Research Article

Geochemical Characteristics of the Middle Devonian Dacaozi-Tanshanping Shale Strata in the Yanyuan Basin, Southwest China: Implications for Organic Matter Accumulation and Preservation

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How the geochemical characteristics of organic matter shale for the carbonate platform facies remain uncertain, which restricts an integrated reconstruction of the model of organic matter accumulation and preservation. Here, we present new results from element geochemical fingerprinting and integrated analyses of paleoclimate, paleoproductivity, paleoredox environment, and terrigenous input of the targeted Middle Devonian Tanshanping and Dacaozi Formations in the Ninglang-Yanyuan Basin, Southwest China. It is worth noting that although the carbonate platform connects with the open sea partially, the redox environment will not be completely controlled by relative sea level variations. Specially, the paleoclimate, paleoproductivity, and paleoredox conditions are the main controlling factors of the accumulation and preservation of organic matter. In view of the paleoclimate indexes, we suggest that both a relatively warm-humid climate characterized by intensified chemical weathering conditions and a higher terrigenous input are identified as two major drivers forcing the reductive environment in the sedimentary waterbody. Finally, a comprehensive model is established for providing new insights into the mechanism of organic matter accumulation and preservation for the carbonate platform facies. The paleoredox environment, paleoproductivity, paleoclimate, and terrigenous input are believed to have exerted a very considerable force on reconstructing the model of organic matter accumulation and preservation for the carbonate platform facies. Specially, the coupling interactions between the paleoproductivity and redox condition are thus also stressed. We found that the preservation condition is much more important than the paleoproductivity, resulting in the degree of organic matter enrichment. Even if the paleoproductivity of a sedimentary waterbody of a depositional period of the Dacaozi Formation was higher, the TOC concentrations were relatively low due to the poor preservation condition by fall of the sea level and increase of the terrigenous input. In another aspect, the better preservation condition of the Tanshanping Formation makes the TOC concentrations higher in the case of lower paleoproductivity in the sedimentary waterbody.

1. Introduction

The mud shale of the Tanshanping Formation in the Ninglang-Yanyuan area is mainly composed of clay minerals and carbonate minerals, and the mud shale of the Dacaozi Formation is mainly composed of clay minerals and siliceous minerals. As organic geochemical characteristic analysis shows, the organic matter types in the middle Devonian of

the Ninglang-Yanyuan region are type II₁ kerogen, reflecting that the maturity is high which is in the overmature dry gas phase, and the maturity increases with the increase of burial depth [1, 2]. Previous studies have proved that the Tanshanping Formation and the Dacaozi Formation are the shale-concentrated sections in the Ninglang-Yanyuan Basin, and they have been important favorable exploration layers for shale gas, which is characterized by large thickness, high

maturity, and high organic carbon content. As the development of the shale exploration in the Tanshanping Formation and the Dacaozi Formation, combined with the deployment of two-dimensional seismic data, we chose a structure favorable site (Lizihe anticline) to deploy a geological survey well called Well Yunningdi-1. Through the analysis and testing, the well drilling by the stable natural gas in the Devonian strata shows that the average total content of analytical gas is 3.25 m³/t. Specially, the total organic carbon content in the Tanshanping Formation was between 0.09% and 1.83% (with an average of 1.14%), and the organic carbon content in the Dacaozi Formation was between 0.32% and 3.48% (with an average of 1.05%).

A series of studies have reported that the Ninglang area in Yunnan is an important area for shale gas exploration and development in the complex tectonic area of Southern China. The Tanshanping Formation and the Dacaozi Formation in the Middle Devonian are components of the main source rocks. Previous studies have shown that the hydrocarbon generation capacity of shale reservoirs depends on the content, type, and thermal evolution of organic carbon [3, 4]. The development of the shale reservoir space is also affected by organic carbon content to some extent [3]. At the same time, the shale which is rich in organic matter tends to have high gas content, which indicates that the organic carbon content has a good correlation with the adsorption performance of shale [5–9]. Therefore, these important scientific issues put forward the necessity to look for more effective evidences to correctly clarify the main control factors of organic matter accumulation and preservation and the resource potential evaluation of Paleozoic shale gas in the Ninglang-Yanyuan area, Yunnan. Many scholars all over the world believe that the favorable conditions for organic matter accumulation in black shale mainly include three modes: high productivity, anoxic preservation, and the combination of the two [10–16]. The model of high productivity is a hypoxic environment which is conducive to the preservation of organic matter when high organic matter is formed under the influence of paleoclimatology, terrestrial organic matter supply, biological productivity of waterbody, and other factors by consuming oxygen in the sedimentary waterbody [17–19]. To sum up, the three models are in the final analysis to discuss the effects of the paleosedimentary environment formed by different factors on the accumulation and preservation of organic matter. Therefore, the reconstruction of the paleosedimentary environment is very important. Many scholars have used the geochemical index of shale to study the sedimentary environment of the organic rich shale [20–25].

At present, most scholars have studied the shale outcrops of the Tanshanping Formation and the Dacaozi Formation of the Devonian in the Ninglang-Yanyuan area in terms of geochemical characteristics, generation and storage characteristics, sedimentary characteristics, and shale gas geological conditions. However, the mechanism of organic matter accumulation and preservation in black shale has not been studied in the Tanshanping Formation and the Dacaozi Formation. In this paper, we took the Well Yunningdi-1 as an example, and systematic elemental geochemistry analysis

was conducted, including the analysis of main elements by X-ray fluorescence spectrometry, the measurement of trace elements and rare earth elements by inductively coupled plasma-mass spectrometry (ICP-MS), the combustion oxidation-nondispersive infrared absorption method, and the measurement of TOC concentrations by the total organic carbon analyzer and summary of its variation characteristics. Moreover, we have studied the elemental chemical characteristics and paleosedimentary environment of the Tanshanping and Dacaozi Formations. On this basis, the main controlling factors of accumulation and preservation of organic matter in shale rocks were discussed in order to provide a theoretical basis for the mechanism of accumulation and preservation of organic matter and the reconstruction of sedimentary model.

2. Geological Background

2.1. Tectonic Position. The Yanyuan Basin is located in the west of Sichuan Basin, at the junction of the Sichuan-Yunnan plateau, and is structurally located in the south-north tectonic belt between western Sichuan and eastern Tibet. Specially, the basin was sandwiched between the Songpan-Ganzi Indosinian fold belt and the Kang-Yunnan ancient land, which is part of the Zhenzhongnappe thrust belt. The northern part of the Yanyuan Basin is controlled by the Xiaojinhe fault, which is adjacent to the Sanjiang island arc orogeny. The west side is controlled by the Guobaoshan-Yanfeng fault, which divides the Yanyuan Basin, the Yongning fault block on the west side and the Ninglang Basin on the southwest side. The east side is controlled by the Jinhe-Jinghe fault and adjacent to the Kangdian ancient land. The Lijiang Basin lies to the south of the Kang-Dian ancient land [26].

2.2. Tectonic Characteristics. The tectonic evolution of the Upper Yangtze plate is mainly controlled by the tectonic activities of the Tethys tectonic domain, which has undergone three major development stages: the proto-Tethys Oceanic basin (Z-O-S), the Guthys Oceanic basin (D-T3), and the New Tethys Oceanic basin (T3-N), reflecting the formation and evolution of the Tethys Ocean basin showed the change of becoming more and more earlier from south to north [27, 28]. Evidence of the disappearance of the New Tethys basin can be seen in the Yaluzangbu river and the Bangongcuo-Nu river Ophiolitic jumble zone in Tibet. At this time, the marine deposition in the western part of the Upper Yangtze river was terminated by the Indochina movement, which was no longer in the category of the tectonic evolution of the New Tethys Basin but was mainly located in the process of sea-land transition facies-continental sedimentary evolution. Paleozoic and Mesozoic marine sedimentary events in the western part of the Upper Yangtze Plate are bounded by the end of Silurian, and the geological period can be divided into two main periods: (1) Proto-Tethyan period of the Sinian-Early Paleozoic and (2) Late Paleozoic-Early Mesozoic Paleo-Tethyan period. Based on the observation and analysis of a large number of drilling data and outcrops, the sedimentary sequence and structural characteristics of

the Yanyuan Basin have been discussed. It is believed that the Yanyuan Basin was formed during the Miocene to Pliocene by the collision and extrusion of the Indian plate and the Eurasian plate. The emergence of this basin indirectly supported and recorded an important collision event of the Indo-Eurasian Plate in the Late Cenozoic [29]. It is important to focus on the tectonic position of the Yanyuan Basin which is in the arc structural belt in front of the Sichuan-Yunnan block, and it is the most obvious area of Cenozoic extrusion in the Qinghai-Tibet Plateau, which is sandwiched between the Xianshuihe fault and Honghe fault. The Sichuan-Yunnan block and its interior were cut by the Xiaojinhe fault, which can be divided into two secondary part blocks called the northwestern Sichuan Block and central Yunnan Block. The sliding velocities of the block boundaries are different between the blocks in northwestern Sichuan and central Yunnan, which reflects the composite motion model of the secondary blocks sliding horizontally and rotating clockwise about the vertical axis [30].

2.3. Sedimentary and Stratum Characteristics

2.3.1. The Ninglang Area. According to the “Yunnan Provincial Regional Geology Records of Ministry of Geology and Mineral Resources,” the Silurian (S) strata are mainly distributed in the Dacaozi area in the northwest and east of the Ninglang Basin, with thickness ranging from 182 m to 659 m. The Lower Silurian is mainly composed of shallow marine facies, with argillaceous limestone and gray limestone shale with a small amount of black siliceous layers. The Upper Silurian is mainly composed of lagoon facies, and a large number of carbonate rocks were developed. As for the Devonian system, Devonian strata are well developed in this area, which mainly outcrops in the Dacaozi, Xilaping, Wenxiang, and other areas, and there are deposits in the Upper, Middle, and Lower Series (Figure 1). The measurement area is divided from bottom to top as follows: The Lower Devonian Daguping Formation (D_1d), with a thickness of 92 m~687 m, is exposed in the eastern Dacaozi and Maoniuping areas, which belongs to coastal and shallow marine facies deposition and be dominated by dark gray shale and siltstone at the top and conglomeratic sandstone at the bottom. It is worth noting that the lithology is in a regular cycle and in parallel unconformable contact with the Silurian system, reflecting an obvious depositional discontinuity. The thickness of the outcrops in the eastern part of the basin is about 91 m, and it is missing in the Xilaping area in the southeast. The Middle Devonian Dacaozi Formation (D_2d) is exposed at Dacaozi and Maoniuping in the east, with a thickness of 266 m~378 m, in which thickness is 266 m at the Dacaozi and missing at the Xilaping in the southeast. The strata of the Dacaozi Formation belong to shallow marine sedimentary facies, which is dominated by dark gray and gray biolimestone, which is interbedded with shale and integrated over the Daguping Formation of Lower Devonian. The Middle Devonian Tanshanping Formation (D_2t) is exposed in the Dacaozi area in the east with a thickness range of 618 m~640 m, and the thickness of the Dacaozi area is 141.3 m, which belongs to shallow marine sedimentary

facies. The lithology is quite different from bottom to top. In particular, the bottom is mainly interbedded with sandstone, conglomeratic sandstone, and black shale, the upper part has experienced a transition that it has less sandy and more calcareous, and the top part is mainly grey limestone, bioclastic limestone, marl, and shale. The thickness of the Tanshanping Formation is about 617 m, and it is in a conformable contact with the Dacaozi Formation. On the whole, the Devonian strata overlay the Lower Ordovician strata. The Upper Devonian Lanniying Formation (D_3l), with a thickness ranging from 476 m to 569 m, is exposed in the Dacaozi, Xilaping, and Luniqing areas in the east, composed of limestone at the top and dolomitic limestone at the bottom, which is integrated above the Tanshanping Formation. The Upper Devonian Gangou Formation (D_3g), with a thickness of 298 m~527 m, is exposed in the Dacaozi, Maoniuping, and other areas in the east, which belongs to shallow marine sedimentary facies, and its lithology is dominated by limestone and oolitic limestone, which is integrated over the Lanniying Formation. Moreover, the Carboniferous system (C), with a thickness range of 266 m~964 m, is exposed in Yaoshan, Zhushan, and other areas in the northwest of China, in which lithology is dominated by dark gray bioclastic limestone and oolitic limestone, with pebbly sandstone and conglomerate at the bottom and chert nodule oolitic limestone at the top [31].

2.3.2. The Yanyuan Area. The strata in the Yanyuan Basin are all exposed from Sinian to Quaternary, except for the absence of Jurassic and Cretaceous. The strata below Triassic are all marine sediments, and the upper Permian has a set of Emei mountain basalt intrusion. The Sinian strata in the basin are exposed in the southeast margin of the basin, which only has a part of the upper Sinian strata; the lithology is mainly dolomite, and the bottom of which is marl, sandy mudstone interlayer. The Lower Paleozoic strata are exposed in the southeast and southwest sides of the basin, and the upper part of the Lower Cambrian to upper Cambrian and upper Ordovician strata are missing, so the Cambrian and Ordovician, Ordovician and Silurian are in parallel unconformable contact. The stratigraphic lithology of the Cambrian is dominated by fine silty clastic rocks, while the dolomite and limestone of the Middle and Upper Ordovician belong to a relative high level of enrichment, and the top is in parallel unconformable contact with the Silurian. As for the Lower Silurian Longmaxi Formation, it belongs to the marine deposit, which consists of graptolite-bearing siliceous argillaceous shale, intercalated argillaceous limestone, argillaceous sandstone, and sandy mudstone. The Middle Silurian is mainly argillaceous limestone, while the Upper Silurian is sand-mudstone and siliceous rock, and the Middle and Upper Silurian is locally dolomite. In terms of the Devonian system, Devonian and Silurian, Carboniferous and Devonian, and Permian and Carboniferous are in parallel unconformity contacts. The lithology of the Lower Devonian is mainly quartz sandstone, fine siltstone, limestone, siliceous rock intercalated with shale, argillaceous siltstone, and black shale. In the upward direction, the gray and sandy matter are reduced, while the argillaceous matter is increased. The Middle and Upper Devonian is dominated by carbonate deposits

FIGURE 1: Comprehensive stratigraphic column of Devonian in Ninglang-Yanyuan [86].

interbedded with calcareous mudstone and argillaceous limestone, while it contains a small amount of sandstone conglomerate. Then, the Carboniferous system is mainly composed of limestone deposits with light gray limestone lithology and a large number of coral fossils. In the end, the lower Permian is dominated by sandy mudstone with local coal intercalation lines, and the middle Permian is dominated by limestone with weathering crust developed at the top, and the upper Permian is invaded by basalt with a thickness of about 2800 m. The top is dominated by fine clastic rocks with black carbonaceous shale mainly.

The Ninglang-Yanyuan Basin is located at the junction of the Songpan-Ganzi fold system and the western margin of the Yangtze platform. It is a component of the Yanyuan-Lijiangtai fold belt on the western margin of the Upper Yangtze block, adjacent to the Sanjiang tectonic belt in the west and the Kangdian ancient land in the east. Accordingly,

this study focuses on Well Yunningdi-1, which is selected as the favorable site for structural preservation in this study (Figure 2).

3. Samples and Methods

3.1. Samples. A total of 52 shale samples in the Tanshanping and Dacaozi Formations were obtained from Well Yunningdi-1 in the Ninglang-Yanyuan Basin. The depth of these shale samples was in a range of 750.28 m~1486.5 m. Specially, the data of shale gas content was provided by the Oil & Gas Resource Survey, China Geological Survey. In this study, 52 shale samples were systematically collected from the black shales of the Devonian Tanshanping and Dacaozi Formations in Well Yunningdi-1 in the Ninglang-Yanyuan Basin. In order to take the next step, pretreatment was performed firstly. After drying the

FIGURE 2: Tectonic position of the Ninglang-Yanyuan Basin and Well Yunningdi-1 (modified from reference [1]).

sample, which had been cleaned by ultrasonic waves with deionized water several times, the sample was ground to 200 mesh with agate mortar.

3.2. Analytical Methods

3.2.1. TOC Analysis. In this study, a total of 52 shale samples from the black shales of the Devonian Tanshanping and Dacaozi Formations were selected for TOC analysis. About 100 mg of powdered samples was prepared and then acidified with 5% HCl in a crucible when the temperature reached approximately 80°C to remove carbonates. The TOC concentration was determined using a Leco CS-230 apparatus at the Oil & Gas Resource Survey, China Geological Survey.

3.2.2. Major Element. All 52 samples were air-dried and crushed into powders before geochemical analysis. The con-

centration of major elements were measured at the Oil & Gas Resource Survey, China Geological Survey, using a Leeman Prodigy (USA) inductively coupled plasma-optical emission spectrometer (ICP-OES) with high-dispersion Echelle optics. Samples were prepared by dilution with tetraborate/lithium metaborate fusion and nitric dissolution processes. Chinese National Rock Standards (GSR-1 and GSR-5) and US Geological Survey (USGS) standard materials (BCR-1, AVG-2, and SCO-1) were used to correct the analytical uncertainties. Analytical precision for most of the major element oxides is more than 98%.

3.2.3. Trace and Rare Earth Elements. Trace element and rare earth element concentrations were determined with the Thermo Scientific Element XR Sector Field Inductively Coupled Plasma Source Mass Spectrometer (ICP-MS). Firstly,

52 test samples were added to lithium metaborate and lithium tetraborate solvent. Then, the powder samples were mixed well and dried at 105°C. Finally, ICP-MS was used to complete the test, which accuracy of for most of the trace and rare earth elements was better than 5%, with higher precision.

4. Results

4.1. Distribution of the TOC. The total organic carbon concentrations of the Tanshanping Formation and the Dacaozi Formation in Well Yunningdi-1 range from 0.10% to 3.48%, with an average of 1.08%. In particular, the total organic carbon concentrations of the Tanshanping Formation are higher than that of the Dacaozi Formation means 1.13% and 1.06%, respectively). Among them, it is worth noticing that the total organic carbon content of the organic-rich shale (1070.6~1088.6 m) in the Tanshanping Formation ranges from 0.92% to 1.43%, with an average of 1.21%. And the total organic carbon content of organic-rich shale (1320.8~1486.5 m) in the Dacaozi Formation ranges from 0.37% to approximately 3.48%, with an average of 1.14%. They were thought to be a good source rock because of the relatively high organic carbon content of these Formation shales, which has reached the standard of good source rock.

4.2. Distribution of Major Elements. The contents of major-element oxides in the shale samples from the Tanshanping Formation and the Dacaozi Formation are presented in Table 1. Table 1 shows that the main elements of the Tanshanping shale are SiO_2 (with an average of 42.55%), Al_2O_3 (with an average of 12.17%), and CaO (with an average of 11.94%), and the total content of these 3 components ranges from 48.96% to 78.34%. In addition, the concentrations of other major element oxides in the Tanshanping Formation are obviously less than 4%, which include Fe_2O_3 (with an average of 3.41%), MgO (with an average of 1.79%), K_2O (with an average of 2.87%), Na_2O (with an average of 1.26%), P_2O_5 , SO_3 , TiO_2 , and MnO (less than 1%). It is worth noting that the main components of the organic-rich shale in the Tanshanping Formation are SiO_2 (with an average of 44.74%), Al_2O_3 (with an average of 12.95%), and CaO (with an average of 11.97%), and the total content of these three components ranges from 63.98% to 73.61%.

The main elements of the Dacaozi shale are SiO_2 (with an average of 56.07%), Al_2O_3 (with an average of 15.95%), Fe_2O_3 (with an average of 5.89%), and CaO (with an average of 4.57%). And the total content of these 4 components ranges from 80.74% to 96.92%. The concentrations of other major element oxides in the Dacaozi Formation are obviously less than 6%, which include K_2O (with an average of 5.53%), MgO (with an average of 1.54%), Na_2O (with an average of 1.44%), P_2O_5 , SO_3 , TiO_2 , and MnO (less than 1%).

The variation trend of the mass fraction of major elements and TOC is similar to the study section of the Tanshanping Formation and the Dacaozi Formation (Figure 3). In the Tanshanping organic-rich shale, the contents of SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , TiO_2 , and MnO decrease with the increase of TOC, while the contents of CaO and MgO increase with the increase of TOC. In the Tanshanping

organic-poor shale, the contents of SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , TiO_2 , and MnO increase with the increase of TOC, while the contents of CaO decrease with the increase of TOC. In particular, TiO_2 content is relatively stable, and K_2O content increases with the increase of TOC in both organic-rich and organic-poor shale segments of the Tanshanping Formation. The variation trend of the mass fraction of major elements and TOC in the Dacaozi Formation is similar to that of the Tanshanping Formation.

4.3. Distribution of Trace Elements. Because the total number of samples from the Dacaozi Formation is obviously larger than the Tanshanping Formation, the Dacaozi Formation is divided into Dacaozi1 and Dacaozi2 in order to indicate the transition of burial depth. Trace and rare earth element (REE) contents were normalized to North America shale composite (NASC) (for trace elements) and chondrite (for REES) in Figures 4(a) and 4(b) [32, 33]. As shown in Figure 4 and Table 2, the shale samples of the study area were standardized by North American shale (NASC). In the samples of the Tanshanping Formation and Dacaozi Formation of Well Yunningdi-1 (52 samples studied), trace elements Zn (ranges from 0.18 to 2.26) and Sr (ranges from 0.22 to 4.45) are relatively rich, while Rb (ranges from 0.02 to 1.30) is relatively poor (Figure 4(a)). In the two shale members, the trace elements have a similar trend of change, but the relative content of the trace elements in the Tanshanping Formation fluctuates slightly more greatly than the Dacaozi Formation (Figure 4(a)). Compared with the Dacaozi1 Formation and the Dacaozi2 Formation, the contents of trace elements in some samples of the Tanshanping Formation fluctuate more greatly, and the peak values of Zn and Sr are lower, while the relative contents of Rb are lower.

4.4. Distribution of Rare Earth Elements. To begin with, the rare earth elements refer to the lanthanides from La to Lu, which exhibit similar chemical properties. Rare earth elements are good tracers and indicators, which are often used in the analysis of paleosedimentary environment of organic-rich shale [34, 35]. REE content of black shales of the Tanshanping Formation and the Dacaozi Formation in Well Yunningdi-1 in the Ninglang-Yanyuan Basin is shown in Table 3. The REE ($\sum\text{REE}$) concentrations of the Tanshanping Formation ranges from 6.00 to 321.24 $\mu\text{g/g}$, with an average of 198.00 $\mu\text{g/g}$, the average is significantly higher than the abundance of North American shale REE (173.21 $\mu\text{g/g}$) and upper crustal abundance (146.40 $\mu\text{g/g}$) [36, 37]. And the REE ($\sum\text{REE}$) concentrations of the Dacaozi Formation ranges from 103.95 to 898.57 $\mu\text{g/g}$, with an average of 337.47 $\mu\text{g/g}$; the value is also significantly higher than the North American shale $\sum\text{REE}$, which is nearly twice as much. From the data above, the REE content of the Dacaozi Formation samples is higher than that of the Tanshanping Formation samples, indicating that the shale of the Dacaozi Formation is farther from the provenance area.

The ratio of $\sum\text{LREE}$ (light rare earth elements) to $\sum\text{HREE}$ (heavy rare earth elements) ($\sum\text{LREE}/\sum\text{HREE}$), reflecting the REE differentiation degree to some extent. The $\sum\text{LREE}/\sum\text{HREE}$ content of the Tanshanping Formation

TABLE 1: Concentrations of major elements (unit: wt%) in samples from the Tanshanping and Dacaozi Formations in the Ninglang-Yanyuan Basin.

Sample code	Member	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	TiO ₂	MnO	CIA
Q1908705	Tanshanping	5.20	27.64	0.46	22.56	1.22	0.95	0.33	0.028	0.012	0.093	0.006	17.9096
Q1908706	Tanshanping	10.33	35.86	3.33	16.92	1.35	1.08	2.33	0.041	0.115	0.297	0.014	33.6900
Q1908709	Tanshanping	16.56	48.83	5.91	4.74	1.97	1.24	6.17	0.114	0.114	0.820	0.055	57.6821
Q1908837	Tanshanping	15.16	44.63	5.25	6.83	2.21	1.18	4.15	0.049	0.139	0.654	0.032	55.4974
Q1908712	Tanshanping	8.44	33.88	1.38	18.56	1.52	1.05	1.69	0.070	0.043	0.209	0.022	28.3799
Q1908713	Tanshanping	9.39	36.74	2.00	18.26	1.31	1.11	2.15	0.075	0.054	0.250	0.034	30.3686
Q1908714	Tanshanping	13.59	49.53	3.59	7.01	2.13	1.35	4.16	0.056	0.088	0.520	0.050	52.0566
Q1908721	Tanshanping	16.22	58.39	5.22	3.73	1.62	1.61	4.07	0.384	0.124	0.897	0.062	63.2941
Q1908723	Tanshanping	15.48	51.07	3.70	8.08	1.58	1.49	3.27	0.136	0.072	0.549	0.044	54.6782
Q1908727	Tanshanping	15.36	44.37	5.32	9.12	1.51	1.43	3.98	0.291	0.116	0.677	0.060	51.3754
Q1908734	Tanshanping	12.64	42.68	4.97	12.11	1.43	1.31	2.74	0.261	0.146	0.472	0.044	43.8976
Q1908843	Tanshanping	8.97	37.41	1.34	17.60	1.37	1.15	1.49	0.122	0.041	0.206	0.029	30.7172
Q1908844	Tanshanping	15.09	49.20	4.04	9.32	1.47	1.48	3.33	0.223	0.084	0.599	0.047	51.6402
Q1908737	Tanshanping	15.11	49.64	4.22	8.84	1.48	1.44	3.16	0.184	0.092	0.618	0.075	52.9244
Q1908847	Dacaozi	14.43	47.19	7.86	8.43	1.34	1.25	6.05	0.683	0.147	0.969	0.116	47.8553
Q1908742	Dacaozi	12.24	41.22	6.43	14.13	1.21	1.11	6.19	0.773	0.122	0.796	0.131	36.3541
Q1908849	Dacaozi	18.81	52.12	7.15	2.60	1.53	1.46	5.35	0.175	0.126	0.903	0.067	66.6623
Q1908745	Dacaozi	17.53	55.07	5.64	3.71	1.62	1.49	4.71	0.152	0.091	0.792	0.079	63.8803
Q1908746	Dacaozi	16.64	61.25	4.18	3.68	1.62	1.64	3.72	0.197	0.086	0.754	0.041	64.8141
Q1908748	Dacaozi	13.69	45.69	3.21	11.80	1.36	1.29	3.48	0.092	0.069	0.452	0.085	45.2417
Q1908751	Dacaozi	17.73	53.91	5.96	4.20	1.60	1.47	4.96	0.141	0.086	0.836	0.107	62.4997
Q1908753	Dacaozi	10.39	39.74	2.28	16.66	1.26	1.14	2.71	0.171	0.055	0.307	0.097	33.6283
Q1908756	Dacaozi	18.43	55.38	6.53	1.94	1.50	1.48	5.60	0.203	0.122	0.971	0.073	67.1236
Q1908759	Dacaozi	10.34	68.08	3.26	6.34	1.44	1.57	1.65	0.172	0.037	0.284	0.092	51.9619
Q1908761	Dacaozi	18.47	48.53	9.52	2.17	1.43	1.39	7.45	0.347	0.146	1.081	0.100	62.6328
Q1908762	Dacaozi	17.56	61.00	4.27	2.35	1.71	1.67	5.46	0.203	0.040	1.045	0.038	64.9155
Q1908765	Dacaozi	11.10	63.61	1.67	8.99	1.44	1.57	2.05	0.126	0.014	0.288	0.118	46.8225
Q1908767	Dacaozi	16.65	62.96	3.70	2.21	1.58	1.60	5.34	0.234	0.041	1.157	0.043	64.5156
Q1908768	Dacaozi	19.84	58.17	8.82	2.65	1.72	1.59	7.69	0.291	0.115	1.228	0.077	62.453
Q1908771	Dacaozi	18.91	52.84	7.47	2.00	1.56	1.48	6.95	0.240	0.111	1.168	0.036	64.4267
Q1908775	Dacaozi	16.99	64.57	3.07	2.14	1.64	1.60	4.76	0.106	0.049	0.668	0.018	66.6216
Q1908777	Dacaozi	19.36	55.03	5.85	2.25	1.60	1.49	6.30	0.115	0.068	0.967	0.060	65.8493
Q1908785	Dacaozi	16.19	57.62	5.06	3.90	1.60	1.47	5.58	0.316	0.075	0.950	0.075	59.6406
Q1908787	Dacaozi	12.86	54.84	3.96	6.89	1.45	1.39	4.25	0.382	0.072	0.751	0.190	50.6456
Q1908789	Dacaozi	12.56	56.29	4.26	12.24	2.00	1.50	4.31	0.483	0.090	0.656	0.294	41.023
Q1908798	Dacaozi	14.99	48.66	10.15	5.81	1.45	1.27	8.08	0.691	0.131	1.166	0.161	49.7102
Q1908800	Dacaozi	18.70	60.29	3.90	2.07	1.79	1.64	5.84	0.123	0.017	1.119	0.032	66.1879
Q1908801	Dacaozi	16.23	61.32	5.32	2.35	1.65	1.56	6.16	0.390	0.059	0.986	0.039	61.721
Q1908802	Dacaozi	16.89	65.21	3.37	1.93	1.57	1.64	4.28	0.055	0.050	0.893	0.024	68.2578
Q1908803	Dacaozi	17.78	56.44	5.95	2.34	1.68	1.47	7.45	0.438	0.027	1.374	0.042	61.2296
Q1908808	Dacaozi	17.71	58.80	5.21	2.31	1.61	1.50	6.68	0.374	0.057	1.102	0.031	62.7902
Q1908811	Dacaozi	12.08	46.26	11.51	4.96	1.08	1.08	11.85	1.853	0.220	1.704	0.064	40.3274
Q1908814	Dacaozi	18.83	57.96	5.53	2.19	1.74	1.60	6.04	0.239	0.040	0.121	0.025	65.6967
Q1908817	Dacaozi	8.91	71.29	4.32	5.89	1.24	1.34	0.14	0.000	0.007	0.120	0.033	54.7409
Q1908819	Dacaozi	16.64	56.06	7.55	2.60	1.52	1.43	7.03	0.591	0.134	0.975	0.081	60.0749
Q1908823	Dacaozi	16.86	64.64	6.61	2.28	1.64	1.34	0.09	0.000	0.007	0.120	0.028	81.9678
Q1908825	Dacaozi	17.66	51.95	8.77	2.15	1.50	1.36	6.93	0.369	0.133	0.992	0.098	62.8532
Q1908826	Dacaozi	17.49	53.96	8.18	1.97	1.63	1.43	5.75	0.197	0.104	0.892	0.078	65.6693

TABLE 1: Continued.

Sample code	Member	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	TiO ₂	MnO	CIA
Q1908828	Dacaozi	17.62	55.90	6.54	2.14	1.66	1.44	6.46	0.311	0.058	1.136	0.039	63.7058
Q1908832	Dacaozi	16.87	59.62	5.68	2.26	1.70	1.47	5.85	0.315	0.052	0.952	0.030	63.7879
Q1908835	Dacaozi	14.01	50.90	9.14	4.53	1.41	1.18	11.22	1.405	0.009	1.755	0.070	45.2838

FIGURE 3: Main element and TOC content of YND-1 well in the Tanshanping Formation and Dacaozi Formation in the Ninglang-Yanyuan area (see Figure 2 for the well position).

ranges from 1.12 to 2.29, with an average of 1.85. And the $\sum\text{LREE}/\sum\text{HREE}$ content of the Dacaozi Formation ranges from 1.17 to 2.59, with an average of 2.01, and light rare earth elements are more enriched. However, the $\sum\text{LREE}/\sum\text{HREE}$ of both shale formations is smaller than that of North American shale (7.44), indicating that there was not much distance between these 2 groups and the provenance area.

The degree of differentiation of rare earth elements can be characterized by the slope of the partition curve of rare earth elements to chondrites, reflecting the higher the slope is, the slower the deposition rate is. LaN/YbN represents the slope of rare earth elements in the normalized chondrite diagram (Figure 4(b)), which can be used to evaluate the sedimental rate of shale. Meanwhile, the higher the deposition

rate is, the closer LaN/YbN is to 1. After the test, we found that the LaN/YbN of the Tanshanping Formation ranges from 0.85 to 1.37, with an average of 1.13. And the LaN/YbN of the Dacaozi Formation ranges from 0.75 to 1.58, with an average of 1.16. It is not difficult to see that the LaN/YbN of the samples of the Tanshanping Formation is closer to 1, leading the deposition rate of shale in the Tanshanping Formation is higher. What is more, the transport distance of the Tanshanping shale is shorter than that of the Dacaozi shale, which can reduce the loss of organic matter effectively.

The geochemical composition of sediments provides important information about the parent rocks from which they derived. The rare earth elements (REEs) are considered to be best indicators of provenance, as they are unlikely to

FIGURE 4: North American shale composite (NASC) normalized (for trace element) and chondrite normalized (for REE) diagrams for samples from the Middle Devonian Tanshanping Formation and Dacaozi Formation in the Ninglang-Yanyuan Basin, Southwest China.

be lost during postdepositional or sedimentary transport processes [38, 39]. In order to eliminate the serrated change of REE abundance with increasing atomic number caused by the even-odd rule of element abundance, REE concentrations were normalized to chondrite in Figure 4(b). Because it is generally accepted that there is no fractionation between LREE and HREE in chondrites, the chondrite standardization enables any separation between REE in the sample to be clearly shown.

The REE distribution pattern of shale samples from the Tanshanping Formation and the Dacaozi Formation in the study area is relatively stable and similar (Figure 4(b)). Figure 4(b) shows that LREE is relatively enriched and HREE is relatively depleted, and the distribution curve has a large slope in the light REE member, while it is flat in the heavy REE member. In addition, Ce and Eu are slightly depleted. On the whole, the REE distribution pattern is right tilted, which means LREE is enriched and HREE is flat. In another aspects, it also reflects the consistency of the provenance of the Tanshanping Formation and Dacaozi Formation in the study area.

5. Discussion

5.1. Paleoredox Condition Control on Deposition of the Tanshanping and Dacaozi Formations. Redox condition was the indispensable factor for organic matter preservation. Considering that particular self-stable and redox-sensitive elements (such as V, Cr, Co, Ni, Sc, and Zr) have been a bit affected or unaffected by diagenetic alternation due to their significantly lower correlation coefficients relative to other element contents [40, 41], the associated redox-sensitive trace elements, especially the trace-element ratios (e.g., V/Ni, Ni/Co, V/Cr, V/Sc, and V/(V + Ni)) are considered empirical indicators of paleoredox conditions. For the above reasons, the ratios of these elements (e.g., V/Ni, V/Cr, V/Sc, Ni/Co, and V/(V + Ni)) are usually considered effective proxies for distinguishing redox conditions of seawater to eliminate the underlying limitation utilizing a single trace

element. Previous studies have suggested that high ratios of these elements reflect reducing conditions.

Previous studies have demonstrated that the redox-sensitive elements were commonly enriched in the anoxic sediments, which could be used as powerful proxies for redox conditions [42]. Redox conditions have an important effect on the preservation of organic matter, the formation of sediments, and the formation and evolution of organisms. Specially, the redox condition indicators including V/Sc, V/Cr, Ni/Co, and V/(V + Ni) were widely used [43–45]. Constraints on the paleoredox conditions and paleoenvironment are provided by the above indicators, which show the discrimination of trace elements in different redox environments of shale in Well Yunningdi-1 (Figure 5). As the indexes to quantitatively evaluate the redox environment of the sedimentary waterbody, it is obvious that the sedimentary environment of the Tanshanping and Dacaozi Formations is different, suggesting that the Tanshanping Formation mainly deposited in a relatively anoxic environment.

On the whole, the redox environments changed greatly in the sedimentary history from the Dacaozi Formation to the Tanshanping Formation. The analysis of this study shows that, influenced by the paleoclimate and terrigenous input, the preservation conditions are triggered to change, reflecting on the TOC concentrations in the end, showing reasonable agreement with the decisive effect of the preservation condition of the mechanism of accumulation and preservation of the organic matter.

5.2. Paleoclimate Control on Deposition of the Tanshanping and Dacaozi Formations. Our investigations on CIA and REE further strengthened overall dysoxic to anoxic conditions of the waterbody during accumulation of the Dacaozi Formation to Tanshanping Formation, which provides the foundation for the following interpretations of the paleoclimate effect on redox environments.

The climatic conditions control the temperature, Eh, and pH of the sedimentary environment [46]. Chemical weathering is a crucial process to control the evolution of the earth surface system, by shaping landscapes, supplying nutrients

TABLE 2: Concentrations of trace elements (unit: $\mu\text{g/g}$) in samples from the Tanshanping and Dacaozi Formations in the Ninglang-Yanyuan Basin.

Sample code	Member	V	Cr	Co	Ni	Rb	Sr	Zr	Mo	Ba	Hf	U	V/Cr	Ni/Co	Th/U	V/Sc	V/(V+Ni)	Sr/Ba	Baxs	P/Ti
Q1908705	Tanshanping	15.47	7.56	1.26	7.09	9.74	208.89	10.25	2.29	26.59	0.31	6.17	2.05	5.62	0.17	6.70	0.69	7.86	26.55	0.30
Q1908706	Tanshanping	137.07	102.71	21.27	68.95	81.52	231.30	92.25	11.01	115.11	3.11	7.53	1.33	3.24	3.11	9.24	0.67	2.01	115.03	0.14
Q1908709	Tanshanping	165.26	184.98	18.04	48.76	175.08	181.33	181.43	1.38	478.90	5.76	6.79	0.89	2.70	2.92	8.32	0.77	0.38	478.78	0.14
Q1908837	Tanshanping	124.37	173.71	15.58	58.45	136.49	152.96	189.48	5.28	294.19	5.85	7.08	0.72	3.75	3.05	9.30	0.68	0.52	294.07	0.07
Q1908712	Tanshanping	56.25	63.88	5.62	19.25	43.14	551.63	55.49	0.86	68.95	1.86	2.41	0.88	3.43	3.06	7.99	0.74	8.00	68.89	0.33
Q1908713	Tanshanping	78.13	43.99	8.69	31.22	59.70	577.97	68.11	3.83	112.01	2.25	3.11	1.78	3.59	3.68	6.64	0.71	5.16	111.94	0.30
Q1908714	Tanshanping	109.32	111.71	11.31	32.65	107.96	121.50	137.41	1.52	202.22	4.17	4.23	0.98	2.89	3.50	10.05	0.77	0.60	202.11	0.11
Q1908721	Tanshanping	140.34	139.53	14.11	34.53	87.22	325.95	272.63	0.72	216.50	7.65	4.94	1.01	2.45	4.88	11.84	0.80	1.51	216.37	0.43
Q1908723	Tanshanping	135.13	137.15	16.79	42.66	104.49	579.60	126.24	1.00	264.89	3.75	4.19	0.99	2.54	3.69	11.18	0.76	2.19	264.77	0.25
Q1908727	Tanshanping	159.17	142.46	17.67	55.93	117.31	992.74	142.33	9.73	574.02	4.22	10.49	1.12	3.16	1.65	12.12	0.74	1.73	573.91	0.43
Q1908734	Tanshanping	112.28	109.49	14.55	46.75	80.03	1105.91	102.26	6.67	246.32	3.19	8.82	1.03	3.21	1.94	8.53	0.71	4.49	246.22	0.55
Q1908843	Tanshanping	69.51	68.67	7.17	31.88	50.82	1335.90	54.31	2.09	141.67	1.70	4.65	1.01	4.45	1.34	10.04	0.69	9.43	141.61	0.59
Q1908844	Tanshanping	138.81	84.27	14.16	38.81	113.76	678.97	134.54	1.89	342.83	4.30	5.39	1.65	2.74	3.14	12.11	0.78	1.98	342.71	0.37
Q1908737	Tanshanping	137.36	77.10	16.42	42.55	97.29	648.31	142.07	1.62	480.04	4.39	4.53	1.78	2.59	3.55	11.36	0.76	1.35	479.93	0.30
Q1908847	Dacaozi	141.02	139.65	18.40	40.86	122.04	560.28	181.83	1.70	622.67	5.36	5.03	1.01	2.22	4.64	9.37	0.78	0.90	622.67	0.70
Q1908742	Dacaozi	128.19	133.17	16.72	45.49	118.83	769.06	121.17	1.28	660.75	3.71	7.10	0.96	2.72	1.90	8.52	0.74	1.16	660.64	0.97
Q1908849	Dacaozi	180.03	167.36	22.38	51.96	159.87	257.43	215.42	4.00	1426.36	6.17	6.13	1.08	2.32	3.21	13.03	0.78	0.18	1426.27	0.19
Q1908745	Dacaozi	156.35	157.74	19.43	46.54	141.12	300.84	177.80	1.55	643.92	5.11	5.06	0.99	2.39	3.23	11.89	0.77	0.47	643.78	0.19
Q1908746	Dacaozi	83.54	72.78	11.57	25.03	77.00	209.36	243.36	0.71	605.66	7.13	3.67	1.15	2.16	3.80	9.20	0.77	0.35	605.53	0.26
Q1908748	Dacaozi	117.42	109.68	13.97	39.92	102.69	1169.57	125.97	1.54	1201.71	3.68	4.69	1.07	2.86	2.84	8.89	0.75	0.97	1201.58	0.20
Q1908751	Dacaozi	177.21	167.37	24.82	61.38	153.49	299.38	187.71	1.15	783.38	5.51	5.15	1.06	2.47	3.64	12.31	0.74	0.38	783.27	0.17
Q1908753	Dacaozi	95.04	91.64	10.15	31.49	71.88	864.32	72.22	0.76	484.48	2.23	3.24	1.04	3.10	2.89	10.05	0.75	1.78	484.34	0.56
Q1908756	Dacaozi	172.35	170.51	20.22	50.68	137.80	148.75	220.54	2.48	802.06	6.30	6.44	1.01	2.51	2.97	11.72	0.77	0.19	801.98	0.21
Q1908759	Dacaozi	22.65	42.21	7.48	18.67	31.21	213.97	118.14	0.76	225.70	3.71	1.52	0.54	2.50	3.18	5.62	0.55	0.95	225.56	0.61
Q1908761	Dacaozi	214.56	189.15	24.12	71.26	175.25	218.80	193.11	2.20	824.44	5.76	6.98	1.13	2.95	3.05	10.93	0.75	0.27	824.36	0.32
Q1908762	Dacaozi	118.20	114.89	13.25	29.14	116.69	124.26	252.55	0.59	766.60	7.32	4.60	1.03	2.20	3.79	9.45	0.80	0.16	766.46	0.19
Q1908765	Dacaozi	33.05	60.59	7.43	11.32	39.04	268.61	97.25	0.51	270.83	2.59	1.55	0.55	1.52	3.53	8.29	0.74	0.99	270.70	0.44
Q1908767	Dacaozi	95.96	113.46	12.11	23.15	104.28	124.51	268.45	0.57	674.62	7.57	4.35	0.85	1.91	3.79	9.31	0.81	0.18	674.53	0.20
Q1908768	Dacaozi	170.67	130.90	23.93	64.94	166.23	157.34	208.30	1.72	891.17	5.76	5.11	1.30	2.71	3.84	9.30	0.72	0.18	891.04	0.24
Q1908771	Dacaozi	175.19	93.09	23.81	44.76	159.06	166.72	281.99	0.99	855.18	7.95	6.64	1.88	1.88	3.25	9.95	0.80	0.19	855.02	0.21
Q1908775	Dacaozi	72.52	74.54	13.46	25.42	93.34	75.93	214.39	0.67	633.45	5.94	2.34	0.97	1.89	4.92	7.91	0.74	0.12	633.30	0.16
Q1908777	Dacaozi	156.78	116.68	23.30	52.99	151.86	169.14	187.90	0.99	926.44	5.36	4.69	1.34	2.27	3.94	8.94	0.75	0.18	926.31	0.12
Q1908785	Dacaozi	177.43	155.47	16.13	47.27	135.69	180.69	194.90	0.69	1648.02	5.79	5.41	1.14	2.93	3.26	15.92	0.79	0.11	1647.87	0.33
Q1908787	Dacaozi	119.68	120.84	12.59	32.08	97.13	259.97	202.79	0.60	1326.24	6.29	4.62	0.99	2.55	3.24	12.14	0.79	0.20	1326.12	0.51
Q1908789	Dacaozi	65.73	99.51	8.09	17.24	69.80	230.26	174.56	0.71	1466.94	4.38	3.85	0.66	2.13	4.40	10.89	0.79	0.16	1466.85	0.74

TABLE 2: Continued.

Sample code	Member	V	Cr	Co	Ni	Rb	Sr	Zr	Mo	Ba	Hf	U	V/Cr	Ni/Co	Th/U	V/Sc	V/(V+Ni)	Sr/Ba	Baxs	P/Ti
Q1908798	Dacaozi	165.72	81.48	27.34	56.88	156.85	282.11	187.85	1.94	928.08	5.65	8.01	2.03	2.08	2.52	9.14	0.74	0.30	927.98	0.59
Q1908800	Dacaozi	135.60	127.17	11.82	28.94	157.10	104.52	274.27	0.61	917.98	7.82	4.29	1.07	2.45	4.30	9.46	0.82	0.11	917.87	0.11
Q1908801	Dacaozi	107.37	84.22	14.21	27.74	123.22	135.11	234.60	0.55	792.74	6.88	4.12	1.27	1.95	3.92	8.93	0.79	0.17	792.60	0.40
Q1908802	Dacaozi	92.21	55.28	11.46	23.65	115.00	77.49	228.30	0.79	710.04	6.66	3.26	1.67	2.06	4.60	9.04	0.80	0.11	709.92	0.06
Q1908803	Dacaozi	158.26	76.84	18.49	41.22	149.39	161.44	222.89	1.25	1337.85	6.41	5.15	2.06	2.23	3.98	9.94	0.79	0.12	1337.72	0.32
Q1908808	Dacaozi	149.66	80.03	20.70	39.16	136.53	127.57	250.59	0.80	788.96	7.24	5.22	1.87	1.89	3.38	12.11	0.79	0.16	788.83	0.34
Q1908811	Dacaozi	139.47	116.24	54.07	110.28	105.93	369.09	191.94	2.05	778.83	5.38	6.94	1.20	2.04	2.10	7.35	0.56	0.47	778.70	1.09
Q1908814	Dacaozi	187.22	148.38	18.14	43.63	161.81	120.21	218.69	0.86	809.75	6.54	5.64	1.26	2.40	3.52	11.09	0.81	0.15	809.66	1.98
Q1908817	Dacaozi	143.57	76.71	20.77	60.50	136.56	188.79	167.92	2.69	778.06	4.85	4.71	1.87	2.91	4.37	8.73	0.70	0.24	777.91	(0.00)
Q1908819	Dacaozi	141.27	72.12	16.49	50.50	122.50	146.01	195.70	2.37	783.05	5.80	4.22	1.96	3.06	3.50	11.40	0.74	0.19	782.98	0.61
Q1908823	Dacaozi	128.65	70.10	16.29	50.09	123.92	154.75	256.60	1.82	646.15	7.47	4.76	1.84	3.07	3.48	9.67	0.72	0.24	646.02	(0.00)
Q1908825	Dacaozi	198.05	156.91	31.41	73.86	177.88	112.78	191.43	1.56	804.79	5.64	6.11	1.26	2.35	3.09	11.62	0.73	0.14	804.66	0.37
Q1908826	Dacaozi	191.23	157.70	27.62	61.27	181.75	101.74	164.83	1.37	907.78	4.95	5.24	1.21	2.22	3.38	11.37	0.76	0.11	907.65	0.22
Q1908828	Dacaozi	205.39	135.73	23.93	50.51	179.94	116.77	201.04	1.30	861.98	6.04	6.19	1.51	2.11	3.25	10.90	0.80	0.14	861.85	0.27
Q1908832	Dacaozi	181.81	76.41	22.08	45.95	157.33	110.49	191.07	0.69	1105.79	5.93	5.24	2.38	2.08	3.32	11.96	0.80	0.10	1105.66	0.33
Q1908835	Dacaozi	196.25	78.93	13.50	43.94	156.97	189.10	157.81	0.34	994.91	4.86	8.70	2.49	3.26	1.89	11.42	0.82	0.19	994.78	0.80

TABLE 3: Concentrations of rare earth elements (unit: $\mu\text{g/g}$) in samples from the Tanshanping and Dacaozi Formations in the Ninglang-Yanyuan Basin.

Sample code	Member	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	LREE	HREE	LREE/HREE	LaN/YbN
Q1908705	Tanshanping	4.11	5.96	0.97	3.75	0.83	0.15	0.79	0.15	0.83	0.19	0.54	0.08	0.47	0.07	29.90	15.78	14.12	1.12	0.85
Q1908706	Tanshanping	28.55	53.15	6.89	25.25	5.17	0.73	4.46	0.86	4.90	1.02	2.99	0.46	2.96	0.45	205.62	119.75	85.87	1.39	0.93
Q1908709	Tanshanping	54.32	84.91	10.80	38.39	7.15	0.95	5.60	1.00	5.59	1.19	3.56	0.58	3.95	0.61	290.17	196.52	93.64	2.10	1.33
Q1908837	Tanshanping	41.21	64.62	7.83	26.83	3.66	0.51	3.32	0.56	3.24	0.81	2.44	0.45	2.94	0.48	216.21	144.66	71.55	2.02	1.36
Q1908712	Tanshanping	16.59	25.13	3.92	14.27	2.82	0.44	2.56	0.47	2.75	0.59	1.73	0.26	1.68	0.26	105.42	63.17	42.25	1.50	0.96
Q1908713	Tanshanping	31.41	67.63	9.15	36.53	7.98	1.33	6.50	1.22	6.61	1.34	3.69	0.55	3.47	0.53	237.28	154.03	83.24	1.85	0.88
Q1908714	Tanshanping	31.98	59.16	8.19	28.38	5.33	0.71	3.90	0.65	3.68	0.74	2.16	0.34	2.26	0.37	192.13	133.74	58.39	2.29	1.37
Q1908721	Tanshanping	48.75	95.01	12.58	46.64	8.45	1.23	7.14	1.27	7.19	1.55	4.64	0.70	4.94	0.76	321.24	212.65	108.6	1.96	0.96
Q1908723	Tanshanping	38.20	61.17	8.28	29.54	4.48	0.62	3.54	0.62	3.18	0.83	2.53	0.40	2.83	0.46	206.99	142.29	64.70	2.20	1.31
Q1908727	Tanshanping	43.59	75.96	10.62	39.20	7.01	1.08	5.94	1.06	5.42	1.24	3.49	0.57	3.83	0.60	269.15	177.46	91.69	1.94	1.10
Q1908734	Tanshanping	40.34	69.82	9.67	40.02	7.76	1.11	6.09	1.09	5.56	1.21	3.14	0.50	3.34	0.50	254.86	168.72	86.14	1.96	1.17
Q1908843	Tanshanping	21.29	28.97	4.55	17.76	3.47	0.59	3.26	0.58	3.08	0.70	1.91	0.30	1.83	0.29	124.22	76.63	47.60	1.61	1.13
Q1908844	Tanshanping	44.66	76.38	9.79	37.38	6.45	0.96	5.67	0.96	5.02	1.15	3.29	0.54	3.28	0.52	258.64	175.62	83.02	2.12	1.32
Q1908737	Tanshanping	42.73	76.73	9.41	37.80	6.40	0.87	4.87	0.87	4.60	1.09	3.26	0.56	3.56	0.54	252.18	173.94	78.24	2.22	1.16
Q1908847	Dacaozi	63.58	128.09	16.57	67.88	14.58	2.65	14.20	2.60	13.99	3.23	8.60	1.38	8.19	1.30	487.72	293.35	194.4	1.51	0.75
Q1908742	Dacaozi	52.66	115.25	15.97	77.00	19.29	3.18	16.56	3.19	15.61	3.17	7.57	1.03	5.47	0.81	460.67	283.36	177.3	1.60	0.93
Q1908849	Dacaozi	58.50	98.35	12.40	47.35	8.05	1.22	6.60	1.07	5.53	1.20	3.45	0.59	3.66	0.57	315.72	225.88	89.83	2.51	1.55
Q1908745	Dacaozi	44.55	74.84	8.90	34.40	5.45	0.81	4.50	0.77	3.86	0.87	2.50	0.45	2.89	0.46	238.56	168.96	69.60	2.43	1.49
Q1908746	Dacaozi	37.69	67.76	8.12	32.31	5.45	0.86	4.62	0.81	4.09	0.92	2.72	0.47	3.00	0.49	219.47	152.19	67.28	2.26	1.22
Q1908748	Dacaozi	41.00	70.30	9.04	36.57	7.12	1.39	5.97	1.14	5.69	1.24	3.39	0.55	3.41	0.52	249.58	165.42	84.17	1.97	1.16
Q1908751	Dacaozi	52.63	85.31	10.30	39.27	6.03	0.90	5.04	0.87	4.41	1.03	3.01	0.53	3.38	0.53	274.72	194.45	80.27	2.42	1.51
Q1908753	Dacaozi	31.44	54.29	7.02	27.46	5.46	0.97	4.99	0.92	4.90	1.13	3.03	0.49	2.98	0.45	199.24	126.63	72.61	1.74	1.02
Q1908756	Dacaozi	53.50	88.45	11.01	38.96	6.57	1.05	5.72	0.99	5.07	1.15	3.47	0.60	4.10	0.66	288.61	199.55	89.06	2.24	1.27
Q1908759	Dacaozi	15.08	25.70	3.85	15.74	3.26	0.57	2.91	0.54	2.84	0.65	1.83	0.29	1.90	0.29	103.95	64.19	39.76	1.61	0.77
Q1908761	Dacaozi	78.79	119.94	15.31	59.35	12.14	1.82	10.24	1.84	9.34	1.97	5.21	0.85	5.25	0.84	417.17	287.35	129.8	2.21	1.45
Q1908762	Dacaozi	47.50	90.96	10.81	40.78	7.67	1.17	6.31	1.06	5.45	1.21	3.34	0.57	3.57	0.58	283.97	198.88	85.09	2.34	1.29
Q1908765	Dacaozi	18.54	32.08	4.70	18.54	3.66	0.64	3.11	0.58	3.00	0.68	1.85	0.29	1.69	0.28	120.83	78.16	42.67	1.83	1.06
Q1908767	Dacaozi	43.99	89.18	10.30	39.67	7.48	1.21	6.06	1.08	5.44	1.21	3.46	0.58	3.72	0.60	276.22	191.82	84.39	2.27	1.15
Q1908768	Dacaozi	56.93	102.05	12.26	46.01	8.72	1.50	7.44	1.32	6.89	1.60	4.57	0.75	4.81	0.74	341.18	227.47	113.7	2.00	1.15
Q1908771	Dacaozi	82.11	126.43	15.99	61.28	10.99	1.73	9.29	1.66	8.68	1.99	5.64	0.96	5.69	0.93	432.21	298.52	133.7	2.23	1.40
Q1908775	Dacaozi	31.99	54.55	6.33	22.34	3.42	0.58	2.85	0.47	2.47	0.60	1.85	0.34	2.35	0.37	169.28	119.21	50.07	2.38	1.32
Q1908777	Dacaozi	60.64	95.84	11.07	38.13	5.16	0.73	4.34	0.73	3.86	0.98	3.02	0.56	3.72	0.59	293.21	211.56	81.64	2.59	1.58
Q1908785	Dacaozi	52.18	87.95	11.34	43.63	8.68	1.50	7.44	1.30	6.39	1.38	3.70	0.60	3.71	0.59	299.77	205.27	94.49	2.17	1.36
Q1908787	Dacaozi	44.90	82.96	10.80	42.91	8.70	1.51	7.67	1.41	7.42	1.63	4.38	0.71	4.35	0.67	292.53	191.78	100.8	1.90	1.00
Q1908789	Dacaozi	42.25	72.90	9.10	36.12	7.28	1.23	6.66	1.22	6.34	1.44	3.95	0.65	3.93	0.60	260.86	168.88	91.99	1.84	1.04

TABLE 3: Continued.

Sample code	Member	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	LREE	HREE	LREE/HREE	LaN/YbN
Q1908798	Dacaozi	68.75	135.40	18.03	76.60	17.64	2.80	14.85	2.90	15.51	3.39	8.67	1.34	7.43	1.14	510.87	319.22	191.7	1.67	0.90
Q1908800	Dacaozi	52.00	86.72	10.22	37.12	5.51	0.81	4.05	0.71	3.95	0.99	3.12	0.57	3.69	0.59	270.41	192.38	78.03	2.47	1.36
Q1908801	Dacaozi	46.41	93.25	11.60	47.27	9.85	1.70	8.25	1.53	7.74	1.71	4.61	0.74	4.33	0.65	318.29	210.08	108.2	1.94	1.04
Q1908802	Dacaozi	36.70	62.21	7.17	24.05	3.92	0.61	3.18	0.57	3.11	0.72	2.21	0.41	2.69	0.42	192.54	134.65	57.89	2.33	1.32
Q1908803	Dacaozi	58.54	103.83	13.02	49.70	9.77	1.75	8.47	1.53	8.03	1.76	4.90	0.80	5.13	0.79	355.28	236.61	118.7	1.99	1.11
Q1908808	Dacaozi	48.59	94.73	12.89	53.23	11.82	2.04	9.13	1.64	7.97	1.62	4.30	0.66	3.95	0.62	328.92	223.30	105.6	2.11	1.19
Q1908811	Dacaozi	100.12	202.13	26.50	120.69	27.70	8.14	31.57	5.82	31.90	7.11	17.07	2.23	11.1	1.61	898.57	485.28	413.3	1.17	0.88
Q1908814	Dacaozi	56.86	109.78	13.74	54.03	10.32	1.63	9.05	1.53	7.78	1.70	4.61	0.76	4.74	0.77	360.64	246.35	114.3	2.16	1.16
Q1908817	Dacaozi	77.20	135.01	17.96	73.54	15.69	3.14	15.45	2.70	14.17	3.17	8.28	1.23	7.02	1.07	517.69	322.53	195.2	1.65	1.07
Q1908819	Dacaozi	50.99	96.93	12.48	49.01	9.95	1.93	9.61	1.65	8.84	2.03	5.48	0.84	4.99	0.77	351.77	221.29	130.5	1.70	0.99
Q1908823	Dacaozi	56.30	116.93	14.98	60.42	12.29	2.27	11.65	2.07	10.78	2.43	6.46	0.99	5.79	0.91	411.00	263.19	147.8	1.78	0.94
Q1908825	Dacaozi	54.32	96.23	12.46	47.93	9.33	1.56	8.43	1.44	7.40	1.62	4.56	0.76	4.53	0.70	337.94	221.82	116.1	1.91	1.16
Q1908826	Dacaozi	51.65	89.92	11.59	43.38	8.01	1.32	6.95	1.19	6.21	1.40	3.93	0.65	4.04	0.63	306.97	205.87	101.1	2.04	1.24
Q1908828	Dacaozi	59.80	113.77	13.98	54.49	10.58	1.67	9.20	1.54	7.79	1.74	4.79	0.80	5.06	0.78	376.63	254.28	122.4	2.08	1.14
Q1908832	Dacaozi	50.44	93.62	12.04	45.81	9.03	1.57	8.34	1.46	7.47	1.69	4.71	0.77	4.74	0.76	327.52	212.51	115.0	1.85	1.03
Q1908835	Dacaozi	57.49	150.23	22.11	101.48	25.87	5.63	24.86	4.39	21.44	4.20	9.69	1.32	7.05	1.06	595.93	362.81	233.1	1.56	0.79

FIGURE 5: Discrimination of trace elements in different redox environments of shale in Well Yunningdi-1.

and trace elements from the lithosphere to the biosphere, and regulating global chemical cycles. In the process of sediment formation, several geochemical indexes have been proposed to assess the degree of chemical weathering [47–50], among which the chemical index of alteration (CIA) is one of the most frequently used indexes. The chemical index of alteration (CIA) is calculated as the ratio $[Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O) * 100]$ in molecular proportions, where CaO represents Ca content in silicate minerals only. It is worth noting that the CIA has been widely used to quantify the degree of chemical weathering for (paleo-)weathering profiles and to reconstruct source region chemical weathering conditions for ancient and modern sediments [51]. In addition, the climate indexes (CIA) display the slowly warming environment, which is often used to reflect the paleoclimate conditions. It means the higher CIA values experienced relatively intense chemical weathering, which indicates a warm and humid climate [52]. It is also consistent with previous studies on the relationship between the CIA and paleoclimate which provides a better standard. As discussed in previous studies, when the value of CIA ranges from 50 to 65, it indicates arid climate. When the value of CIA ranges from 65 to 85, it indicates semiarid climate. When the value of CIA ranges from 85 to 100, it indicates warm and humid climate [53, 54]. Specially, the shale-dominated the Dacaozi Formation and Tanshanping Formation experienced a moderate to weak degree of chemical weathering as evidenced by the

significant decrease of CIA (mean 58.5 and 43.2, respectively) (Figure 6 and Table 1). Besides, the $\sum REE$ ($\sum REE = Sc + Y + La + Ce + Pr + Nd + Sm + Eu + Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu + Th$) can also indicate climate conditions [55]. It is noticed that the climate became more dry-cold from the Dacaozi Formation to the Tanshanping Formation as evidenced by the significant decrease of $\sum REE$ (mean 337.5 and 198.0, respectively) (Figure 6 and Table 1).

Therefore, these considerable variations likely reflect the impact of alternating climatic conditions of warm-humid and cool-arid, which confirm a relatively intensive weathering and its associated warm-humid setting that occur during the deposition of shales of the Dacaozi Formation.

In summary, there are several lines of evidence that it is more conducive to form a higher paleoproductivity in the context of a relatively warm-humid climate which promote biological growth in the sedimentary waterbody. From the above discussion of the values (CIA, $\sum REE$) from the Dacaozi Formation to the Tanshanping Formation, we have found that although the climate is relatively warm-humid during the deposition of the Dacaozi Formation, the weak preservation condition leads to destroy the accumulation of organic matter, which shows the lower TOC concentrations in the end.

5.3. Paleoproductivity Control on Deposition of the Tanshanping and Dacaozi Formations. In particular, the initial productivity of waterbody can be characterized by the

FIGURE 6: Paleoproductivity, paleoredox, paleosalinity, paleoclimate, relative sea level, and TOC content of Well Yunningdi-1 in the Tanshanping Formation and Dacaozi Formation in the Ninglang-Yanyuan area (see Figure 2 for the well position).

nutrient richness and organic carbon flux of surface water, and the change of initial productivity plays a key role in the accumulation of organic matter.

The Ba content is an indicator widely used to reflect the paleocean bioproductivity [56–60]. There is a high concentration of SO_4^{2-} ions reoxidized by H_2S on the surface of decayed organic matter. These ions will react with the Ba^{2+} in seawater to form BaSO_4 and result in sedimentation. Therefore, the area with a higher bioproductivity also has a higher content of BaSO_4 [61, 62]. The trace elements in rocks are composed of terrigenous input constituents and authigenic ones. Only the latter can reflect the characteristics of the paleosedimentary environment [63–65]. The Ba produced under the biological action is known as excess Ba (Ba_{xs}). The Late Archean Australian Shale standard is commonly used to calculate excess barium (Ba_{xs}) to characterize paleoproductivity. It is worth noticing that the higher values

of Ba_{xs} are indicators of higher paleoproductivity in the sedimentary waterbody of the Dacaozi Formation (Figure 6).

Furthermore, phosphorus (P) is considered to be one of the ultimately limited elements in marine environment, and also, it belongs to the most important nutrient elements for plankton [66] and a major component of skeletal material. Therefore, P is widely used as an indicator of paleoproductivity. Organic matter and authigenic minerals may have a dilutive effect on the absolute P content in the terrigenous detrital matter. To eliminate the effect, the P/Ti ratio is used to evaluate the paleoproductivity rather than the absolute P content [67, 68] because Ti is usually derived from the terrigenous detrital matter [69, 70]. The higher ratios of P/Ti of the Dacaozi Formation (which is higher than the P/Ti ratio of the black flint in the Ubara profile with medium productivity (with an average of 0.34)) reported in Figure 6 can also imply relatively high paleoproductivity throughout the depositional

sequence of shales, which coincides with the better provenance supply as argued above in a relatively warm-humid sedimentary setting, which provided favorable conditions for the accumulation of organic matter.

Since the depth of water controls the redox conditions and Ce depletion degree of water, Ce anomaly can also be used to indicate the relative change of the sea level. With the rise of sea level, the oxygen content of bottom water and the δCe of sediments are reduced [71].

From the above discussion, we can get a stronger idea that detailed analysis of the paleoredox conditions and further investigation of the paleoclimatic and paleoproductivity forcing mechanisms operating during sedimentation indicate that the Dacaozi organic-rich shales was deposited in the more warm-humid environments. Climatic fluctuations resulted in the difference degree of the terrigenous input of the Dacaozi and Tanshanping Formations, which coincide well with the water paleoproductivity changes and redox environmental evolution [72]. Specifically, during the deposition of the Dacaozi Formation, significant increases in the temperature and humidity led to the relatively high terrigenous inputs with more nutrient inputs. The terrigenous inputs promoted abundant planktons and favoring organic matter accumulation [73]. In addition, the shallow waterbody made it easier for sunlight to penetrate the waterbody, which coincides with the relatively high paleoproductivity. However, the preservation condition of the organic matter in the Dacaozi Formation was generally poor, as often the relative sea level was so low that it trend to accumulate more oxygen [74]. Specially, the higher terrigenous input diluted more organic matter, and the longer distance of transportation and lower deposition rate have accelerated the destruction of preservation conditions. Due to the worse preservation conditions, the TOC concentrations of the Dacaozi Formation were lower. On the contrary, we have found that the paleoproductivity during the sedimentary period of the Tanshanping Formation was lower than that of the Dacaozi Formation, reflecting the relative cold-dry climate and lower terrigenous input. It is obvious that the paleoproductivity in the waterbody was worse, and that is mainly because it did not have enough terrigenous input, reflecting the limited provenance supply. In another aspects, we found that the range of the penetration from sunlight was relatively narrow, for the sea level was relatively high. Nevertheless, the higher sea level supports a reductive and stable bottom waterbody (Figure 7). And the lower terrigenous input indicates the decrease of fresh water input, leading to be more reductive in the waterbody. In addition, it is worth to emphasis on the shorter distance of transportation during the sedimentary period of the Tanshanping Formation, which enhance the preservation ability in the sedimentary center.

6. Mechanism of Accumulation and Preservation of Organic Matter

The study area was in the sedimentary environment of the carbonate platform. The high biological productivity, anoxic, and reducing environment were conducive to the accumulation and preservation of organic matter in shale [75]. In order

to reconstruct the model of accumulation and preservation of organic matter in the carbonate platform facies, it is essential to clear up the relationship between TOC and relative sea level, paleoproductivity, and redox conditions of the unique sedimentary facies which has many unconventional features. Therefore, this study preliminarily discusses the accumulation and preservation mechanism of shale organic matter in Well Yunningdi-1 in the Ninglang-Yanyuan area by using the evolution of water redox conditions combined with the research results of sea level change, paleoproductivity, paleoclimate, and terrigenous input.

6.1. Relationship between TOC and Relative Sea Level Variations. In considering sea level variations during the sedimentary period, the relative sea level and regional paleoclimate are suggested here as two distinct factors for the influence of accumulation and preservation of organic matter at different scales.

On the one hand, the difference of the redox environment of the Tanshanping and Dacaozi Formations can be analyzed from the relative sea level. Previous studies have shown that water depth is one of the elements which controls the redox condition and Ce depletion degree. With the rise of sea level, both of the oxygen content of bottom water and the δCe of sediments decrease [71]. The value of δCe in the Tanshanping Formation is lower than that in the Dacaozi Formation (mean 0.763 and 0.824, respectively), reflecting the rise of the relative sea level. The research of the redox environment emphasized the importance of the relative sea level response in the process of deposition of the carbonate platform and throw light on whether the relative sea level variations control the redox environment of the sedimentary waterbody in the carbonate platform.

On the other hand, the anoxic environment in the sedimentary waterbody of the Tanshanping Formation is ascribed to the regional paleoclimate effect during the sedimentary period. At the same time, the terrigenous inputs promote planktons' propagation and growth.

This implies that the combined effects of relative sea level variations and regional paleoclimate driving mechanisms favored the accumulation and preservation of organic matter in the study area. To summarize, the combined impact of these factors is ultimately reflected in the TOC.

6.2. Relationship between TOC and Paleoproductivity. Based on the above researches, Ba_{xs} indicates that the paleoproductivity of the sedimentary waterbody in the Dacaozi Formation is higher than that of the Tanshanping Formation (mean 856.29 and 254.49, respectively), which are shown in Figure 6 and Table 2. Considering that the accumulation and preservation of the organic matter in the Dacaozi Formation is largely controlled by paleoproductivity due to their significantly higher correlation coefficients between TOC and paleoproductivity indexes (e.g., Pb and Ni/Al) [76], which are shown in Figures 7(d) and 8(e). In addition, the associated indexes of climate and terrigenous input (e.g., REE and CIA values) are considered important indicators of paleoproductivity. However, due to the damage of the preservation condition, there is more oxygen enrichment of

FIGURE 7: A conceptual model illustrating the influence of the changes of relative sea level, paleoredox condition, paleoproductivity condition, and paleoclimate condition on organic matter accumulation and preservation for the Tanshanping Formation and the Dacaozi Formation. (a) The Tanshanping Formation. (b) The Dacaozi Formation.

the sedimentary waterbody of the Dacaozi Formation, which led to the lower TOC concentrations of the Dacaozi Formation.

6.3. Relationship between TOC and Redox Conditions and Terrigenous Inputs. The redox conditions are crucial in the mechanism of accumulation and preservation of the organic

matter, which shown in Figure 7. As most scholars believe, this is in close agreement that the redox environment of sedimentary waterbody is not only affected by redox indexes but also affected by terrigenous input.

On the one hand, we have supported the idea that the accumulation and preservation of the organic matter in the Tanshanping Formation are largely controlled by paleoredox

FIGURE 8: Crossplots of redox indexes (Cr, Cu/Zn, and δU) versus TOC content and paleoproductivity indexes (Pb and Ni/Al) versus TOC content of the Tanshanping and Dacaozi shales.

due to their significantly higher correlation coefficients between TOC and paleoredox indexes (e.g., Cr, Cu/Zn, and δU), which have been considered reliable redox indexes [77, 78], reflecting in Figures 8(a)–8(c).

On the other hand, terrigenous input is also considered an important element, coinciding reasonably well with the paleoproductivity and paleoredox environment.

From the above discussion, we can get a stronger idea that CIA and $\sum REE$ can reflect paleoclimate and terrigenous input together. The CIA and $\sum REE$ values of the Dacaozi Formation are higher, reflecting the relatively warm-humid

paleoclimate and higher terrigenous input. At the same time, the higher terrigenous input diluted more organic matter. According to the previous studies, both of the paleoclimate and terrigenous input led to oxidation of the sedimentary waterbody of the Dacaozi Formation. On the contrary, it was relatively dry-cold during the sedimentary period of the Tanshanping Formation, which reflects lower terrigenous input. The lower terrigenous input has effectively decreased the dilution of organic matter, leading a reductive environment of sedimentary waterbody in the Tanshanping Formation.

6.4. Model of Accumulation and Preservation of Organic Matter

6.4.1. The Interactions between the Relative Sea Level, Paleoproductivity, Redox Condition, and Carbonate Platform Sedimentation. As one of the key research points of the Ninglang-Yanyuan Basin, the Tanshanping and Dacaozi Formations of Well Yunningdi-1 have the following features.

According to previous studies, we have done a lot of works about the marine facies and pure continental facies. Specially, the sedimentary position of the study area is different from the previous researches, which belongs to the carbonate platform facies (Figure 7).

Unlike marine deposits, sedimentary water bodies of the carbonate platform are partially connected with the open sea, showing reasonable agreement that the accumulation and preservation of organic matter will be partially affected by the open sea (Figure 7). However, the connection area with the open sea is really limited in the sedimentary waterbody here, it will be greatly affected by other multiple factors (such as paleoclimate, paleoproductivity, terrigenous input, and redox conditions) within the sedimentary waterbody.

Aiming at the mechanism of accumulation and preservation of the carbonate platform, this paper takes the Tanshanping Formation and Dacaozi Formation as an excellent example and focuses on the analysis of the dialectical relation between the paleoproductivity and paleoredox environment and the accumulation and preservation model of shale in the study area.

In terms of paleoproductivity and redox condition, it is obvious to know that both of them affect the accumulation and preservation of organic matter. In the study on the accumulation and preservation mechanism of organic matter in the Tanshanping and Dacaozi Formations, the comprehensive results of the combined effects of paleoproductivity and redox conditions form a marked contrast.

From the above discussion, we have summarized a view. Based on the example of the Dacaozi Formation, the TOC of the study shale member is not necessarily higher in the context of higher productivity waterbody. The reason why it shows lower TOC concentrations is that the sedimentary waterbody of the Dacaozi Formation had more oxygen because of the fall of the sea level and the dilution from the terrigenous input. In another aspect, based on the example of the Tanshanping Formation, the paleoproductivity was lower, for the relatively dry-cold climate has blocked biological growth. As a complement, the range of the penetration from sunlight was relatively narrow because of the rise of the sea level. However, the waterbody was more reductive during this depositional period, because the lower terrigenous input which was reflected by the dry-cold climate indicates the decrease of fresh water input. All of the conditions guarantee a better preservation condition of organic matter. On the whole, the TOC concentrations of the study shale are not necessarily lower although the paleoproductivity is relatively poor.

6.4.2. Depositional Model for Organic-Rich Shale of Carbonate Platform. In terms of sedimentary facies, the Dacaozi Formation developed saline lagoon facies, which belongs to shallow

water deposits farther from the sedimentary center. During the deposition period of the Dacaozi Formation, the water energy was low, which was mainly due to weak tidal action. It is noticed that only a limited number of organisms developed in the waterbody because of the abnormal salinity of the waterbody. Based on the above factors, it can be seen that the organic matter enrichment capacity of the Dacaozi Formation was relatively poor. As for the sedimentary period during the Tanshanping Formation, it developed the reef deposit with rich reservoir performance. It developed closer to the sedimentary center. Due to the rich nutrients and clean water, there were a lot of organisms growing in the waterbody during the sedimentary period of the Tanshanping Formation.

According to the detailed analysis of the paleoredox conditions and further investigation of the multifaceted studies about relative sea level, paleoclimate, terrigenous input, and paleoproductivity during sedimentation, we have purposed the conceptual model illustrating the influences of the relative sea level variations, paleoredox condition, paleoproductivity condition, and paleoclimate condition on organic matter accumulation and preservation for the Tanshanping Formation and the Dacaozi Formation.

Detailed analysis of the paleoredox conditions and further investigation of the paleoproductivity forcing mechanisms operating during sedimentation indicate that the shales of the Dacaozi and Tanshanping Formations were deposited under the controlling of paleoredox conditions. During the deposition period of the Dacaozi Formation, which was deposited in the more warm-humid shallow water environments, we found that significant increases in the temperature and humidity led to more fresh water inputs and a high degree of chemical weathering [79–83]. The higher terrigenous inputs, promoting abundant planktons and better condition of organic matter accumulation, coincides with the higher level of penetration from sunlight. From the above factors, it is obvious to exhibit a higher paleoproductivity in the sedimentary waterbody of the Dacaozi Formation. However, the preservation condition of the organic matter in the Dacaozi Formation was poor, as often the relative sea level was so low that it tend to accumulate more oxygen. Specially, the higher terrigenous input diluted more organic matter, and the longer distance of transportation and lower deposition rate have accelerated the destruction of preservation conditions. As we can see in Figure 7(b), there were a few dead planktons left in the bottom water, in which their bodies were damaged to varying degrees because of the poor preservation condition. Due to the worse preservation conditions, the TOC concentrations of the Dacaozi Formation were lower. During our investigation of the mechanism of accumulation and preservation of organic matter in the Tanshanping Formation, the depositional model for organic-rich shale of the Tanshanping Formation has been discovered. Our previous work has summarized that the paleoproductivity during the sedimentary period of the Tanshanping Formation was lower than that of the Dacaozi Formation, which reflects the relative cold-dry climate and lower terrigenous input. As the relative sea level rise, increased water depth would decrease the mixing chance of surface oxygenated water into sediment-water interface, and increased sea level also trapped clastic flux inshore,

which reflects lower terrigenous input [84]. In addition, the range of the penetration from sunlight was relatively narrow, for the sea level was so high that it blocks sunlight from entering into the water. Nevertheless, it supports a reductive and stable bottom water because of the rise of the sea level (Figure 7(a)), showing reasonable agreement with the influence of the decrease of fresh water input which is attributed to the fall of terrigenous input. Moreover, the shorter distance of transportation of terrigenous detritus during the sedimentary period of the Tanshanping Formation enhances the preservation ability in the sedimentary center. As is shown in Figure 7(a), the number of plankton carcasses greatly increases due to the lack of oxygen in the waterbody or catastrophic events. Decomposition of these carcasses consumes large amounts of oxygen and form H_2S gas, which further ensures the anoxic condition of the bottom water [85]. It is worth noting that there are a large number of plankton carcasses in the bottom water, which were hardly destroyed by external forces because of the stable anoxic waterbody and the shorter distance of transportation of terrigenous detritus.

To sum up, the significance of establishing the accumulation and preservation model of organic matter lies in discussing the coupling interactions between the paleoproductive forces and paleoredox environment. Because of the unique features of the carbonate platform facies, the examples of the Dacaozi Formation and the Tanshanping Formation are used to illustrate: the TOC concentrations of the study shale member are not necessarily higher although the paleoproductivity is relatively high, and the TOC concentrations of the study shale is not necessarily lower although the paleoproductivity is relatively poor. The considerable fluctuations in the TOC concentrations are reasonably attributed to the redox environment of the Tanshanping and Dacaozi Formations, which determines the preservation conditions.

These findings highlight the importance of coupling between the paleoproductivity and redox environment in the more specific carbonate platforms in further research.

7. Conclusions

On the basis of our results from TOC concentrations, major, trace, and rare earth elemental fingerprints and comprehensive analyses on the special features of the carbonate platform facies in the Tanshanping and Dacaozi Formations, this current study provides a good opportunity for documenting the major controlling factors of the accumulation and preservation of organic matter and for revealing new insights into the response of the coupling interactions between the paleoproductivity and redox environment. The achievements are thus conducted to generate a comprehensive and specific depositional model for the carbonate platform facies as evident in the case of the Tanshanping and Dacaozi Formations, Ninglang-Yanyuan Basin, Southwest China, and the following conclusions have been drawn:

- (1) The variation trend of the content of major elements and TOC is similar to the study shales of the Tanshanping and Dacaozi Formations. Com-

pared to the Dacaozi Formation, the value of the trace elements (Ni/Co, V/Cr, and V/Sc) in our study confirms that the shale of the Tanshanping Formation was deposited in an reductive environment. As for the rare earth element, the shale members of the Middle Devonian Tanshanping and Dacaozi Formations are both enriched in LREE and depleted in HREE, with negative anomalies of Ce and Eu

- (2) Specially, the sedimentary position of the study area is different from the previous researches, which belongs to the carbonate platform facies. We have concluded that the main controlling factors are the paleoclimate, paleoproductivity, terrigenous input, and paleoredox conditions in the sedimentary waterbody. Aiming at the mechanism of accumulation and preservation of the carbonate platform, this paper takes the Tanshanping Formation and Dacaozi Formation as an excellent example and focuses on the analysis of the coupling interactions between the paleoproductivity and paleoredox environment. On the whole, these above features show its uniqueness, which deserved to be analyzed
- (3) Dacaozi organic-rich shales were deposited in the more warm-humid environments. In addition, the shallow waterbody made it easier for sunlight to penetrate the waterbody, which coincides with the relatively high paleoproductivity. However, the preservation condition of the organic matter was generally poor, as often the relative sea level was so shallow that it tend to accumulate more oxygen. Specially, the higher terrigenous input diluted more organic matter, leading to the destruction of preservation conditions. Due to the worse preservation conditions, the TOC concentrations of the Dacaozi Formation were lower. On the contrary, the paleoproductivity during the sedimentary period of the Tanshanping Formation was lower. Nevertheless, the higher sea level and the lower terrigenous input reduced input of fresh water and supported a reductive bottom waterbody. Through a combination of the above factors, the TOC concentrations of the Tanshanping Formation shale were relatively high
- (4) The significance of constructing the accumulation and preservation model of organic matter lies in discussing the coupling interactions between paleoproductive forces and redox environment. The examples of the Dacaozi and Tanshanping Formations are used to illustrate the following: the TOC concentrations of the study shale member are not necessarily higher although the paleoproductivity is relatively high. In the same way, the TOC concentrations of the study shale are not necessarily lower although the paleoproductivity is relatively poor. As a result, the preservation conditions have been the decisive factor in the accumulation and preservation model of organic matter of the carbonate platform

Data Availability

Some of the data are contained in a published source cited in the references. All the data in this article is accessible to the readers.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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