Weiyuan, Luzhou, and Changning areas, respectively) and sublayer 4 (1.31-4.57 wt%, 1.64-3.52 wt%, and 3.88-4.49 wt% in Weiyuan, Luzhou, and Changning areas, respectively). There is no enrichment of OM in submember 2 of Longmaxi formation (TOC = 0.19 0.57 wt% in the Weiyuan area).
- (2) The paleoenvironment changed from oxic to suboxic during O_3 w in Luzhou area, and that of Weiyuan, Luzhou, and Changning is a process of gradual transition from anoxic to oxic during the S_1l_1 , while the paleoproductivity reached the highest in sublayer 2. However, a slightly hot and dry climate happened in the early sublayer 2 period. Weiyuan area was continuously diluted by terrigenous debris during S_1l_1 , and the influence of it was the greatest in the sublayer 4 depositional period, while Luzhou area was also continuously diluted by terrigenous debris during O_3 w, but the influence was much stronger than that of S_1l_1 in the Weiyuan area
- (3) Luzhou area was in a restricted water column in O_3w , and during the depositional period of S_1l_1 , Weiyuan, Luzhou, and Changning areas were affected by the seasonal upwelling, and the water column was relatively open during sublayer 1, 2, and 3. Due to the shallow water column in sublayer 4, Weiyuan area was in a restricted environment, while the water column was still open in other areas
- (4) Under the influence of tectonic differentiation, the enrichment of OM in O_3w was controlled by the paleotectonic pattern, the suboxic environment caused by a restriction of the water column and middle-high paleoproductivity, while that of S_1l_1

benefits from the extensive anoxic environment caused by deep water (i.e., redox conditions) and high paleoproductivity, and other conditions have little effect on the enrichment of it. Changes in global sea level (redox environment), tectonic patterns, and paleoproductivity control the development of organic-rich shales conjointly

Based on predecessors and combined with the actual production materials, this study makes a more refined stratification of the shale at the turn of Ordovician-Silurian and makes a comparative analysis of the OM enrichment from the perspective of major and trace elements. Further research can use test and analysis methods such as metal isotopes. In addition, controlled by the drilling cost, the core samples and test analysis taken in this paper do not involve the formation of the first member of Longmaxi formation.

Data Availability

Data used to support the result of this study can be found in this manuscript text.

Conflicts of Interest

The authors did not report any conflicts of interest regarding the contents of this paper.

Acknowledgments

This research was supported by the Science and Technology Project of PetroChina Exploration and Production Company (Project No. kt2021-11-01) and Hubei Provincial Natural Science Foundation of China (Grant No. 2021CFB182).

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