

Sedimentary environment and major controlling factors of organic matter-rich shale from the Wufeng-Longmaxi formation in eastern Sichuan Basin, China

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Abstract The major controlling factors of organic matter and its enrichment model of the black shale from the Wufeng-Longmaxi Formation were explored by investigating the vertical variation characteristics, as well as major element and trace element abundances in the Wuxi Bailu section. The results show that the sedimentary tectonic setting of the Wufeng-Longmaxi Formation in the north-east margin of the upper Yangtze platform is located on the active continental margin, which is a passive continental margin and continental island arc. The parent rock in the source area is mainly felsic volcanic rocks mixed with small amounts of sedimentary recycling materials. Due to increased plate activity and a drop in sea levels, terrigenous pyroclastic input increased. The palaeoclimate was semi-humid, and a robust dysoxic-reduction environment and a high level of palaeoproductivity, causing the formation of the organic-rich shale in the Wufeng Formation. At the base of the Longmaxi Formation, the sedimentary water body was affected by global transgression, showing a strong anoxic-reductive environment, and the paleoclimate was a warm and humid condition. The palaeoproductivity level was high, resulting in the formation of organic shale. Due to the sea level drop at the top of the Longmaxi Formation, the sedimentary water was in an oxic-reduced environment, but the input of terrigenous pyroclastic matter increased. Because the paleoclimate was warm and humid and the palaeoproductivity level was high, organic-rich shale was formed. The findings demonstrate that terrigenous clastic input circumstances, palaeoproductivity conditions, and paleoredox conditions had the greatest influence on the enrichment of organic matter in the Wufeng-Longmaxi

Formation. Thus, organic matter enrichment was controlled by multiple paleoenvironmental factors.

Keywords Wufeng-Longmaxi Formation, organic-rich shale, organic matter enrichment, depositional palaeoenvironment, eastern Sichuan Basin

1 Introduction

The Wufeng (WF)-Longmaxi (LMX) Formation marine shale in the eastern Sichuan Basin has a large sedimentary thickness, a high organic matter content, and a high porosity (Zou et al., 2010; Liang et al., 2012). Thus, it is regarded as the principal region for China's future shale gas discovery and development. An important indicator for assessing the potential for shale gas is the organic matter level. On the one hand, it impacts the shale's ability to produce hydrocarbons; on the other hand, it also significantly affects the size of the shale storage space (Borjigin et al., 2017). However, the studies on the primary controlling elements and enrichment types of organic matter in northeast Chongqing are rare.

The enrichment and accumulation of organic matter are impacted by numerous factors, primarily including input from the land source, paleoclimate, palaeoredox conditions, and palaeoproductivity (Liu et al., 2018; Liao et al., 2019; Shang et al., 2020; Bai et al., 2022; Wu et al., 2022). The preservation model and the productivity model are two organic matter accumulation models that can be categorized based on the factors that influence organic matter enrichment (Talbot, 1988; Carroll and Bohacs, 1999). The preservation model assumes that the sedimentary water environment mainly controls the organic material enrichment (Arthur et al., 1998), while

the productivity model identifies primary productivity as the primary fundamental regulating element of the enrichment of organic matter (Wignall and Newton, 2001). The convergence of these two models typically leads to the buildup of organic materials in sediments.

The enrichment degrees of oxidation-reduction sensitive elements V, U, Ni, and Co are significantly different under different oxidation-reduction conditions; thus, they can be used as indicators to measure the oxidation-reduction conditions of water bodies (Algeo and Li, 2020; Algeo and Liu, 2020). In general, Cu, Ba, Ni, and Zn are closely related to biological activities and can effectively indicate the palaeoproductivity level (Algeo and Maynard, 2004; Ding et al., 2022). Cu, Mn, and Cr are easily enriched in a humid environment, while Sr, Ba, and K are easily enriched in an arid environment; thus, they are widely used to measure palaeoclimate conditions (Ross and Bustin, 2009; Adegoke et al., 2015). Terrigenous detritus is the primary source of stable chemical elements like Al, Zr, and Ti, which are crucial geochemical indicators for a qualitative description of the flux variations of terrigenous detritus (Sugisaki et al., 1982; Murphy et al., 2000).

Many scholars have discussed the factors governing the richness of organic material in marine shale from the WF-LMX Formation through elemental geochemical analysis of marine shale in the Yangtze area (Wang et al., 2017; Chen et al., 2021; Wu, 2022), but there are regional variations in the WF-LMX Formation's marine shale's organic material enrichment factors. The amount of organic matter enriched in the WF-LMX Formation in the Changning-Qianjiang-Xiushan region is affected by many factors, such as palaeoproductivity, oxidation-reduction conditions, water restriction conditions, and regional tectonic activities (Wu, 2022). WF-LMX Formation enrichment with organic material in the Yichang region is primarily controlled by oxidation-reduction conditions, followed by palaeoproductivity, and paleoclimatic circumstances (Chen et al., 2021). To the best of our knowledge, the main factors controlling the buildup of organic matter in marine shale in the WF-LMX Forma-

tion in the eastern Sichuan Basin are still unclear.

Thus, the WF Formation-LMX Formation of the Bailu section in the eastern Sichuan Basin was selected as the main research object. Then, systematic elemental geochemical analyses, including major and trace elements, were carried out. The WF-LMX Formation's variation rules of vertical land source input, paleoclimate, palaeoredox conditions, and palaeoproductivity are clarified in conjunction with the change in total organic carbon (TOC) content. Additionally, the factors governing organic material enrichment and the mode of organic material enrichment of the WF-LMX Formation shale are discussed to provide a conceptual framework for shale gas development.

2 Geological setting

The study area is located in the northeastern Sichuan Basin. It is located in the high and steep fold belt of eastern Sichuan and is close to the Daba Mountain platform margin fold belt (Fig. 1(a)). During the period from Late Ordovician to Early Silurian, the study area was strongly influenced by Caledonian activity and the upper Yangtze Plate underwent compression and folding, which led to the continuous expansion of the central Sichuan uplift, forming the central Guizhou uplift, Xuefeng uplift, and Miao Ling uplift. However, in the middle and upper Yangtze regions, the large-scale distribution limitation-retention basin led to the development of a low energy, under-compensated, and dysoxic environment over a large area, and the WF-LMX Formation's black shale was formed.

There was a set of dark siliceous rock and siliceous mudstone strata in deep water. The Kunyinchiao Bed overlying the Ordovician/Silurian boundary was affected by global glaciation, and the sea level generally declined (Liu et al., 2019). A set of bioclastic marl, silty mudstone, fine sandstone of shallow water, and land shelf facies were deposited and developed. When the LMX Formation was being formed in the study region, due to global

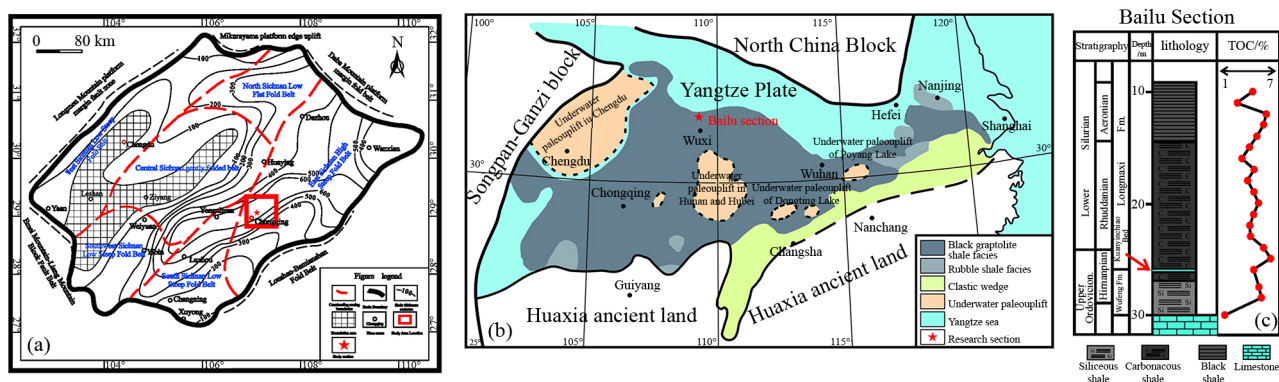


Fig. 1 (a) Geotectonic zoning of the Sichuan Basin and location of the study area; (b) early paleogeographic map and research profile of Silurian Dan Lu in southern China; (c) stratigraphic column of the Bailu section.

climate change, the sea level rose and fell in stages, and a group of dark gray carbonaceous mudstone and mudstone of deep-water shelf facies were deposited (Yan et al., 2019) (Figs. 1(b) and 1(c)).

3 Sample and analysis

3.1 Sample

Twenty representative samples were collected from the Bailu section and analyzed. The Bailu section (N31°37'14.6", E109°40'30.6") is located 500 m north of Bailu Town, Wuxi County, Chongqing, on the northeast edge of the upper Yangtze platform. The lithology of the section is relatively complete, and the stratum is nearly vertical owing to the influence of tectonism. Four samples were taken from the section's WF Formation, which is mostly black siliceous shale mixed with carbonaceous shale, and 16 samples, mostly of graptolite-rich black shale, from the LMX Formation.

3.2 Experimental method

Geochemical analysis, including TOC content and Element analysis, was carried out on the samples. Element analysis was performed at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. For whole rock major element analysis, the sample pretreatment was the melting method, and the major elements were analyzed using a Zsx Primus II wavelength dispersive X-ray fluorescence spectrometer. Trace element analysis was conducted on an Agilent 7700e ICP-MS. TOC measurements were conducted on an HCS-0A at Jiangsu Design Institute of Geology for Mineral Resources.

3.3 Data processing

The majority of the trace elements in sediments are made up of terrigenous debris and authigenic components, and only the authigenic components in sediments can reflect the evolution characteristics of the sedimentary environment in geological history. However, rock composition is complex and diverse, and there is some deviation in judging its enrichment only by the content of trace elements and standard shale. To eliminate terrigenous detrital components from having an impact on authigenic components, trace element concentration is usually standardized by using the Al element with relatively stable properties during diagenesis (Calvert and Pedersen, 1993). Briefly, the Post Archean Australian shale (PAAS) was used for standardized calculation, and the enrichment factor (EF) of elements was calculated as follows:

$$X - EF = (X/Al)_{\text{sample}} / (X/Al)_{\text{PAAS}}, \quad (1)$$

The EF of element X is represented by X -EF, the measured concentrations of elements X and Al in the examined samples are represented by $(X/Al)_{\text{sample}}$, and the X/Al ratio in PAAS is represented by $(X/Al)_{\text{PAAS}}$. X -EF greater than 1 means that some element is richer than the PAAS, while X -EF less than 1 means that an element is more deficient than the PAAS (Ding et al., 2018).

To assess palaeoproductivity more accurately, the Ba_{bio} content in sediments was also calculated (Casacci et al., 2016) utilizing the equation below:

$$Ba_{\text{bio}} = [Ba_{\text{sample}}] - [Al_{\text{sample}} \times (Ba/Al)_{\text{PAAS}}], \quad (2)$$

where Ba_{sample} is the measured content of element Ba in the samples under study, $(Ba/Al)_{\text{PAAS}}$ are the ratios of Ba/Al in Post Archean Australian shale (PAAS) and Ba_{bio} represents the Ba content produced by biological processes, and the estimated content in terrigenous debris is generally subtracted from the total amount in the sample.

4 Results

4.1 TOC

The WF-LMX Formation shale's TOC in the Bailu section changes with time. The TOC values of the WF and LMX Formation shale range 1.14 wt%–4.28 wt% (average 3.84 wt%) and 2.48 wt%–6.1 wt% (average 4.35 wt%), respectively. The results show that the total organic carbon content in Bailu section is higher than 2 wt%. Overall, the TOC values in the middle and upper WF Formation and the lower LMX Formation are the higher while that in the middle LMX Formation is lower, and the TOC values in LMX Formation changes greatly with time (Fig. 2).

4.2 Major element geochemistry

The main composition of marine mudstones and shales is SiO_2 , Al_2O_3 , and CaO (Ross and Bustin, 2009) (Table 1). SiO_2 is the most abundant mineral in all samples. The SiO_2 contents in the WF Formation, Kunyinchiao Bed, and LMX Formation are 80.55%–94.67% (average 85.93%), 86.78%, and 72.09%–87.79% (average 81.17%), respectively. The Al_2O_3 contents are 1.74%–6.83% (average 4.86%), 4.15% and 3.52%–10.70% (average 6.20%) in the WF Formation, Kunyinchiao Bed, and LMX Formation, respectively. The CaO contents are the least with 0.13%–0.23% (average 0.18%) in the WF Formation, 0.14% in the Kunyinchiao Bed, and 0.08%–0.34% (average 0.17%) in the LMX Formation. The sum of the three minerals ranges 82.89%–96.53% (average 88.23%). In addition to the three minerals with the

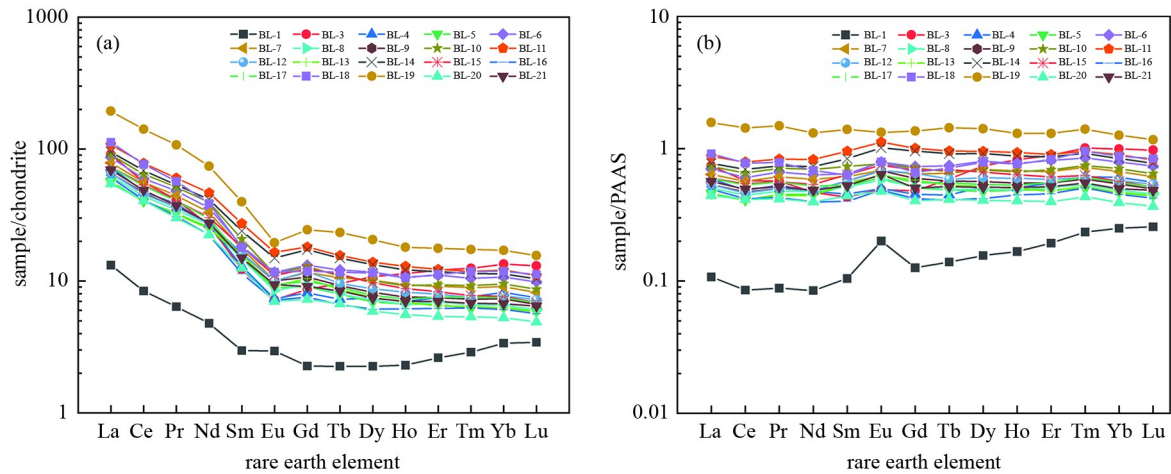


Fig. 2 (a) Normalized REE concentration of chondrites in Bailu section; (b) PAAS normalized REE concentration in Bailu section.

Table 1 Results of TOC analysis and major element content of shale samples from the Wufeng Formation-Longmaxi Formation in the Bailu section

Formation	Sample No.	TOC/%	SiO ₂ /%	TiO ₂ /%	Al ₂ O ₃ /%	TFe ₂ O ₃ /%	MnO/%	MgO/%	CaO/%	Na ₂ O/%	K ₂ O/%	P ₂ O ₃ /%	CIA ^a /%
Wufeng Formation	BL-1	1.14	94.67	0.07	1.74	0.73	0.005	0.20	0.13	0.13	0.44	0.02	66.52
	BL-3	5.1	80.55	0.43	6.83	1.10	0.001	0.54	0.18	0.75	1.73	0.06	67.46
	BL-4	4.82	82.58	0.33	6.01	1.24	0.001	0.47	0.23	0.50	1.74	0.07	67.16
	BL-5	4.28	86.78	0.22	4.15	0.61	0.001	0.36	0.14	0.36	1.18	0.05	67.38
	BL-6	6.1	76.75	0.35	6.77	1.58	0.005	0.46	0.08	0.75	1.86	0.05	67.26
Longmaxi Formation	BL-7	5.33	77.21	0.31	6.16	3.34	0.005	0.44	0.09	0.65	1.69	0.05	67.69
	BL-8	3.93	85.97	0.23	4.54	0.51	0.001	0.32	0.24	0.45	1.26	0.03	64.71
	BL-9	3.85	85.57	0.27	5.17	0.98	0.001	0.35	0.09	0.46	1.40	0.07	69.52
	BL-10	4.28	81.20	0.39	7.21	1.22	0.003	0.46	0.09	0.67	1.91	0.07	69.35
	BL-11	4.76	73.75	0.45	8.97	3.47	0.007	0.51	0.17	1.19	2.26	0.15	67.20
	BL-12	4.29	84.10	0.27	5.16	1.21	0.004	0.34	0.14	0.51	1.37	0.09	68.63
	BL-13	3.63	87.36	0.19	3.94	1.19	0.004	0.25	0.14	0.36	1.07	0.07	68.16
	BL-14	4.31	78.51	0.37	7.03	2.65	0.007	0.44	0.19	0.80	1.81	0.12	67.73
	BL-15	2.99	87.79	0.18	3.52	1.57	0.004	0.22	0.24	0.36	0.92	0.06	64.99
	BL-16	3.83	84.91	0.23	4.66	1.44	0.005	0.28	0.12	0.52	1.25	0.07	67.22
	BL-17	4.61	82.85	0.30	5.77	1.20	0.005	0.36	0.17	0.61	1.58	0.07	66.76
	BL-18	5.36	74.69	0.45	8.52	1.89	0.008	0.58	0.34	0.93	2.34	0.13	66.09
	BL-19	5.63	72.09	0.58	10.70	1.34	0.004	0.77	0.22	1.19	2.91	0.05	66.47
	BL-20	2.48	85.50	0.25	4.82	1.98	0.005	0.33	0.24	0.51	1.27	0.07	66.00
	BL-21	4.18	80.47	0.28	6.27	2.53	0.004	0.52	0.12	0.46	1.69	0.07	70.47

Note: a) CIA = mol[Al₂O₃/(Al₂O₃ + CaO* + Na₂O + K₂O)] × 100.

highest contents, there are also relatively high K₂O and TFe₂O₃ contents with averages of 1.58% and 1.59%, respectively. MgO, Na₂O, and TiO₂ contents are relatively low, 0.41%, 0.51%, and 0.31%, respectively.

4.3 Trace element geochemistry

Trace elements of marine mudstone and shale samples from the WF Formation to the LMX Formation in the

Bailu section were measured, and trace elements Co, V, Cr, Ga, Rb, Zr, Ba, Ni, U, Th, and Cu were tested. Results showed that the Ba and V contents are high, 912.95×10^{-6} to 3181.66×10^{-6} (average 2097.28×10^{-6}) and 53.46×10^{-6} to 709.2×10^{-6} (average 311.99×10^{-6}), respectively. The other trace element contents are relatively small: Cr contents are 15.58×10^{-6} to 67.22×10^{-6} (average 39.62×10^{-6}) and Ni contents are 22.96×10^{-6} to 122.08×10^{-6} (average 72.98×10^{-6}). The Th, U,

Co, and Ga contents are low: the U contents are 1.74×10^{-6} and 28.59×10^{-6} (average 15.73×10^{-6}), while the Th contents are 1.84×10^{-6} and 13.74×10^{-6} (average 7.61×10^{-6}).

4.4 Rare earth element (REE)

The chondrite-normalized REE concentrations show similar REE distribution curves of the shale samples in the Bailu section (Fig. 2(a)) and relatively rich light REE (LREE) (Table 2). Except for BL-1, which only slightly favors Anomaly in Eu ($\delta Eu = 1.14$), all other samples show negative Anomaly in Eu (δEu 0.63–0.80). The Ce content of mud shale samples from the WF Formation to LMX Formation are all close to 1, and there is no obvious abnormal trend ($\delta Ce = 0.90$ – 1.0 , average 0.95). The REEs standardized in the PAAS show that the REE concentration model standardized by PAAS is flatter than that standardized by chondrite, indicating that the enrichment degree of LREE and heavy REE (HREE) in the study sample is consistent with that of PAAS (Fig. 2(b)). The total REEs (ΣREE) of mud shale samples in the Bailu section are in the range of 25.40×10^{-6} to

312.69×10^{-6} (average 134.45×10^{-6}), slightly lower than that of the Upper Continental Crust, which was 146.40×10^{-6} (Taylor and McLennan, 1985). It is lower than that of the North American Shale Composite, which is 173.01×10^{-6} , and PAAS, which is 184.77×10^{-6} (Taylor and McLennan, 1985).

5 Discussion

5.1 Tectonic setting and provenance characteristics

The tectonic setting of the source area can affect the composition and properties of the sediment source and then control the input of provenance debris in the sedimentary basin, while the provenance characteristics of shale can control the source rock potential. Thus, it is crucial to examine the tectonic settings and provenance characteristics of the samples. REEs, transition elements (V, Cr, Co, Ni, etc.), and high field strength elements (Hf, Se, etc.) are strongly distinguished from other elements, and are preferentially enriched in sediments. During the transportation of detritus, they have strong stability and

Table 2 Rare earth elements (REE) abundances ($\mu\text{g/g}$) and relevant geochemical indexes of shale samples from the Wufeng-Longmaxi Formation in the Bailu section

Formation	Sample No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	$\Sigma REE^a)$	LREE/HREE	$\delta Ce^b)$	$\delta Eu^c)$
Wufeng Formation	BL-1	4.10	6.80	0.78	2.87	0.58	0.22	0.59	0.11	0.73	0.17	0.55	0.09	0.71	0.11	5.40	1.61	25.40	5.03	0.92	1.14
	BL-3	28.35	45.49	5.03	15.84	2.39	0.53	2.24	0.45	3.47	0.82	2.54	0.40	2.81	0.42	27.03	6.06	143.87	7.42	0.92	0.70
	BL-4	22.63	38.47	4.69	16.14	2.52	0.54	2.11	0.34	2.40	0.50	1.57	0.25	1.71	0.24	16.60	5.61	116.33	9.32	0.90	0.72
	BL-5	17.58	32.54	3.99	15.26	2.90	0.65	2.36	0.38	2.23	0.48	1.40	0.20	1.32	0.19	15.50	3.68	100.66	8.53	0.94	0.76
	Longmaxi Formation	BL-6	26.78	48.27	5.87	21.48	3.58	0.85	3.41	0.57	3.76	0.77	2.32	0.34	2.23	0.32	27.01	6.04	153.62	7.78	0.93
BL-7		24.40	45.22	5.42	19.89	3.42	0.74	3.00	0.50	3.26	0.67	1.91	0.29	1.89	0.26	22.04	5.48	138.40	8.40	0.95	0.71
BL-8		19.25	35.39	4.22	16.11	2.86	0.62	2.42	0.38	2.31	0.48	1.46	0.21	1.37	0.19	16.22	3.57	107.07	8.88	0.95	0.73
BL-9		20.37	37.52	4.40	16.39	3.16	0.74	2.77	0.44	2.64	0.54	1.57	0.24	1.53	0.21	18.28	4.64	115.44	8.31	0.95	0.76
BL-10		28.13	52.11	6.28	23.68	4.07	0.83	3.33	0.52	3.22	0.66	1.97	0.30	1.99	0.28	21.88	6.92	156.17	9.38	0.94	0.69
BL-11		33.43	63.10	7.36	28.02	5.32	1.21	4.69	0.74	4.47	0.93	2.57	0.38	2.53	0.35	29.10	8.09	192.30	8.31	0.97	0.74
BL-12		20.42	36.76	4.41	16.39	3.19	0.74	3.05	0.45	2.82	0.59	1.67	0.24	1.62	0.23	19.84	4.59	117.00	7.68	0.93	0.72
BL-13		17.10	32.50	3.90	15.01	3.08	0.67	2.70	0.41	2.42	0.50	1.36	0.21	1.31	0.19	15.80	3.35	100.49	7.95	0.96	0.71
BL-14		29.54	55.61	6.54	24.86	4.67	1.10	4.48	0.71	4.29	0.87	2.48	0.37	2.37	0.33	28.32	6.03	172.56	7.69	0.96	0.73
BL-15		22.77	43.22	4.96	18.17	3.54	0.81	3.20	0.53	3.12	0.63	1.74	0.25	1.59	0.22	20.40	2.81	127.97	8.27	0.98	0.74
BL-16		18.84	33.33	3.77	13.42	2.22	0.53	1.96	0.31	1.97	0.44	1.30	0.20	1.27	0.18	14.51	3.84	98.10	9.44	0.95	0.77
BL-17		22.67	42.46	4.95	17.73	2.93	0.69	2.57	0.43	2.51	0.52	1.58	0.24	1.56	0.22	17.92	4.45	123.43	9.49	0.96	0.77
BL-18		34.93	62.00	6.95	23.23	3.49	0.86	3.08	0.55	3.70	0.76	2.36	0.38	2.48	0.36	27.23	7.04	179.40	9.62	0.96	0.80
BL-19		60.18	114.10	13.15	44.45	7.77	1.43	6.33	1.11	6.63	1.29	3.72	0.56	3.57	0.50	40.61	7.29	312.69	10.17	0.98	0.63
BL-20		16.90	32.92	3.68	13.43	2.44	0.51	1.88	0.32	1.90	0.40	1.13	0.17	1.10	0.16	11.99	3.30	92.26	9.88	1.00	0.73
BL-21		21.58	39.41	4.54	16.49	2.92	0.69	2.36	0.40	2.39	0.50	1.47	0.22	1.40	0.21	15.59	5.67	115.83	9.56	0.96	0.80

Notes: a) $\Sigma REE = LREE + HREE$; $LREE = La + Ce + Pr + Nd + Sm + Eu$; $HREE = Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu$; b) $\delta Eu = \frac{Eu_N}{(Sm_N + Gd_N)^{\frac{1}{2}}}$; c) $\delta Ce = \frac{Ce_N}{(La_N \times Pr_N)^{\frac{1}{2}}}$; Subscripts N values present = chondrites normalized value.

are controlled by the rock composition of provenance, and the influence of diagenesis and alteration in the later stage is weak. Thus, indicators of crop source identification and structural background analysis are commonly used (McLennan, 1989; Cullers, 2000).

At the turn of Ordovician-Silurian, the North China Plate and the Yangtze Plate collided, and the northern margin of the Yangtze Plate was typically in the collision-convergence environment of the plate active edge or island arc (Wang et al., 2017), the Bailu section's outcrop is situated in the area where the Yangtze and North China Plates collide, on the northeast edge of the upper Yangtze Platform. It is obvious that the collision and joint between the Yangtze Plate and the North China Plate is the key factor in controlling the shale organic material accumulation in the WF-LMX Formation in the Bailu section. The tectonic setting was analyzed based on the discrimination diagram of K_2O/Na_2O versus SiO_2 ; the samples of the Bailu section all fall into the passive continental margin (Fig. 3(a)), but the major elements are easily disturbed by

weathering, transportation, and diagenesis, which makes the judgment index of major elements unreliable. However, trace elements and REEs have more obvious advantages in determining the tectonic setting. The most popularly used are the La/Sc-Ti/Zr, Th-Co-Zr/10, and La-Th-Sc diagrams (Bhatia, 1985), suggesting that the mudstone samples of the Bailu section mainly fall near the active continental margin and a few fall near the continental island arc and passive continental margin (Figs. 3(b) and 4).

The La/Th-Hf provenance discrimination results show that the shale samples of the Bailu section fall near the felsic/basic provenance-mixed area and a few samples fall in the felsic acid island arc source area and andesite island arc source area (Fig. 5(a)). The Co/Th-La/Sc and La/Yb-REE provenance discrimination results show that the mud shale samples of the Bailu section fall near the source area of felsic volcanic rocks and some samples of the LMX Formation are placed near the granite source area (Fig. 5(b)). The La/Yb- Σ REE discrimination

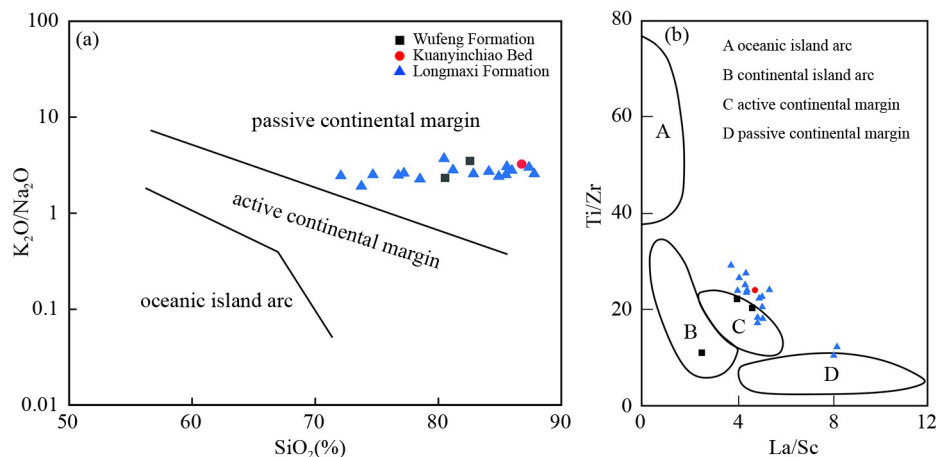


Fig. 3 Tectonic setting diagram for mud shale of WF-LMX Formation in eastern Sichuan Basin (after Bhatia, 1985; Roser and Korsch, 1988). (a) K_2O/Na_2O-SiO_2 ; (b) $La/Sc-Ti/Zr$.

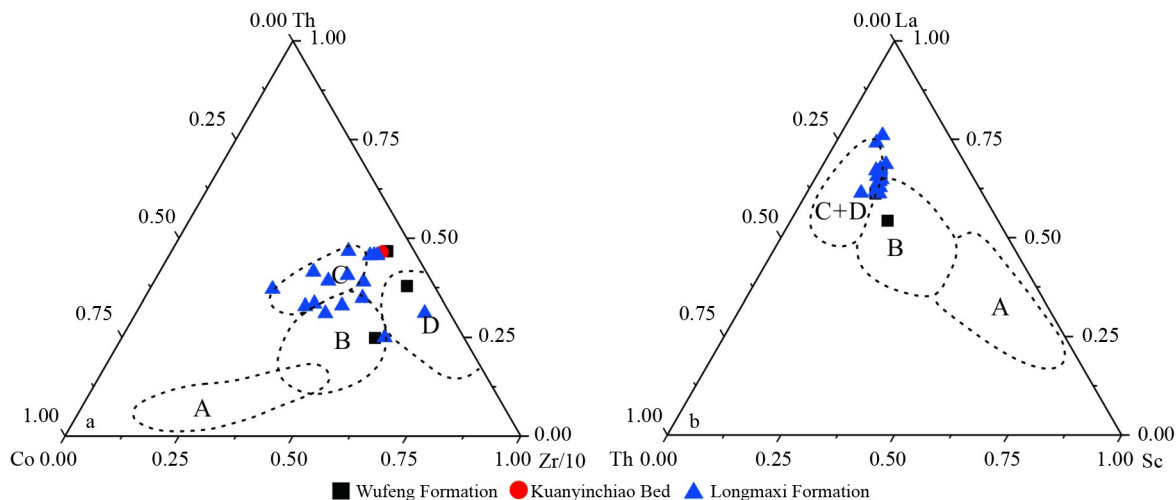


Fig. 4 Tectonic setting diagram for mud shale of WF-LMX Formation in eastern Sichuan Basin (Bhatia and Crook, 1986). (a) $Th-Co-Zr/10$; (b) $La-Th-Sc$; A-oceanic island arc; B-continental island arc; C-active continental margin; D-passive continental margin.

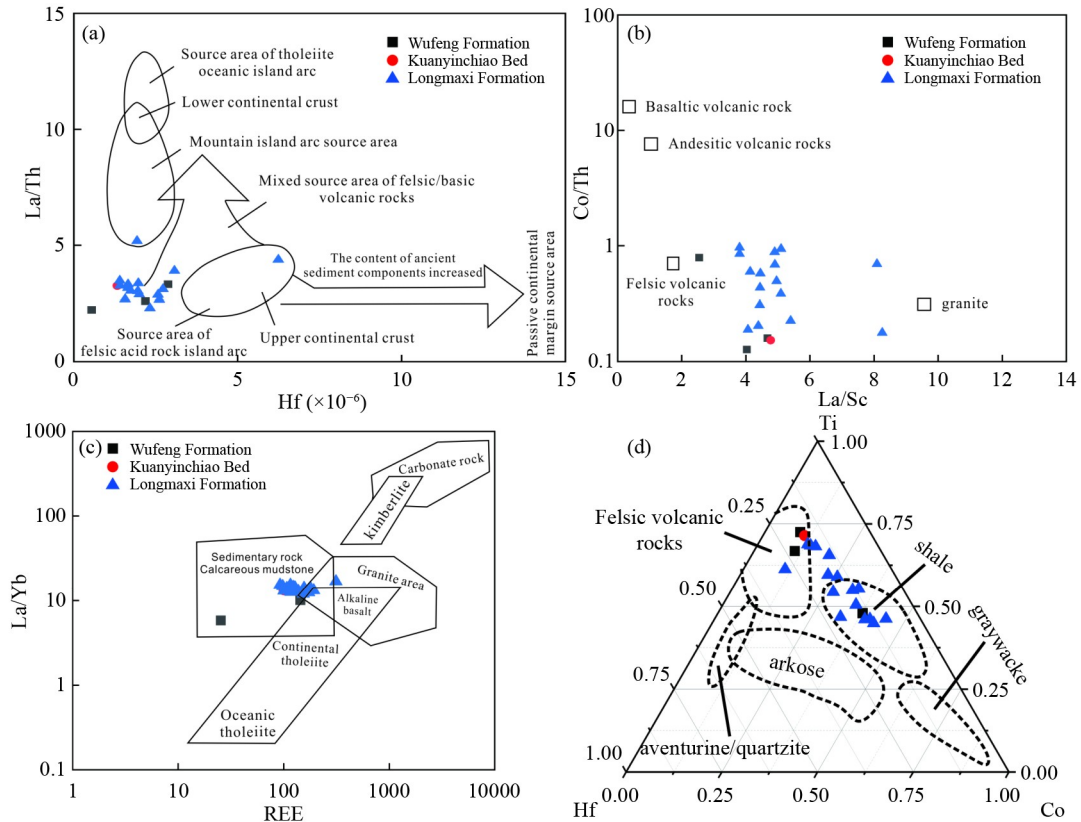


Fig. 5 Source and compositional discrimination for mud shale of WF-LMX Formation in eastern Sichuan Basin. (after Allègre and Minster, 1978; Floyd and Leveridge, 1987). (a) Hf versus La/Th diagram; (b) La/Sc vs. Co/Th diagram; (c) ΣREE vs. La/Yb diagram; (d) Th-Hf-Co discrimination.

diagram shows that LMX Formation samples fall near the source area of the calcareous mudstone of sedimentary rocks while the WF Formation samples and a small amount of LMX Formation samples fall into the overlapping source area of calcareous mudstone, granite, and alkaline basalt of sedimentary rocks (Fig. 5(c)). The Th-Hf-Co provenance discrimination results reveal that the WF Formation samples fall into the felsic volcanic source area and the LMX Formation samples fall near the shale source area (Fig. 5(d)).

The active continental margin reflected by the element geochemistry of the shale of the WF-LMX Formation in the Bailu section has the characteristics of a passive continental margin and continental island arc tectonic background. The weathering and denudation products formed by a set of intermediate-acid volcanic lava, pyroclastic rocks, and some sedimentary rocks formed by tectonic collision are the main body to provide terrigenous clastic components of mud shale of the WF-LMX Formation.

5.2 Paleoclimate

5.2.1 Terrigenous flux proxies

Al, Zr, Ti, and other elements have stable chemical pro-

erties and are less affected by weathering, transportation and diagenesis and are usually used to indicate the flux change of terrigenous debris (Murphy et al., 2000). Based on the vertical variation trend of Al, Zr, Ti, Y/Ho, and K₂O/Rb, similar vertical variation trends of the Al, Zr, and Ti in the WF Formation of the Bailu section. It shows that the input of terrigenous debris decreases first and then increases in the sedimentary stage of Wufeng Formation (Fig. 6). In the middle of the WF Formation the Al, Zr, and Ti contents increase in a thin interval, then decrease and reach the lowest in the upper portion of the WF Formation (Fig. 6). Moreover, the Y/Ho ratio of the mud shale samples of the WF Formation is close to that of PAAS (Y/Ho = 27), indicating that the sediments are greatly affected by the land-based input. The K₂O/Rb ratio gradually increased in the center portion of the WF Formation, indicating the deposition of numerous felsic pyroclastic rocks in the sedimentary basin in the later and middle stages of the WF Formation (Fig. 6). This may reflect that the collision between the Yangtze Plate and the North China Plate in the center portion of WF Formation resulted in increased terrigenous clastic content and then the sea level dropped, due to glaciation, which shifted the sedimentary basin away from the provenance area, decreasing the input of provenance detritus.

Y/Ho and K₂O/Rb ratios, as well as the vertical

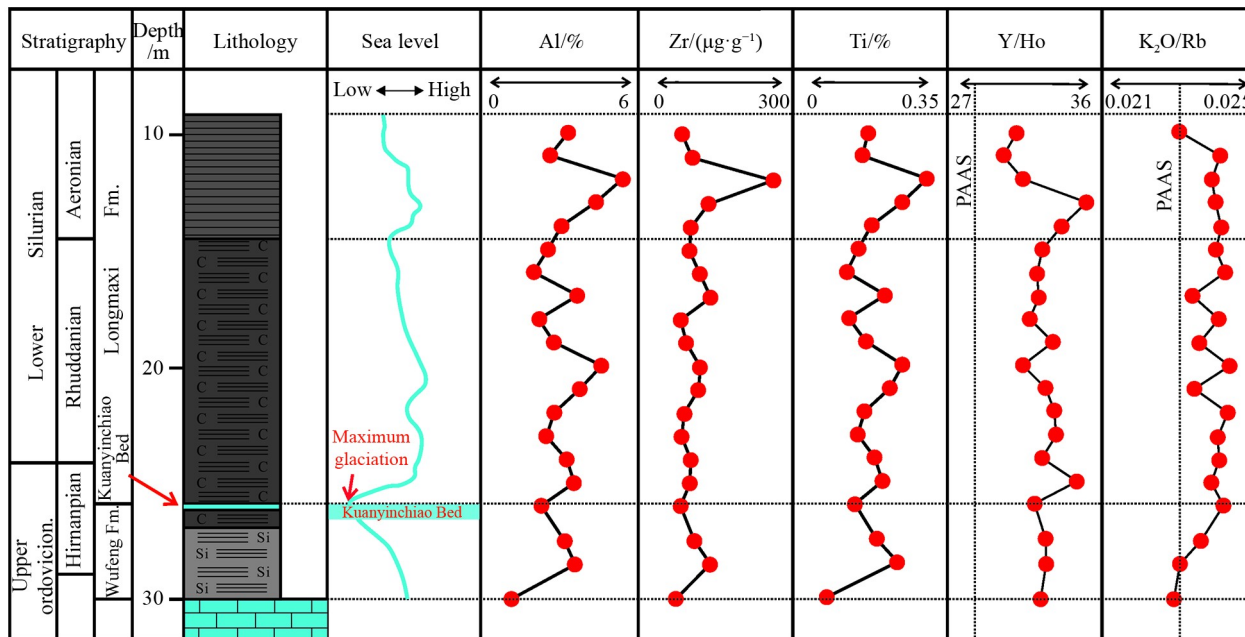


Fig. 6 Vertical variations of Al (%), Zr ($\mu\text{g/g}$), Ti (%), Y/Ho, and $\text{K}_2\text{O/Rb}$ of sediments in BL section.

variation trend of the Al, Zr, and Ti contents, at the base of the LMX Formation, the Al, Zr, and Ti contents, and the Y/Ho ratio are slightly increased but remain at low levels. In the middle of the LMX Formation, the Y/Ho ratio is increased and the Al, Zr, and Ti contents are increased and then decreased while in upper portion of the LMX Formation the Al, Zr, and Ti contents and Y/Ho ratio are increased rapidly (Fig. 6). The $\text{K}_2\text{O/Rb}$ ratio fluctuates in the middle of the LMX Formation, indicating that the provenance area at this stage is not only felsic pyroclastic but also disturbed by mixed sedimentary rocks. The $\text{K}_2\text{O/Rb}$ ratio in the upper part of the LMX Formation is increased, indicating deposition of a large amount of felsic pyroclastic rocks in the sedimentary basin at the late stage of the LMX Formation, which may reflect that the initial stages of the LMX Formation, the Yangtze plate further collided with the North China plate and the tectonic activity enhanced volcanic activity increasing the input of terrigenous clastic rocks. However, owing to the end of glaciation and the rapid rise of sea levels, the provenance region was located distant from the sedimentary basin; thus, the bottom of the LMX Formation maintained a low terrestrial input. After that, due to the further intensification of tectonic activity, in the early stage of the LMX Formation, the input of terrigenous detritus reached a high level (Fig. 6). However, in the middle of the LMX Formation sedimentary stage, tectonic activity was relatively calm, volcanic activity decreased, provenance debris mixed with a small amount of sedimentary recycling materials, and the input of terrigenous debris decreased. In the late sedimentary stage of the LMX Formation, tectonic activity intensified again, volcanic activity intensified, and the sea level dropped, which made the sedimentary

basin close to the provenance area and increased the input of terrigenous debris (Fig. 6).

5.2.2 Paleoclimate

Paleoclimatic change is the main factor affecting the depositional environment, and the warm and humid climate is a favorable factor for the formation of organic matter. Studying the changes in paleoclimatic conditions can provide a basis for organic matter enrichment. Fe, Mn, Cr, V, Ni, and Co are enriched in humid climate, while Ca, Mg, K, Na, Sr, and Ba are enriched in dry climate. The palaeoclimate index C ($\sum(\text{Fe} + \text{Mn} + \text{Cr} + \text{V} + \text{Ni} + \text{Co})/\sum(\text{Ca} + \text{Mg} + \text{K} + \text{Na} + \text{Sr} + \text{Ba})$) indicate the change in palaeoclimate conditions from hot and dry to warm and humid (Cao et al., 2012), with C values less than 0.2 referring to arid climate conditions, C values in the range of 0.2–0.6 referring to semi-arid and semi-humid climatic conditions and C values greater than 0.6 referring to humid climatic conditions. The Sr/Cu proportion is a sensitive indication of palaeoclimate, with values above 10 indicating a dry and hot climate and Sr/Cu ratios of 1–10 reflecting warm and humid climatic conditions (Cao et al., 2012).

To reconstruct paleoclimates, the chemical index of alteration (CIA) is frequently used. A high CIA value represents strong chemical weathering and alteration intensity, thus indicating that the climate is hot and humid (Bai et al., 2015). C , Sr/Cu, and CIA have been used in this work to characterize the paleoclimate characteristics in the sedimentary period.

The C and Sr/Cu values of the WF Formation shale in the Bailu section are 0.26–0.68 (average 0.32) and 0.51–10.34 (average 3.81), respectively, indicating that

the whole WF Formation was in a semi-arid-semi-humid and humid climate during the sedimentary period. Moreover, in the deposition stage of the Kuyinchiao Bed, the *C* value reached the valley value, and the Sr/Cu reached the peak value, indicating that the deposition stage of the Guanyin Bridge was under arid climate conditions (Fig. 7). Also, the CIA of WF Formation shale is between 66.5% and 67.5%, indicating that the WF Formation is in a medium chemical weathering condition in the sedimentary stage (Fig. 7).

The LMX Formation's shale has *C* values that range from 0.21 to 1.0 (average 0.53), demonstrating that the LMX Formation's sedimentary stage is located in a warm, humid climate that is both semi-arid and semi-humid. The Sr/Cu values are in the range of 0.67–4.78 (average 1.87), indicating that the sedimentary stage is also in a warm and humid climate. Also, the CIA values of the LMX Formation samples are in the range of 64.7%–70.4% (average 67.4), indicating that the LMX Formation was located in a warm, humid environment with modest chemical weathering. Based on the *C* and Sr/Cu vertical variation chart, the palaeoclimate conditions fluctuated during the deposition period of the LMX Formation. In the early stage of the LMX Formation, *C* and Sr/Cu changed in a wide range in a relatively small interval and the climate fluctuated between drought and

humidity (Fig. 7), which may be related to the change between cooler and warmer conditions caused by the Hernandez Ice Age events. In the middle of the deposition stage of the LMX Formation the climate was hotter and wetter, but in the middle and late deposition stage of LMX Formation the climate conditions gradually changed from humid to semi-arid to semi-humid. These changes occurred over a long time interval, which may be related to the large-scale regressive movement of the Early Silurian and Late LMX Formation (Fig. 7).

5.2.3 Palaeoredox conditions

V, U, Ni, and Co are redox-sensitive trace elements (RSTEs) that easily dissolve in seawater under oxidation conditions but easily precipitate into sediments under reduction conditions, which can effectively indicate and restore redox conditions of sedimentary water bodies (Tribouillard et al., 2006). Moreover, REE Ce exists in the form of Ce⁴⁺ ions in an oxidizing environment, which is not easily adsorbed by clay minerals and organic matter, but in a reducing environment, it is easily enriched in sediments, while other REEs do not have this characteristic. The redox environment of water areas is frequently determined using Ce/La and other rare earth indicators (Berry and Wilde, 1978). This study uses

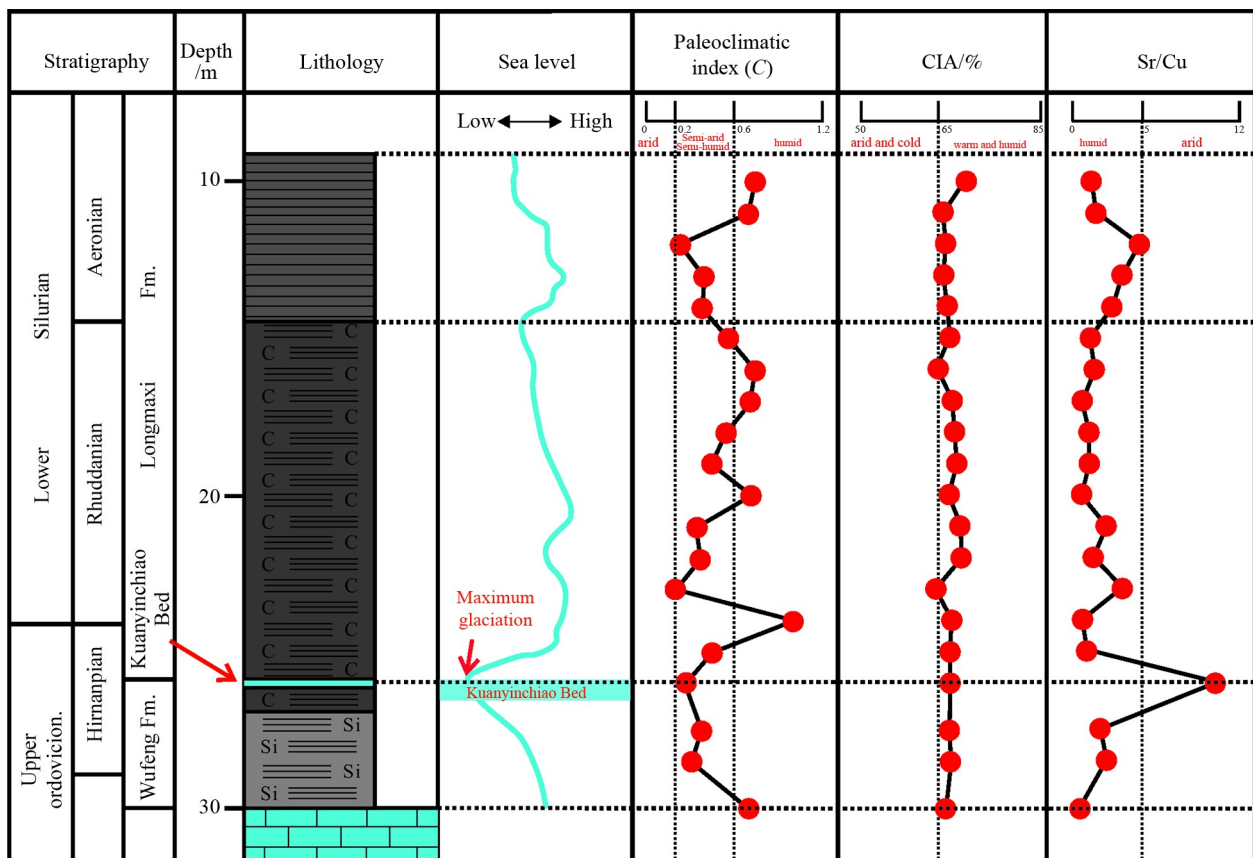


Fig. 7 Vertical variations of paleoclimate index “C”, chemical alteration index “CIA”, and Sr/Cu of sediments in BL section.

V/(V + Ni), U/Th, Ni/Co, V/Cr, and Ce/La to reconstruct the redox conditions surrounding the deposition of the WF-LMX Formation. Prior research has established the reference standard of the ratio of redox-sensitive elements to distinguish oxic, dysoxic, and anoxic grades (Lewan and Maynard, 1982; Hatch and Leventhal, 1992; Tribouillard et al., 2006) (Table 3).

Before judging the redox state of the sedimentary environment RSTE data reliability should be evaluated first to determine whether RSTE data has been influenced hydrothermally. The RSTE data have been evaluated by the Al-Fe-Mn triangle diagram (Zhang et al., 2019), which ruled out the possibility of RSTE data being affected by the hydrothermal influence (Fig. 8).

The V/(V + Ni), U/Th, Ni/Co, V/Cr, and Ce/La of the WF Formation in the Bailu section have averages of 0.83, 1.66, 60.73, 5.55, and 1.70, respectively. There are some differences in the reactions of various redox indexes. The vertical trend diagram of U/Th, Ni/Co, and Ce/La shows that the bottom-to-top ratio of the WF Formation gradually increases, indicating that the degree of anoxia is

gradually strengthened at this stage. U/Th and Ce/La reflect that the sedimentary environment has changed from a dysoxic state to an anoxic state, reflecting that the water body's oxidation is weakened and its reduction is enhanced; V/(V + Ni) and V/Cr show that the sedimentary water is always in an anoxic environment. The palaeoredox indicators all show that the sedimentary water was in a strong anoxic-reduction environment at the deposition stage of the Kunyinchiao Bed. In the deposition stage of the WF Formation the sedimentary water was in a dysoxic and anoxic palaeoredox environment (Fig. 9). Moreover, the cross-plot of palaeoredox substitutes supports this conclusion (Figs. 10(a) and 10(b)). The reason may be that the anaerobic degree of the sedimentary water of the WF Formation continues to deepen under the combined influence of Gondwana continental glaciation and plate activity. In the early deposition stage of the WF Formation the sea level decreased gradually owing to glaciation and the oxygen content of seawater increased in the early stage. After that, with the intensification of tectonic activity, a large amount of pyroclastic materials poured into sedimentary water, increasing the nutrient content in the sedimentary water body, and numerous plankton multiplied, which made the degree of anoxia in the sedimentary water body continuously intensified (Fig. 9).

The V/(V + Ni), U/Th, Ni/Co, V/Cr, and Ce/La ratios of the LMX Formation have average values of 0.78, 2.16, 23.28, 7.74, and 1.85, respectively. The vertical variation diagram of the oxidation-reduction index is consistent. In the sedimentary stage of the middle and lower LMX Formation, it was always in the condition of anoxic-reductive sedimentary water. In the upper portion of

Table 3 Criteria for judging redox conditions of the WF-LMX Formation in eastern Sichuan Basin

Element index	Oxygen-deficient environment		Oxic
	Anoxic	Dysoxic	
V/Cr	> 4.25	2.00–4.25	< 2.00
V/(V + Ni)	> 0.60	0.46–0.60	< 0.46
Ni/Co	> 7.00	5.00–7.00	< 5.00
U/Th	> 1.25	0.75–1.25	< 0.75
Ce/La	> 1.8	1.5–1.8	< 1.5

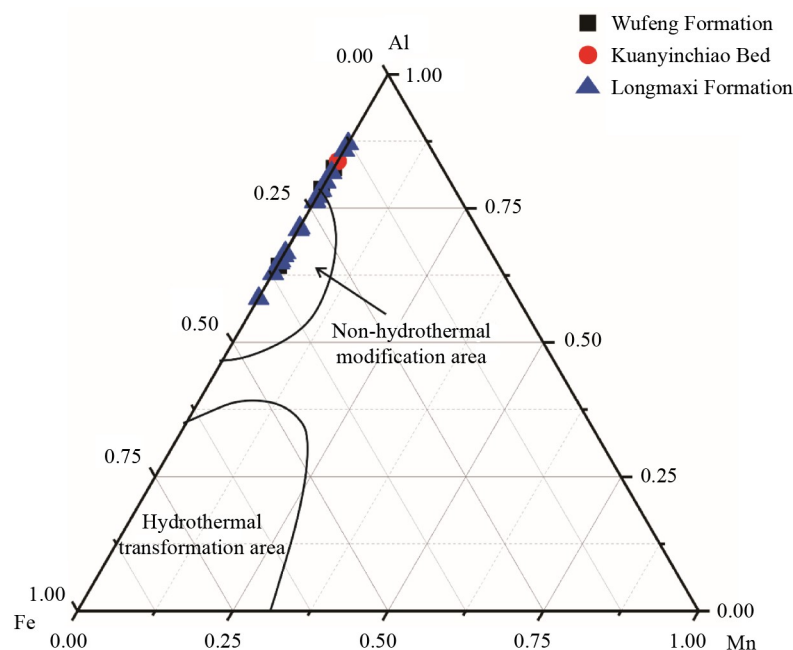


Fig. 8 Al-Fe-Mn triangle map (the plate was revised according to Zhang et al., 2019).

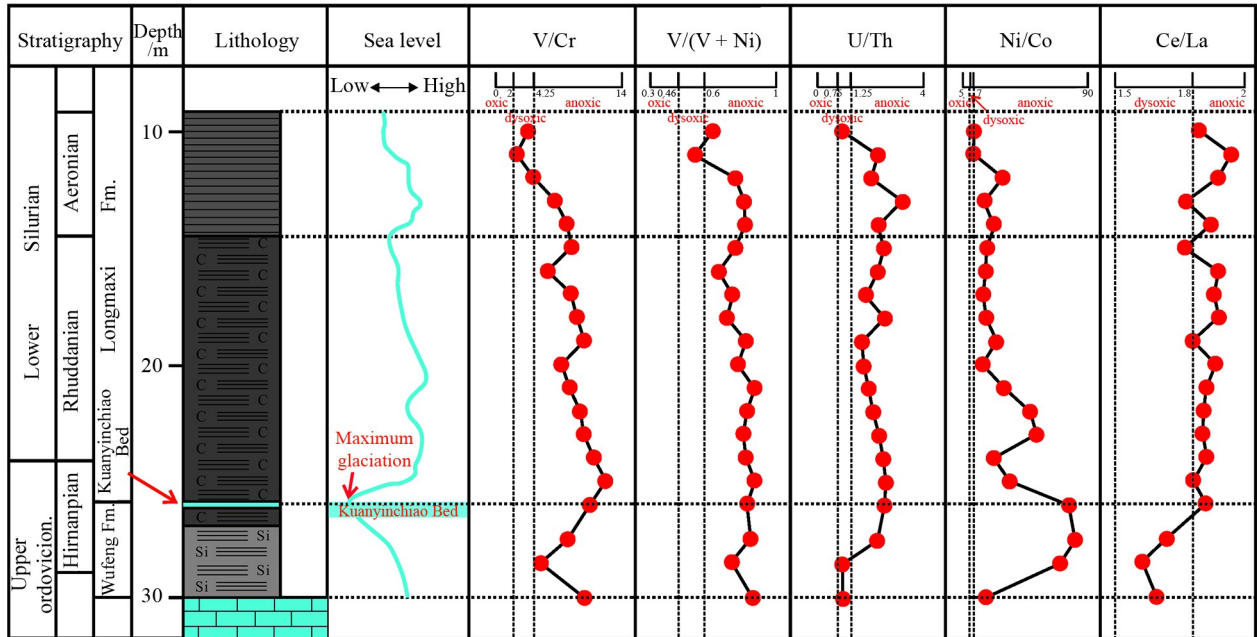


Fig. 9 Vertical variations of V/(V + Ni), U/Th, Ni /Co, V /Cr, and Ce/La of sediments in BL section.

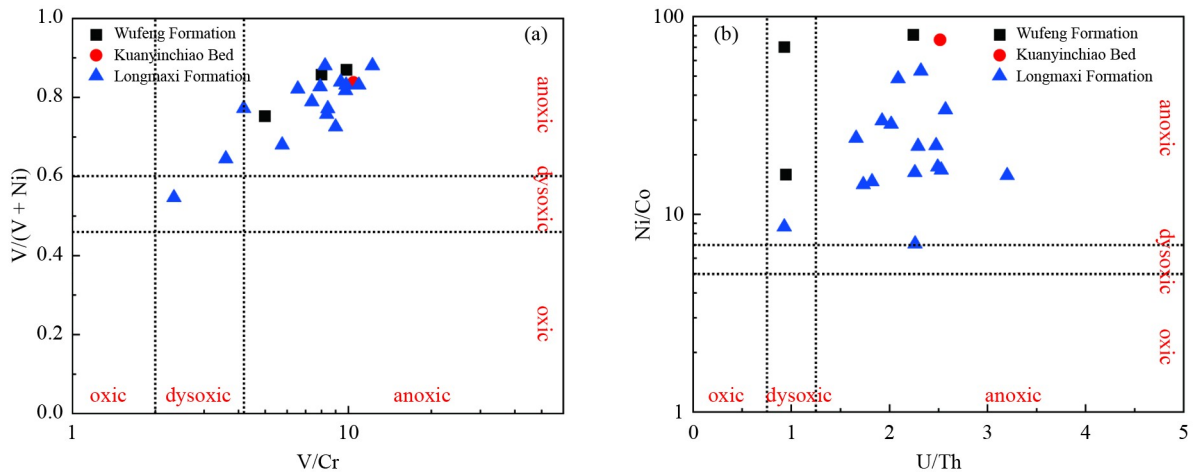


Fig. 10 Crossplots of paleoredox indicators for different systems tracts of the WF-LMX Formations in Bailu section. (a) V/Cr vs. V/(V + Ni); (b) U/Th vs. Ni/Co.

LMX Formation, the ratio of palaeoredox indicators showed a decreasing trend and the sedimentary water environment changed from an anoxic environment to a dysoxic environment (Fig. 9). The cross diagram of ancient redox substitutes showed that the LMX Formation samples are in an anoxic environment as a whole and a few samples are in a dysoxic environment (Fig. 10). It is speculated that the degree of oxidation-reduction in sedimentary water is jointly controlled by tectonic activity and sea level. In the LMX Formation's early sedimentary period, due to the end of glaciation and the increasing sea level, the sedimentary basin formed a stable stratified water column, and the sedimentary water was in an anoxic-reducing environment. With the weakening of tectonic activity and the decrease in sea levels, the oxygen content of the sedimentary water body

rose but the whole body was still in an anaerobic environment. In the late sedimentary stage of the LMX Formation, the stable stratified water column was broken owing to the sea-level drop. The ratio of palaeoredox indicators all showed a decreasing trend and vertically showed an evolution from an anaerobic environment to an anaerobic environment (Fig. 9). This is consistent with the previous conclusion that the shale sedimentary water of the LMX Formation in the Yangtze Plate is in a dysoxic environment and the oxidation of water increases along the longitudinal direction (Wu, 2022).

5.2.4 Palaeo-oceanic productivity

Palaeo-oceanic productivity is the process by which organisms produce and accumulate organic substances

from the external environment through life activities, providing the material basis for organic enrichment. Various geochemical elements are used to characterize the paleo-oceanic primary productivity (Tribouillard et al., 2006; Shen et al., 2015).

The Ba_{bio} content has been widely used as a palaeoproductivity proxy in shale sediments. Nutrient elements Ni, Cu, and Zn are also used to effectively evaluate the ancient productivity, which are closely related to biological activities (Tribouillard et al., 2006). These elements were normalized by Al to eliminate the influence of terrigenous detritus input, and their ratios were widely used as palaeoproductivity indicators (Yuan et al., 2020).

In the deposition stage of the WF Formation the Ba_{bio} content showed an upward trend, while in the deposition stage of Kuanynchiao Bed, Ba_{bio} content decreased. Previous studies have suggested a biogenic barium content of approximately 1000–5000 ppm ($\times 10^{-6}$) in the modern equatorial Pacific Ocean waters. The Ba_{bio} content of WF Formation shale is 1533.54 ppm on average. It shows that WF Formation had high palaeo-

productivity during the deposition period (Fig. 11). However, the changing trend of Ni/Al shows that it has always maintained a certain palaeoproductivity level in the deposition stage of WF Formation (Fig. 11). Ba_{bio} content and Ni/Al show a high level of palaeoproductivity, which may be because the organic matter deposition center of the Bailu section is close to the collision junction area between Yangtze Plate and North China Plate. Moreover, in the middle deposition period of the WF Formation, the Yangtze Plate and the North China Plate began to collide and join, and the sea level gradually decreased. Semi-humid paleoclimate conditions transport a large amount of volcanic ash and terrigenous pyroclastic to the ocean, providing abundant nutrients for the surface waters of the ocean. It promotes the growth of primary producers, thus improving the palaeo-oceanic primary productivity.

In the LMX Formation's stage of deposition, the Ba_{bio} content in the middle (average 1995.24 $\mu\text{g/g}$) and lower (average 1782.69 ppm) part of the LMX Formation is relatively stable, and in the upper portion (average 1995.24 $\mu\text{g/g}$) of the LMX Formation is increasing. The

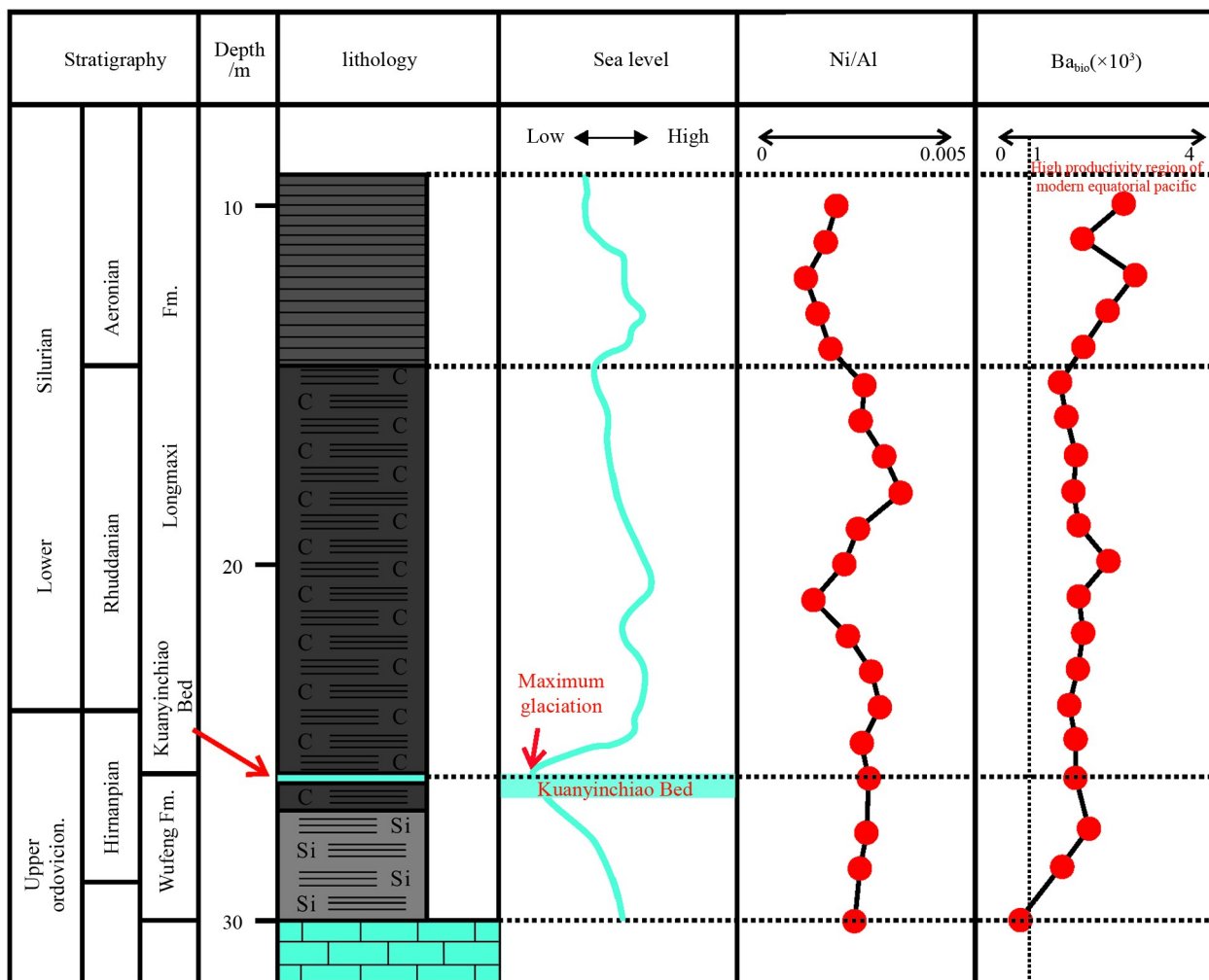


Fig. 11 Vertical variations of Ba_{bio} and Ni/Al of sediments in BL section.

sedimentary water body representing the LMX Formation has a high productivity level, and the palaeoproductivity level of the LMX Formation gradually rises vertically. Ni/Al ratios increased during the beginning of the LMX Formation, which may be due to the end of glaciation and the abundant nutrients provided by large-scale transgression (Fig. 11). With the warm and humid paleoclimate conditions the early palaeoproductivity of the LMX Formation was improved (Yan et al., 2019). From the early sedimentary stage to the middle sedimentary stage of the LMX Formation a descending interval appeared, which may be related to the intensification of tectonic movement at that time. The strong volcanic activity worsened the nature of seawater, and after some creatures could not adapt to it and died on a large scale, the level of ancient productivity declined slightly. The palaeoproductivity level was rising rapidly. The reason may be that tectonic activity is in the intermittent stage. Moreover, with the decline in sea levels, the sedimentary basin was close to the source area and numerous terrigenous pyroclastic materials entered the ocean with runoff, providing nutrients for the prosperity of marine palaeontology, resulting in a great increase in palaeoproductivity.

5.2.5 Upwelling impact

Upwelling environments at continental margins can impact organic matter enrichment in the ocean. The upwelling current can bring nutrients and organic matter from the bottom of the ocean to the surface of the ocean. Therefore, it can promote the growth and reproduction of marine surface paleontology and increase the ocean's primary productivity. Metallic elements (Mn and Co) exhibit different geochemical behaviors in water environments (restricted and upwelling). Therefore, it is often used to indicate the characteristics of the marine water environment (Lan and Shen, 2022). Previous studies used

Al-Co × Mn and Al-Co-EF × Mn-EF plates to identify the sedimentary water environment (Sweere et al., 2016; Lan and Shen, 2022). The plate shows that when Co × Mn < 0.4 and Co-EF × Mn-EF < 0.5 deposited water environment is in an open/upwelling current environment (Fig. 12).

The Co × Mn values of the mud shale samples of the Wufeng Formation in the Bailu section range from 0.0006 to 0.0056 (average 0.002), and the Co-EF × Mn-EF is between 0.0041 and 0.338 (average 0.352). It shows that the sedimentary basin is in an open / rising ocean current with strong water flow (Fig. 13). The Co × Mn value of the Longmaxi Formation shale is between 0.001 and 0.0056 (average 0.045), and the Co-EF × Mn-EF is between 0.007 and 0.19 (average 0.085), which also indicates that the sedimentary basin is in open/upwelling ocean currents. Moreover, the value of Co-EF × Mn-EF decreases, which indicates that the ocean current in the sedimentary stage of the Longmaxi Formation is enhanced (Fig. 13). In the sedimentary stage of the Wufeng-Longmaxi Formation, the rising ocean current has been active. This leads to a large amount of nutrients at the bottom of the deep sea to the ocean's surface water. Thus, it promotes the reproduction of marine paleontology. The ancient ocean in the sedimentary stage has been at a high level of paleoproductivity, proving this point. It is speculated that the seafloor hydrothermal fluid was upwelling due to the collision between the Yangtze Plate and the North China Plate. Therefore, it triggers a strong upwelling. The large amount of volcanic debris in the shale also proves volcanic hydrothermal activity on the seabed.

Since Mo was missing from the trace element test, the combined Co × Mn and Cd/Mo plates could not discriminate the main control factors of organic matter enrichment in the sedimentary environment (Shang et al., 2020). However, the analysis shows that the upwelling current has an important influence on marine paleoproductivity.

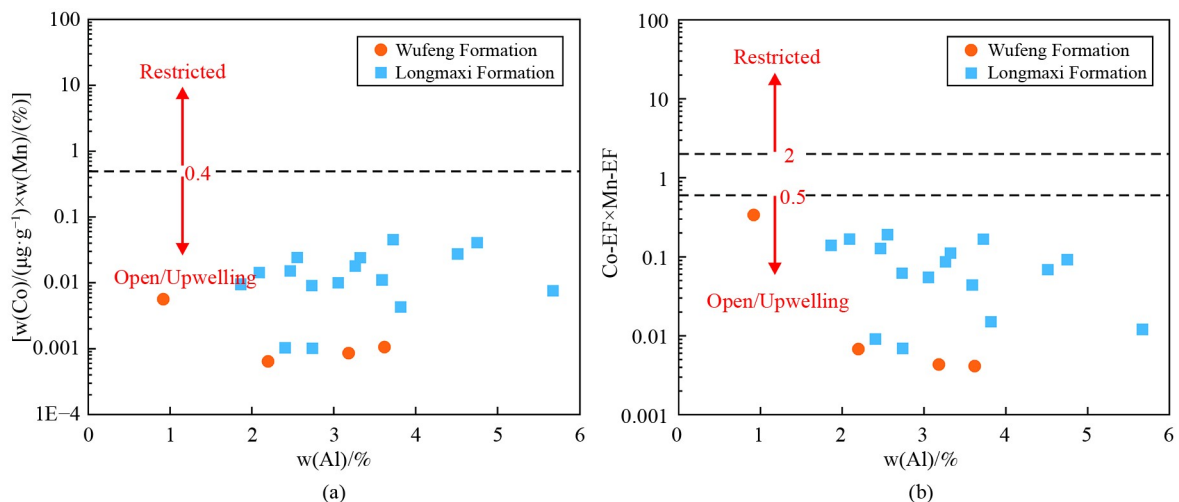


Fig. 12 (a) Co × Mn vs. Al. (b) Co-EF × Mn-EF vs. Al; The patterns of Co × Mn-Al and Co_{EF} × Mn_{EF} - Al are modified from (Sweere et al. 2016).

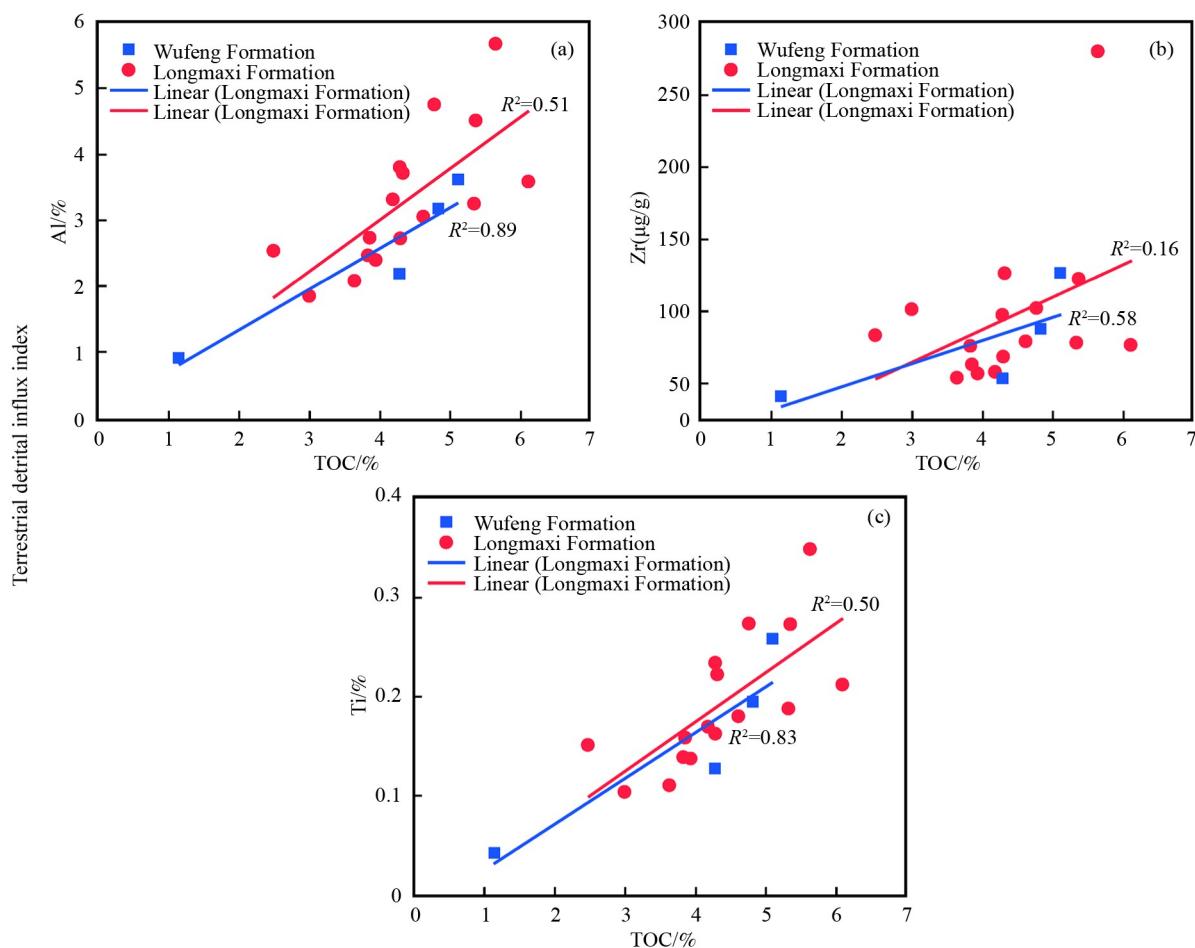


Fig. 13 Cross plots of TOC vs. clastic influx index of the shale samples from the WF-LMX Formations in Bailu section.

5.3 Controls of the sedimentary environment on the OM enrichment

The change in organic matter content in various stages of shale deposition in the WF-LMX Formation is the result of coupling control of many factors. The organic matter content is the final result of the superposition of positive and negative effects, corresponding to the main control factors. The main controlling factors of organic matter enrichment in the Bailu section were investigated by linear correlation analysis and gray correlation analysis between palaeoenvironmental conditions (Terrigenous flux proxies, Paleoclimate, Palaeoredox conditions, and Palaeo-oceanic productivity) and TOC content.

5.3.1 Analysis of the impact of single deposition environmental factors

1) Terrestrial debris input is an important factor controlling organic matter enrichment. The TOC content of the WF Formation shale and the concentrations of Al, Ti, and Zr show a strong positive association (R^2 : 0.89, 0.83, and 0.58, respectively). In the LMX Formation shale, there is a substantial positive association between TOC and the

Al, Ti, and Zr concentrations ($R^2 = 0.51, 0.50, \text{ and } 0.16$, respectively) (Fig. 13). It can be inferred that the input of detrital materials is an important factor to controlling accumulation of organic matter in the WF-LMX Formation shale deposits in the Bailu section. Moreover, the input of terrigenous detrital materials has double promotion effects on the accumulation of organic matter in shale. On the one hand, the mixed deposition of fine-grained minerals and organic matter in terrigenous detritus can physically protect organic matter through adsorption and promote the burial and preservation of organic matter (Zeng et al., 2015). On the other hand, terrigenous clastic parent rocks are mainly felsic volcanic rocks and materials are rich in nutritional elements, which promotes the rapid prosperity of marine surface producers, improves marine productivity, and produces a great amount of organic matter.

2) Paleoclimate is an important factor in controlling the degree of weathering of rocks and the prosperity of paleontology. Warm and humid climatic conditions promote the growth of organisms and is conducive to enriching organic matter (Chen et al., 2020). In this study, the paleoclimate index C , CIA, and TOC content are shown in scatter diagrams (Fig. 11). The diagram of CIA

and TOC content shows that the abundance of organic matter decreases with the increase of climate drought (Fig. 11). The rest of the illustrations do not display this relationship (Figs. 11(a) and 11(b)). A large amount of terrigenous volcanoclastic material is hypothesized to flow into sedimentary basins. It leads to deviations in the content of some paleoclimatic elements (e.g., Cu, Fe, Zn, etc.) (Yuan et al., 2020). In short, it shows that organic matter enrichment is not controlled by a single paleoenvironmental condition but by other factors.

In the black shale samples of the WF Formation in the Bailu section, the correlation coefficient R^2 between TOC content and paleoclimate indicators CIA is 0.89, showing a strong correlation (Fig. 14). It can be inferred that the organic matter enrichment of the WF Formation in the Bailu section is very dependent on the paleoclimate conditions at that time. The correlation coefficient's R^2 between TOC content and palaeoclimatic indicators CIA in the black shale samples of the LMX Formation is 0.01, far less than 1, indicating that paleoclimatic circumstances were not the primary determining factor of the organic material accumulation in the LMX Formation (Fig. 14).

3) Paleo-redox conditions as one of the key factors

controlling organic matter enrichment (Wang et al., 2022). Correlation analysis has been performed between the ancient redox indexes V/(V + Ni), U/Th, Ni/Co, and V/Cr and the TOC of the black shale in the WF Formation of the Bailu section. The correlation coefficient's R^2 of TOC content with V/(V + Ni), U/Th, Ni/Co, and V/Cr are 0.36, 0.18, 0.92, and 0.33, respectively (Fig. 15). In addition to the high correlation with Ni/Co, in the WF Formation of the Bailu profile, other indicators have a low correlation with TOC, indicating that this component may have the effect of redox environment, but it is not the dominant factor. The correlation coefficients' R^2 of TOC content with V/(V + Ni), U/Th, Ni/Co, and V/Cr in the black shale samples of the LMX Formation in the Bailu section are 0.45, 0.03, 0.04, and 0.16, respectively (Fig. 15). Except for a certain correlation between TOC and V/(V + Ni), other indicators show poor correlation, indicating that the redox conditions of sedimentary water have not significantly affected the organic matter accumulation of the LMX Formation.

4) Paleoproductivity condition is another key factor in the enrichment of organic matter in hydrocarbon source rocks (Xu et al., 2022). According to the black shale samples of the Wufeng Formation in the Bailu section,

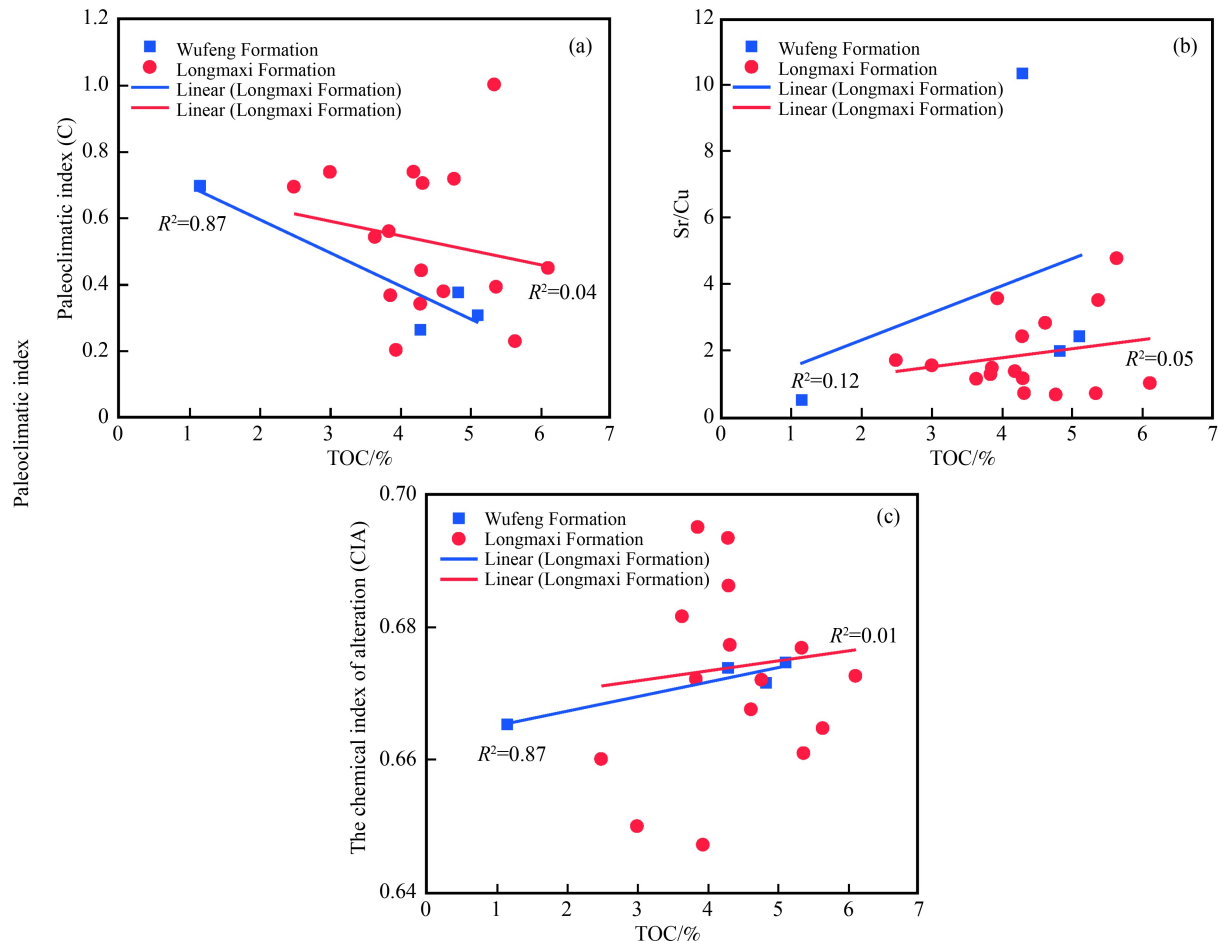


Fig. 14 Crossplots of TOC vs. paleoclimatic index of the shale samples from the WF-LMX Formations in Bailu section.

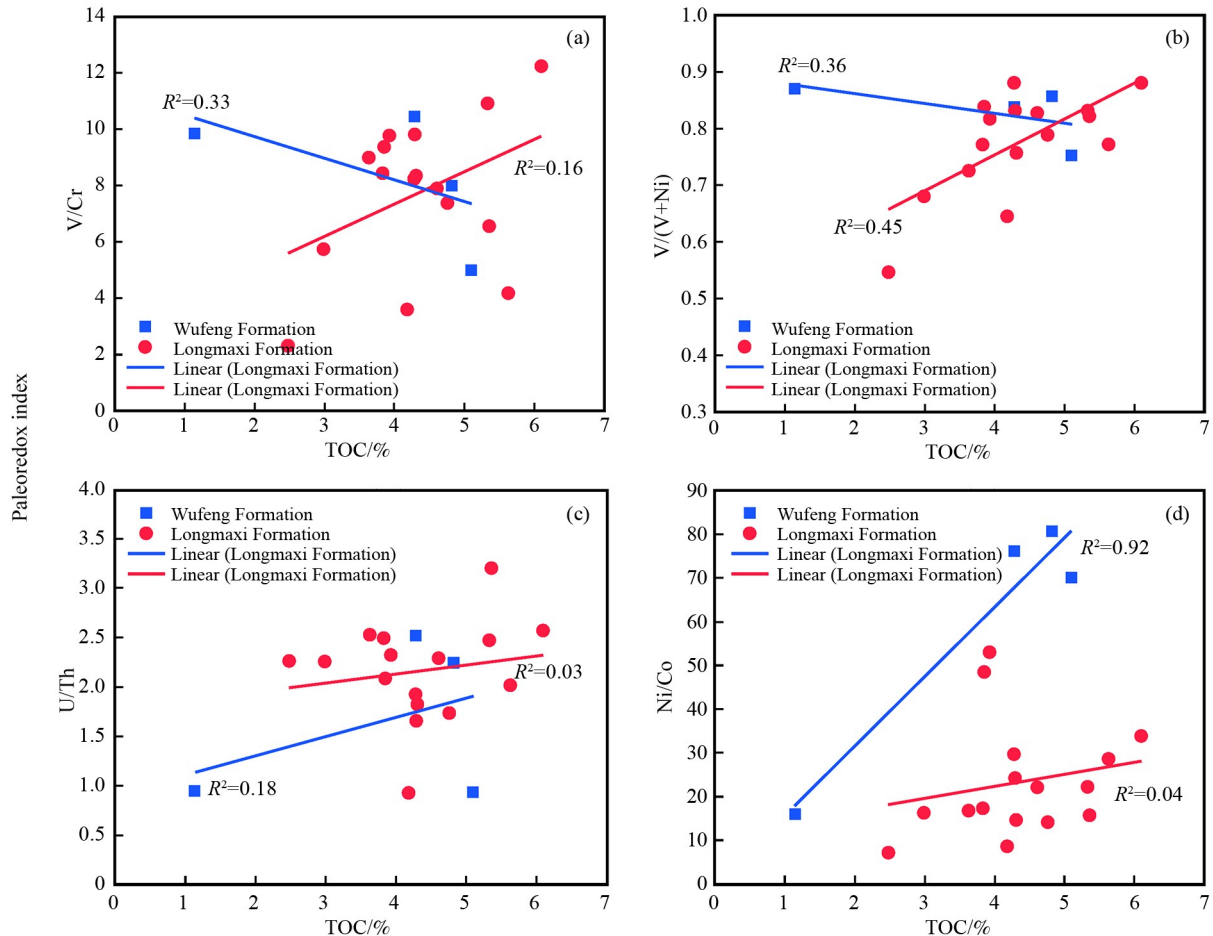


Fig. 15 Crossplots of TOC vs. paleo redox index of the shale samples from the WF-LMX Formations in the Bailu section.

TOC content is positively correlated with Ni/Al and Ba_{bio} content and its correlation coefficients' R^2 were 0.51 and 0.80. This shows that primary productivity is one of the related control factors of organic matter enrichment in the Wufeng Formation (Fig. 16). According to the black shale samples of the Longmaxi Formation in the Bailu section, TOC content is weakly negatively correlated with Ni/Al and weakly positively correlated with Ba_{bio} content. The correlation coefficients' R^2 were 0.03 and 0.14, respectively, with a weak correlation. It is speculated that this is due to the change of terrigenous debris input which leads to a decrease of marine autochthonous productivity. Therefore, the influence of paleoproductivity conditions on the enrichment of organic matter in Longmaxi Formation shale is limited (Fig. 16).

5.3.2 Multivariate statistical analysis of organic matter enrichment control factors

The principle of gray relational analysis is to determine the geometric similarity between the reference sequence (TOC content) and several comparative data columns (palaeoenvironmental parameters). Thus, it reflects the degree of correlation between curves. The gray

correlation method can be used to explore the correlation between organic matter content and paleoenvironmental factors. The influence of paleoenvironmental factors on TOC content can be evaluated by comparing the gray correlation degree of each paleoenvironmental factor. For more details on the basic steps of gray correlation analysis, please see (Yin et al., 2019).

The gray correlation degree between environmental factors and TOC content was calculated. The gray correlation degree of Wufeng Formation shale in the Bailu section from high to low is Paleoredox (Ni/Co) > Detrital flux (Al%) > Paleoproductivity (Ba_{bio}) > Paleoclimate (CIA). The gray correlation degree between paleo redox index, terrigenous debris input, paleoproductivity, and TOC content is greater than 0.9 (Fig. 17(a)). It shows that the enrichment of organic matter in the study area is mainly controlled by the paleo-redox index, terrigenous debris input, and paleoproductivity conditions. It is similar to the results of the above single environmental factor study. The gray correlation degree between the paleoclimate index and TOC is 0.809. It shows that the paleoclimatic conditions have limited control over the enrichment of organic matter in the Wufeng Formation in the study area.

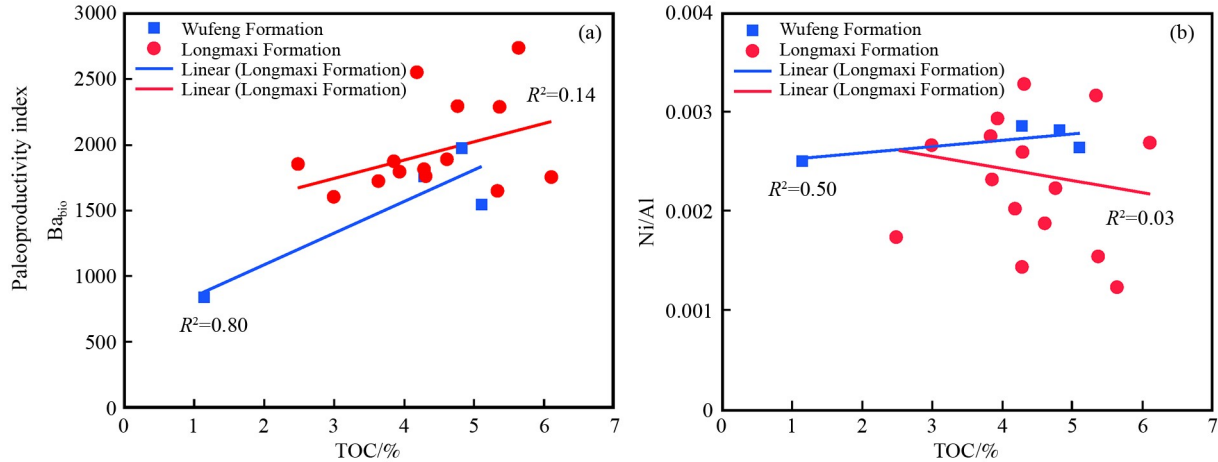


Fig. 16 Crossplots of TOC vs. paleoproductivity index of the shale samples from the WF-LMX Formations in Bailu section.

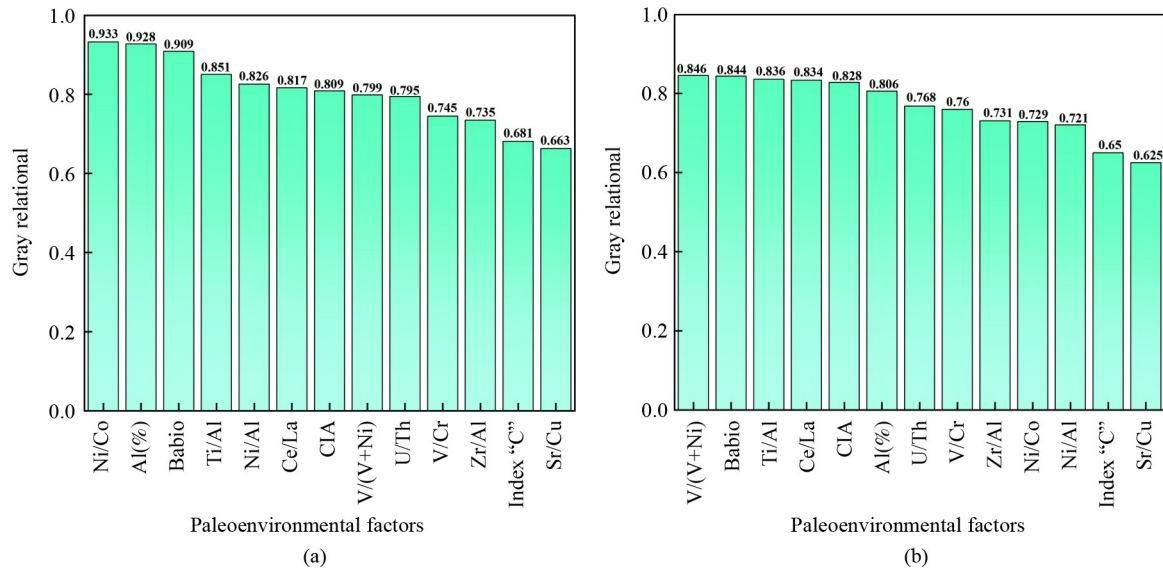


Fig. 17 Paleoenvironmental factors and gray correlation for shale samples from the WF-LMX Formations in the Bailu section. (a) Wufeng Formation samples; (b) Longmaxi Formation samples.

The gray correlation of each environmental factor in Longmaxi Formation shale is Paleoredox (V/V + Ni) > Paleoproductivity (Ba_{bio}) > Detrital flux (Ti/Al) > paleoclimate (CIA) from high to low. The gray correlation degree between the paleo-redox index, paleoproductivity index, and the TOC content is similar. It shows that paleo-redox conditions and paleoproductivity conditions have a great influence on the enrichment of organic matter in Longmaxi shale in the study area. Followed by terrigenous debris input conditions. The gray correlation degree between the paleoclimate index and TOC content is the lowest. It shows that the ancient climate conditions have little effect on the enrichment of organic matter in the study area (Fig. 17(b)).

The above studies show that the enrichment of organic matter in the Wufeng Formation shale of the Bailu section is controlled by terrigenous debris input, paleoproductivity, and paleo-redox conditions. In the sedimentary

stage of the Longmaxi Formation, paleo-redox conditions, paleoproductivity, and terrestrial debris input conditions are the main factors controlling the enrichment of organic matter. In summary, the enrichment of organic matter in the Wufeng-Longmaxi Formation shale of the Bailu section in north-eastern Sichuan is not controlled by a single paleoenvironmental factor, it is the result of the superposition of many factors.

5.4 Organic matter accumulation model

The organic matter enrichment model of the Wufeng-Longmaxi Formation in the eastern Sichuan Basin is discussed based on the four environmental parameters of terrigenous debris input change trend, paleoclimatic characteristics, palaeoredox environment, and palaeoproductivity conditions analyzed above, combined with the tectonic evolution characteristics, upwelling current

characteristics, and previous views.

During the Katian stage, owing to the influence of Guangxi tectonic movement, the uplifts of central Guizhou, central Sichuan, and Xuefeng have risen successively and the passive continental margin of the northern margin of the Yangtze Plate is in the development stage of shrinking and filling (Ji et al., 1990). The upper Yangtze region is transformed into a barrier basin, and the water circulation of the basin is weakened (Fig. 18(a)). In the middle and late Katian period, tectonic activity have intensified and volcanic activity occurred frequently, resulting in masses of felsic volcanic debris. Tectonic activities lead to frequent changes in terrigenous debris supply. A large number of

pyroclastic materials have entered the surface water body, providing nutrients for the reproduction of plankton such as graptolite. Moreover, during this period, the whole area was under semi-wet-semi-arid climatic conditions and the upwelling currents acted intensively, which promoted plankton blooms, thus making the primary productivity of the ocean higher. Furthermore, the proliferation of numerous plankton makes the oxygen content of the sedimentary water drop rapidly, forming a dysoxic-reduction water body environment. With the passage of time, the oxygen content of the sedimentary water body decreases continuously, forming an anoxic-reductive water body environment. Therefore, strong tectonic activity, climatic conditions suitable for biolo-

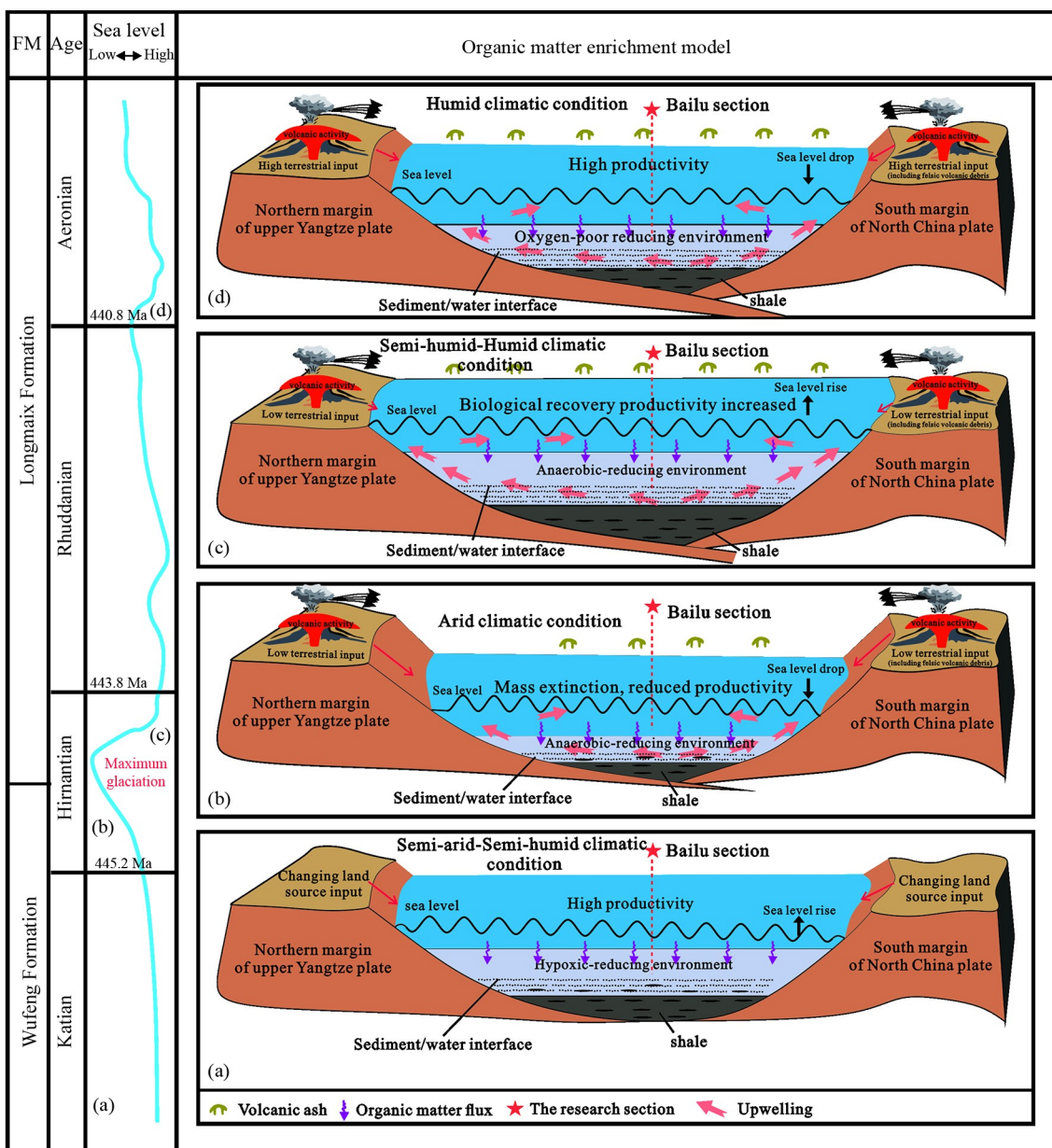


Fig. 18 Organic matter enrichment model of WF-LMX organic-rich shales in eastern Sichuan Basin. the data of sea-level are from Liu et al., (2019).

gical growth, dysoxic-reductive water environment, a large amount of pyroclastic input, and strong palaeoproductivity conditions form high-quality source rocks in the Katian stage.

During the collision between the Yangtze and North China Plates, the tectonic movement in this area was more intense in the mid-Hirnantian period. There is frequent volcanic activity, and a large amount of volcanic terrigenous detrital material pours into the ocean. However, due to the Gondwana continental glacier, it reached its peak. The global sea level decreased significantly, which caused the sedimentary basin to be far away from the continental denudation area. The supply of terrestrial pyroclastic decreases. Additionally, tectonic activity weakened the water circulation of the sedimentary basin again and glaciation reduces the oxygen content at the bottom of seawater, forming an anoxic-reduction water environment. Owing to the influence of glaciation a mass extinction event occurred and the primary productivity of the ocean declined. It resulted in the formation of a set of thin calcareous marl and silty mudstone with wide distribution in the middle and late periods of the Hirnantian stage, corresponding to the Kunyinchiao Bed (Fig. 18(b)).

At the end of the Hirnantian Stage, the subduction of the Yangtze Plate resulted in the formation of abundant volcanic clastic bodies in the North China Plate. The global sea levels rose rapidly and upwelling currents were strengthened due to the melting of Gondwana's glaciers. Marine transgression occurred again in the upper Yangtze area, shifting the sedimentary basin far away from the provenance, and the input of terrestrial pyroclastic decreased. In this period the sedimentary environment as a whole was in a semi-humid climate conditions, the organisms gradually recovered, rich nutrients were provided by the upwelling currents, and the abundance of large-scale marine microorganisms stimulated the increase in marine productivity. Moreover, due to the rapid rise of sea levels, the sedimentary basin formed a stable stratified water column. Additionally, a large number of biological remains decomposed, further consuming the oxygen content of the deposited water, rendering the sedimentary water body in an anoxic-reducing environment. Therefore, there is low terrigenous pyroclastic input, but the warm and humid climate environment, high marine primary productivity, and anoxic-reductive sedimentary environment prompted the formation of a set of organic-rich shale in the late Hernandez stage (Fig. 18(c)).

During the end of the Rhuddanian era, the Yangtze Plate was further subducted to the North China Plate, and water circulation in the sedimentary basin was weakened again. In the upper Yangtze region, the sea level drops. With increasing oxygen content in surface water, the anoxic environment of the sedimentary water body was destroyed and an oxic environment appeared. The regres-

sion makes the sedimentary basin close to the source area, and a large number of felsic pyroclastic rocks were deposited in the sedimentary basin, which provided nutrients for the prosperity of marine life. Additionally, the climate was warm and humid in this period, increasing the primary productivity of the ocean. Despite the fact that organic matter cannot be preserved in oxic sedimentary water, high marine primary productivity conditions and a significant contribution of volcanic terrigenous detritus input are beneficial to organic matter enrichment. Thus, in the Rhuddanian stage's late deposition, a group of organic-rich shale was subsequently produced (Fig. 18(d)).

6 Conclusions

1) The black shale deposition period of the WF Formation-LMX Formation in the Bailu Section. The source area of sediment parent rock is mainly felsic volcanic rock source area, with a mixed small amount of deposited recycled materials. The sedimentary background is located on the active continental margin, which has the characteristics of a passive continental margin and continental island arc.

2) The organic matter of the Wufeng Formation in the Bailu section is mainly controlled by terrestrial debris input, paleoproductivity, and paleo-redox conditions. The enrichment of organic matter in the Longmaxi Formation is mainly controlled by paleo-redox conditions, paleoproductivity, and terrigenous debris input conditions. In conclusion, the enrichment of organic matter in the Wufeng-Longmaxi Formation shale of the Bailu section in north-eastern Sichuan is not controlled by a single paleoenvironmental factor, it is the result of multiple factors.

3) During the Katian stage numerous volcanic detritus entered the sedimentary basin. The sedimentary basin developed an anoxic-reductive water environment. The whole sedimentary period was in a warm and humid climate. High primary productivity conditions form a set of high-quality source rocks in the Katian stage.

4) During the middle Hirnantian stage, tectonic activity intensified and the sea level dropped. The terrigenous detritus content decreased and the sedimentary basin developed an anoxic-reductive water environment. Gondwana glaciation caused the mass extinction of organisms, resulting in the decrease of ancient productivity, and the development of calcareous marl and silty mudstone in the middle Hirnantian stage. During the late Hirnantian stage, the glaciation ended, the climate was warm and humid, and the primary productivity of the ocean increased. The sedimentary basin formed an anoxic-reductive water environment, and the input of volcanic land sources decreased, forming a set of shale rich in organic matter.

5) In the late Rhuddanian stage, the whole sedimentary period was in a warm and humid climate. With increasing oxygen content in the water body, the sedimentary basin formed an oxic water environment. Moreover, with decreasing sea levels, the basin approached the provenance area, the input of volcanic terrigenous detritus increased and the primary productivity of the ocean increased, leading to the development of a set of organic shale in north-east Chongqing.

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References

- Adegoke A K, Abdullah W H, Hakimi M H, Yandoka B M S (2015). Geochemical characterisation and organic matter enrichment of Upper Cretaceous Gongila shales from Chad (Bornu) Basin, northeastern Nigeria: bioproductivity versus anoxia conditions. *J Petrol Sci Eng*, 135: 73–87
- Algeo T J, Li C (2020). Redox classification and calibration of redox thresholds in sedimentary systems. *Geochim Cosmochim Acta*, 287: 8–26
- Algeo T J, Liu J S (2020). A re-assessment of elemental proxies for paleoredox analysis. *Chem Geol*, 540: 119549
- Algeo T J, Maynard J B (2004). Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem Geol*, 206(3–4): 289–318
- Allègre C J, Minster J F (1978). Quantitative models of trace element behavior in magmatic process. *Earth Planet Sci Lett*, 38(1): 1–25
- Arthur M A, Dean W E, Laarkamp K (1998). Organic carbon accumulation and preservation in surface sediments on the Peru margin. *Chem Geol*, 152(3–4): 273–286
- Bai J K, Zhang S H, Liu C Y, Jia L B, Luo K Y, Jiang T, Peng H (2022). Mineralogy and geochemistry of the Middle Permian Pingdiquan Formation black shales on the eastern margin of the Junggar Basin, north-west China: implications for palaeoenvironmental and organic matter accumulation analyses. *Geol J*, 57(5): 1989–2006
- Bai Y Y, Liu Z J, Sun P C, Liu R, Hu X F, Zhao H Q, Xu Y B (2015). Rare earth and major element geochemistry of Eocene fine-grained sediments in oil shale- and coal-bearing layers of the Meihe Basin, northeast China. *J Asian Earth Sci*, 97: 89–101
- Berry W B N, Wilde P (1978). Progressive ventilation of the oceans: an explanation for the distribution of the Lower Paleozoic black shales. *Am J Sci*, 278(3): 257–275
- Bhatia M R (1985). Rare earth element geochemistry of Australian Paleozoic graywackes and mudrocks: provenance and tectonic control. *Sediment Geol*, 45(1–2): 97–113
- Bhatia M R, Crook K A W (1986). Trace element characteristics of graywackes and tectonic setting discrimination of sedimentary basins. *Contrib Mineral Petrol*, 92(2): 181–193
- Borjigin T, Shen B J, Yu L J, Yang Y F, Zhang W T, Tao C, Xi B B, Zhang Q Z, Bao F, Qin J Z (2017). Mechanisms of shale gas generation and accumulation in the Ordovician Wufeng–Longmaxi Formation, Sichuan Basin, SW China. *Pet Explor Dev*, 44(1): 69–78
- Calvert S E, Pedersen T F (1993). Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record. *Mar Geol*, 113(1–2): 67–88
- Cao J, Wu M, Chen Y, Hu K, Bian L Z, Wang L G, Zhang Y (2012). Trace and rare earth element geochemistry of Jurassic mudstones in the northern Qaidam Basin, northwest China. *Geochemistry*, 72(3): 245–252
- Carroll A R, Bohacs K M (1999). Stratigraphic classification of ancient lakes: balancing tectonic and climatic controls. *Geology*, 27(2): 99–102
- Casacci M, Bertinelli A, Algeo T J, Rigo M (2016). Carbonate-to-biosilica transition at the Norian–Rhaetian boundary controlled by rift-related subsidence in the western Tethyan Lagonegro Basin (southern Italy). *Palaeogeogr Palaeoclimatol Palaeoecol*, 456: 21–36
- Chen L, Jiang S, Chen P, Chen X H, Zhang B M, Zhang G T, Lin W B, Lu Y C (2021). Relative sea-level changes and organic matter enrichment in the Upper Ordovician–Lower Silurian Wufeng–Longmaxi Formations in the Central Yangtze area, China. *Mar Pet Geol*, 124: 104809
- Chen Y H, Wang Y B, Guo M Q, Wu H Y, Li J, Wu W T, Zhao J Z (2020). Differential enrichment mechanism of organic matters in the marine–continental transitional shale in northeastern Ordos Basin, China: control of sedimentary environments. *J Nat Gas Sci Eng*, 83: 103625
- Cullers R L (2000). The geochemistry of shales, siltstones and sandstones of Pennsylvanian–Permian age, Colorado, USA: implications for provenance and metamorphic studies. *Lithos*, 51(3): 181–203
- Ding J H, Sun J S, Zhang J C, Yang X T, Shi G, Wang R Y, Huang B, Li H L (2022). Elemental geochemical evidence for controlling factors and mechanisms of transitional organic matter accumulation: the upper Permian Longtan Formation black shale in the Lower Yangtze region, south China. *J Nat Gas Sci Eng*, 98: 104385
- Ding J H, Zhang J C, Tang X, Huo Z P, Han S B, Lang Y, Liu T (2018). Elemental geochemical evidence for depositional conditions and organic matter enrichment of black rock series strata in an inter-platform basin: the Lower Carboniferous Datang Formation, Southern Guizhou, southwest China. *Minerals*, 8(11): 509
- Floyd P A, Leveridge B E (1987). Tectonic environment of the Devonian Gramscatho basin, south Cornwall: framework mode and geochemical evidence from turbiditic sandstones. *J Geol Soc London*, 144(4): 531–542
- Hatch J R, Leventhal J S (1992). Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U. S. A. *Chem*

- Geol, 99(1–3): 65–82
- Ji R S, Qin D Y, Gao C L (1990). Closing of eastern Qinling palaeocean and collaging between the North China and Yangtze Blocks. *Petroleum Geo Experiment*, 12(4): 353–365
- Lan Z K, Shen J J (2022). Depositional paleo–environments of Lower Cambrian Qiongzhusi Formation in the Western Middle Yangtze Block and its controlling effect on the organic matter enrichment. *Energies*, 15(10): 3761
- Lewan M D, Maynard J B (1982). Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochim Cosmochim Acta*, 46(12): 2547–2560
- Liang C, Jiang Z X, Yang Y T, Wei X J (2012). Shale lithofacies and reservoir space of the Wufeng–Longmaxi Formation, Sichuan Basin, China. *Pet Explor Dev*, 39(6): 736–743
- Liao Z W, Hu W X, Cao J, Wang X L, Hu Z Y (2019). Petrologic and geochemical evidence for the formation of organic–rich siliceous rocks of the Late Permian Dalong Formation, Lower Yangtze region, southern China. *Mar Pet Geol*, 103: 41–54
- Liu S X, Wu C F, Li T, Wang H C (2018). Multiple geochemical proxies controlling the organic matter accumulation of the marine–continental transitional shale: a case study of the Upper Permian Longtan Formation, western Guizhou, China. *J Nat Gas Sci Eng*, 56: 152–165
- Liu Y, Wu B, Gong Q S, Cao H Y (2019). Geochemical characteristics of the lower Silurian Longmaxi Formation on the Yangtze Platform, South China: implications for depositional environment and accumulation of organic matters. *J Asian Earth Sci*, 184: 104003
- McLennan S M (1989). Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. *Rev Mineral Geochem*, 21(1): 169–200
- Murphy A E, Sageman B B, Hollander D J, Lyons T W, Brett C E (2000). Black shale deposition and faunal overturn in the Devonian Appalachian Basin: clastic starvation, seasonal water–column mixing, and efficient biolimiting nutrient recycling. *Paleoceanography*, 15(3): 280–291
- Roser B P, Korsch R J (1988). Provenance signatures of sandstone–mudstone suites determined using discriminant function analysis of major–element data. *Chem Geol*, 67(1–2): 119–139
- Ross D J, Bustin R M (2009). Investigating the use of sedimentary geochemical proxies for paleoenvironment interpretation of thermally mature organic–rich strata: examples from the Devonian–Mississippian shales, Western Canadian Sedimentary Basin. *Chem Geol*, 260(1–2): 1–19
- Sugisaki R, Yamamoto K, Adachi M (1982). Triassic bedded cherts in central Japan are not pelagic. *Nature*, 298(5875): 644–647
- Shang F H, Zhu Y M, Hu Q H, Wang Y, Li Y, Li W, Liu R Y, Gao H T (2020). Factors controlling organic–matter accumulation in the Upper Ordovician–Lower Silurian organic–rich shale on the northeast margin of the Upper Yangtze platform: evidence from petrographic and geochemical proxies. *Mar Pet Geol*, 121: 104597
- Shen J, Schoepfer S D, Feng Q L, Zhou L, Yu J X, Song H Y, Wei H Y, Algeo T J (2015). Marine productivity changes during the end–Permian crisis and Early Triassic recovery. *Earth Sci Rev*, 149: 136–162
- Sweere T, van den Boorn S, Dickson A J, Reichart G J (2016). Definition of new trace–metal proxies for the controls on organic matter enrichment in marine sediments based on Mn, Co, Mo and Cd concentrations. *Chem Geol*, 441: 235–245
- Talbot M R (1988). The origins of lacustrine oil source rocks: evidence from the lakes of tropical Africa. *Geological Society*, 40: 29–43
- Taylor S R, McLennan S M (1985). *The Continental Crust: Its Composition and Evolution*. Oxford: Blackwell Scientific Publications, 1–328
- Tribouillard N, Algeo T J, Lyons T, Riboulleau A (2006). Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem Geol*, 232(1–2): 12–32
- Wang Y M, Li X J, Dong D Z, Zhang C C, Wang S F (2017). Major controlling factors for the high–quality shale of Wufeng–Longmaxi Formation, Sichuan Basin. *Energ Explor Exploit*, 35(4): 444–462
- Wang Y Y, Chen J F, Shen W B, Li M (2022). Mechanism of organic matter accumulation in black shales of the Yuertusi Formation in the Tarim Basin: insights from paleoenvironmental variation during the Early Cambrian. *Front Earth Sci (Lausanne)*, 10: 879658
- Wignall P B, Newton R (2001). Black shales on the basin margin: a model based on examples from the Upper Jurassic of the Boulonnais, northern France. *Sediment Geol*, 144(3–4): 335–356
- Wu B (2022). The sedimentary geochemical characteristics and geological significance of the Wufeng–Longmaxi Formation accumulation of organic matter black shale on the southeastern Sichuan Basin, China. *Geofluids*, 2022: 1900158
- Wu Z R, He S, He Z L, Li X C, Zhai G Y, Huang Z Q (2022). Petrographical and geochemical characterization of the Upper Permian Longtan Formation and Dalong Formation in the Lower Yangtze region, South China: implications for provenance, paleoclimate, paleoenvironment and organic matter accumulation mechanisms. *Mar Pet Geol*, 139: 105580
- Xu L F, Cheng Y S, Zhang J C, Liu Y, Yang Y Y (2022). Controls on the organic matter accumulation of the marine–continental transitional Shanxi Formation shale in the southeastern Ordos Basin. *ACS Omega*, 7(5): 4317–4332
- Yan D T, Chen D Z, Wang Z Z, Li J, Yang X R, Zhang B (2019). Climatic and oceanic controlled deposition of Late Ordovician–Early Silurian black shales on the North Yangtze platform, south China. *Mar Pet Geol*, 110: 112–121
- Yin K, Xu J, Li X M (2019). A new grey comprehensive relational model based on weighted mean distance and induced intensity and its application. *Grey Systems–Theory and Application*, 9(3): 374–384
- Yuan W, Liu G D, Zhou X X, Xu L M, Li C Z (2020). Palaeoproductivity and organic matter accumulation during the deposition of the Chang 7 organic–rich shale of the Upper Triassic Yanchang Formation, Ordos Basin, China. *Geol J*, 55(4): 3139–3156
- Zeng S Q, Wang J, Fu X G, Chen W B, Feng X L, Wang D, Song C Y, Wang Z W (2015). Geochemical characteristics, redox conditions, and organic matter accumulation of marine oil shale from the Changliang Mountain area, northern Tibet, China. *Mar Pet Geol*, 64: 203–221
- Zhang L C, Xiao D S, Lu S F, Jiang S, Lu S D (2019). Effect of

sedimentary environment on the formation of organic-rich marine shale: insights from major/trace elements and shale composition. *Int J Coal Geol*, 204: 34–50

Zou C N, Dong D Z, Wang S J, Li J Z, Li X J, Wang Y M, Li D H, Cheng K M (2010). Geological characteristics and resource potential of shale gas in China. *Pet Explor Dev*, 37(6): 641–653