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ORIGINAL PAPER-EXPLORATION GEOLOGY

The accumulation model of organic matters for the Niutitang Formation shale and its control on the pore structure: a case study from Northern Guizhou

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Abstract

Shale gas reservoir is a fine-grained sedimentary rock with component of clastic particles and organic matters, and the accumulation of the organic matters would determine the effective development of shale gas. The paleoclimate, detrital influx, redox of the water and paleoproductivity are effective geochemical indicators that could help to find the favorable shale gas reservoir stratum. In this study, the shale samples collected from Niutitang Formation (Northern Guizhou, China) were launched the measurements of the content of major elements and trace elements, and the characteristics of geochemical indicators were analyzed, which can be used to discuss the accumulation model of organic matters. Besides, the pore structure of shale sample controlled by the enrichment of organic matters is also discussed. The paleoclimate is dominant cold and dry, and it changes to warm and humid at the later Niutitang period, and the detrital influx also increased at the later Niutitang period; the water environment of Niutitang Formation shale presents as reductive, and the paleoproductivity of the Niutitang Formation shale is commonly high. The enrichment of organic matters in the Niutitang Formation is dominantly controlled by the redox of the water, while the hydrothermal activity and the paleoproductivity lead to the difference enrichment of organic matters in the Niutitang Formation shale. The accumulation model of organic matters also influences the characteristics of pore structure from the Niutitang Formation shale, and the pore structure could be divided into two types. The shale with high content of organic matters also features high content of quartz and pyrite, and these minerals contribute to the preservation of pore space in the shale, while that of the clay minerals is contrary. The high content of organic matters and preferable pore characteristics indicate the Niutitang Formation favors the development of shale gas, especially that for the lower Niutitang Formation.

Keywords Niutitang Formation shale · Geochemical indicators · Accumulation of organic matter · Pore structure · Northern Guizhou

Introduction

Shale gas has attracted the attention of researchers in the unconventional oil and gas field recent years. The exploration and development of shale gas dominantly focus on the Middle Triassic Yanchang Formation, Lower Silurian Longmaxi Formation and Lower Cambrian Niutitang Formation in China (Wang et al. 2020a, b). The Longmaxi Formation shale gas has successfully conducted commercial development, while that for the Yanchang Formation shale gas just is still in the primary exploration stage. As the key development stratum of shale gas in South China, the Niutitang Formation shale gas in Hubei Province has acquired major breakthrough (Wang et al. 2020a, b).

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The accumulation of organic matter is the result of multifactors, including sedimentary environment, tectonic movement, the preservation of organic matter and so on. The difference accumulation of organic matters could be investigated with the geochemical method with various geochemical indicators (Ross and Bustin 2009a, b). The organic matter accumulation models could be summarized with two types, preservation model and productivity model, respectively (Talbot 1988; Carroll and Bohacs 1999). The preservation model concentrates on the water environment that controls the preservation of the organic matters (Demaison and Moore 1980; Arthur and Sageman 1994; Arthur et al. 1998), while the productivity model persists the organisms contribute to the preservation of organic matter (Wignall and Newton 2001). In fact, the accumulation of organic matters commonly shows the comprehensive effect of preservation model and productivity model, especially that for the marine–continental transitional shale (Liu et al. 2018). Geochemistry characteristics are effective method to recover the paleogeographical and paleoclimate, which would finally summarize the difference accumulation of the organic matter. There are several geochemical indicators that could be used. Chemical index of alteration (CIA) is commonly utilized to analyze the paleoclimate (Wedepohl 1971; Nesbitt and Young 1982; McLennan 1993; Ross and Bustin 2009a, b); the ratio of content of SiO_2 and Al_2O_3 (SiO_2/Al_2O_3), the ratio of content of MnO and TiO_2 (MnO/TiO_2) and the ratio of content of yttrium and holmium (Y/Ho) are used to indicate the amount of the detrital influx (Ryuichi et al. 1982; Webb and Kamber 2000); the ratio of content of vanadium and (vanadium plus nickel) (V/(V + Ni)), the ratio of content of vanadium and chromium (V/Cr), the ratio of content of nickel and cobalt (Ni/Co), EF_{Mo}, EF_U, EF_V, EF_{Ni}, the ratio of content of uranium and thorium (U/Th) and the ratio of content of cuprum and zincum (Cu/Zn) could indicate the redox environment of water (Algeo and Maynard 2004; Ross and Bustin 2009b; Pi et al. 2014; Zhu et al. 2018), and the ratio of content of phosphorus and titanium (P/Ti) and ratio of content of barium and aluminum (Ba/Al) could present the paleoproductivity (Dean et al. 1997; Algeo et al. 2011; Liu et al. 2018). Currently, the accumulation characteristics of organic matter with the geochemical method for Niutitang Formation shale in China mainly focus in south of Yangtze platform (Liu et al. 2015, 2016; Xia et al. 2015; Wu et al. 2017; Zhou et al. 2017, 2019; Li et al. 2018, 2019; Zhang et al. 2018; Ma et al. 2019; Awan et al. 2020). The lithofacies of Niutitang Formation shale in South China could be divided into five types, including organic matter-rich siliceous shale, silty-siliceous shale, argillaceous shale, calcareous shale and silty-siliceous mixed shale (Yang et al. 2016; Wu et al. 2017).

The pores in the Niutitang Formation shale are dominantly mineral matrix pore with poor connectivity, and the organic pores are rare (Wang et al. 2016a). The shape of the Niutitang Formation pores is various, including conical, ink bottle, spherical, elliptical, beaded, irregular, plate-like intersecting micro-fractures and so on (Sun et al. 2020). The micropores in the Niutitang Formation shale mainly occur in the organic matter (Sun et al. 2016), while large amount of these pores are closed pore (Sun et al. 2018). The mesopores and macro-pores are dominantly contributed by the minerals (Sun et al. 2016). The content of TOC, quartz and clay minerals and the thermal evolution degree are the key factors that determine the characteristics of pore structure in the Niutitang Formation shale (Shang et al. 2021; Wang et al. 2021). The thermal evolution degree determines the development of the organic matter. When R_o of shale is less than 1.5%, the amounts of the organic pores are less, and the pore aperture is also small. Once the R_o exceeds 3%, the organic pores in the shale nearly disappear (Wang et al. 2016a, b, c; Gu et al. 2018; Wang et al. 2020a, b). The content of quartz is high in the Niutitang Formation shale (Qin et al. 2019), and the quartz presents with five different types, silt-size/sand-size detrital quartz, siliceous skeletons, overgrowth nucleated around detrital quartz, matrix-dispersed microcrystalline quartz and aggregates of euhedral quartz, respectively, and the authigenic quartz is the dominant type (Dong et al. 2021). However, Liu et al. (2018) reported that the high content of quartz in the Niutitang Formation shale profits from the biogenetic quartz (Dong et al. 2021). For the Niutitang Formation shale in Guizhou, the content of quartz is also high, and the quartz comes from both continental detrital quartz and biogenetic quartz (Sun et al. 2021). The intergranular pores and organic pores are developed in Niutitang Formation siliceous shale (Niu et al. 2021), while Wang et al. (2020a, b) found that the organic pores are rarely developed in the Niutitang Formation shale. For the argillaceous shale in the Niutitang Formation, the intergranular pores are less developed, and the cleavage-sheet intraparticle pores are developed in the clay minerals (Niu et al. 2021). The content of TOC ($<6.5\%$) and quartz favor the development of pores for the siliceous shale, especially that for the micropores (Wang et al. 2016b, c; Niu et al. 2021). The quartz features as rigid mineral, it can resist a certain compaction, which will finally preserve the pore space (Xi et al. 2019). Besides, the dissolution of feldspar could also promote the development of pores (Guo et al. 2021). When it comes to the argillaceous shale, the pore structure characteristics are mainly influenced by the content of illite (Niu et al. 2021).

There have been a detailed study on the accumulation of organic matters and the characteristics of pore structure for the Niutitang Formation shale in South China, while the accumulation characteristics of organic matter for Niutitang Formation shale in North Guizhou is rare. The accumulation of organic matter is influenced by the sedimentary environment, and it will lead to various lithology characteristics, which will finally determine the different pore structure of shale. In this study, the Niutitang Formation shale samples were collected from a shale gas well in Northern Guizhou, with the detailed analysis of the characteristics of major and trace elements, the accumulation characteristics of organic matters is discussed with multi-geochemical indicators; combined with the lithology characteristics of the Niutitang Formation, the pore structure characteristics influenced by the organic matter accumulation model is studied.

Samples and method

The geological setting and samples

The study area locates in the northern Guizhou Province, China. Guizhou has experienced the Xuefeng movement, Caledonian movement, Hercynian movement, Indo-China movement, Yanshan movement and Himalayan movement during the geologic history, the complicated tectonic movements lead to the seven secondary structure units in Guizhou currently (Fig. 1). At the later period of Mesoproterozoic Era, the sedimentary environment of the study area is marine, and it continuously expands to the north. At Silurian, the continental crust transforms from active continental margin to stable platform and finally turns into stable continental crust at the late Silurian. The shale samples used in this study collected from a shale gas well in Guizhou Province, and the nine shale samples were collected with interval method (Fig. 2). To avoid the probable sample pollution, the collected shale samples were packaged with independent plastic bag.

Measurements

The content of TOC is measured with the TOC-Control L/V organic carbon analyzer produced by Shimadzu, and the determination of total organic carbon in sedimentary rock (GB/T 19,145–2003, Chinese Standard) is consulted. Firstly, the shale samples were crushed with a size less than 80 mesh; following that, excess dilute hydrochloric acid was added to get rid of the inorganic carbon in the samples; after that, the shale samples would be burned with oxygen under high temperature, which would change the TOC to carbon

Fig. 1 The location of the research area (modified from Liu et al. 2018)

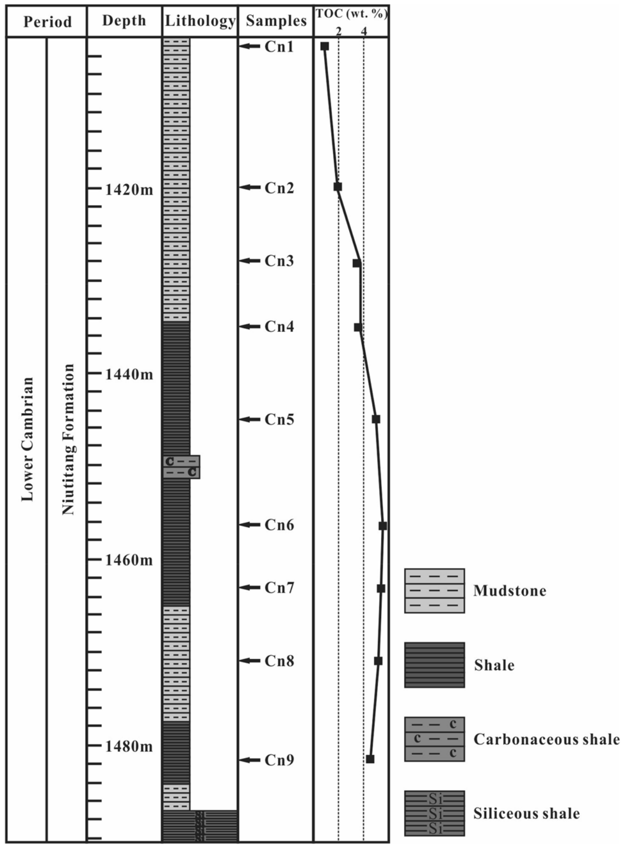


Fig. 2 The stratigraphic column and vertical distribution of TOC content of the Niutitang Formation

dioxide; finally, the content of TOC was measured with the infrared detector. The parallel samples were set, the deviation of the measurement result less than 0.1% is thought to be reliable.

The shale samples were crushed to 200 mesh before the geochemical characteristics are analyzed. The content of the major elements were measured with the X-ray fluorescence spectrometry method according to the methods for chemical analysis of silicate rocks (GB/T 14,506.28-2010, Chinese Standard). The shale samples would be prepared with the glass melting method and then be analyzed with the Axios Max X-ray fluorescence spectrometry analyzer. With the chemical reagent–general rules for inductively coupled plasma mass spectrometry (GB/T 39,486–2020, Chinese Standard), the content of the trace elements was measured with the inductively coupled plasma mass spectrometer. Firstly, the crushed shale samples (approximately 25 mg) would be dried under 105 °C; secondly, the dried samples would be placed in the seal gland, with 0.5 ml HF solution, the samples would be dried again at 120 °C to dissolve the SiO_2 in the samples; thirdly, the samples would be handled with the mixture of HF solution (1 ml) and HNO_3 (0.5 ml) under 190 °C for 24 h; after that, the samples would be soaked with the 30% (v/v) HNO_3 under 130 °C for another 3 h; finally, the samples would be cooled and analyzed. The accuracy is controlled below 5%.

The view of scanning electron microscope (SEM) was launched with the MAIA3 model 2016 (LM) ultra-high-resolution field emission scanning electron microscope. The shale samples would be polished with the Fischione argon ion polishing instrument, then the surface of the samples would be sprayed with gold. With a size of 10 mm × 10 mm × 1 mm, the D8 ADVANCE X-ray diffraction analyzer was used to view the pore structure characteristics.

With the determination of the specific surface area of solids by gas adsorption using the BET method (GB/T 19,587–2017, Chinese Standard), the pore structure of the shale samples was measured with the TriStar II specific surface area analyzer.

The enrichment factor (EF) of various elements is commonly used to describe the enrichment degree, which can reflect the deviation degree of the element in the shale samples when it compares with the average marine shale (Wedepohl 1971), and it can be calculated with Eq. (1) (Ross and Bustin 2009b).

$$\mathrm{EF} = (\mathrm{element}/\mathrm{Al})_{\mathrm{sample}}/(\mathrm{element}/\mathrm{Al})_{\mathrm{averageshale}} \quad (1)$$

CIA could be acquire as follow,

$$\mathrm{CIA} = 100 \times \left[\mathrm{Al_2O_3}/\left(\mathrm{Al_2O_3} + \mathrm{CaO}* + \mathrm{Na_2O} + \mathrm{K_2O}\right)\right] \quad (2)$$

where CaO* is the content of CaO, it should be adjusted with the content of P_2O_5, $CaO_{adjust} = CaO\text{-}P_2O_5 \times 10/3$, when $CaO_{adjust} > Na_2O$, $CaO^* = Na_2O$; if not, $CaO^* = CaO_{adjust}$. The contents of the elements used in Eq. (2) should be molar percent form (McLennan 1993).

Results

TOC characteristics

The content of TOC ranges from 0.90 to 5.54% for the Niutitang Formation shale. Except for Cn1 and Cn2 samples, the content of TOC for the shale samples exceeds 2%. It can be found that the content of TOC is higher for the lower Niutitang Formation shale, and it tends to be decrease for the upper Niutitang Formation shale (Fig. 2).

Major elements geochemistry characteristics

The three end-member figure is used to present the content of the dominant inorganic minerals, including SiO_2, Al_2O_3 and CaO. Figure 3 shows the Niutitang Formation shale

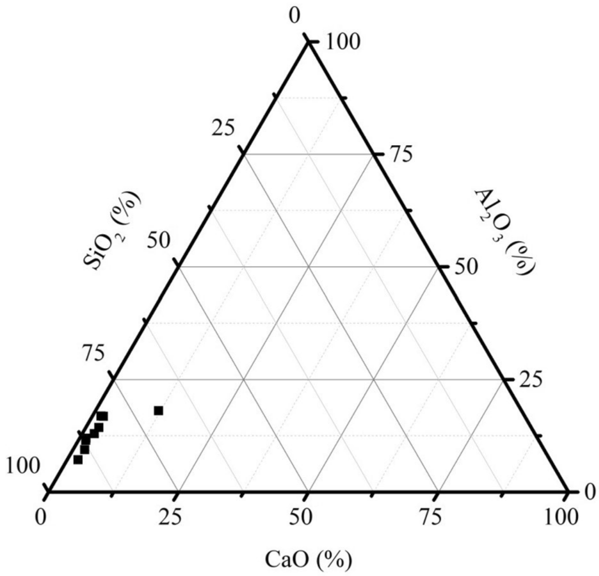


Fig. 3 Ternary diagram of quartz, clays and carbonates in Niutitang Formation shale samples

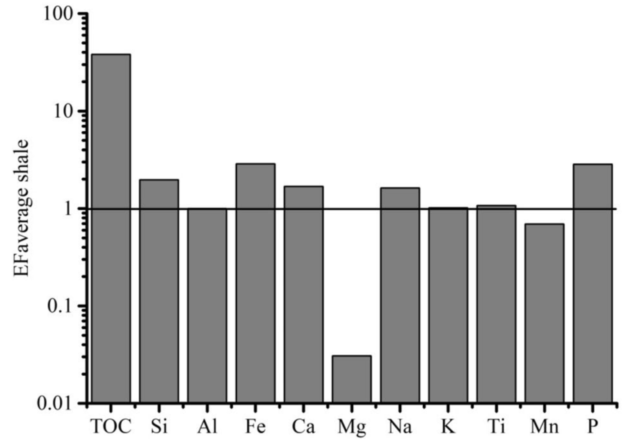


Fig. 4 Enrichment factors of TOC and major elements in Niutitang Formation shale samples

feature as SiO_2 enrichment. The content of SiO_2 ranges from 50.12 to 71.38%, the content of Al_2O_3 varies from 5.64 to 13.23%, and that for CaO ranges from 0.97 to 8.69%. The lower Niutitang Formation shale features higher content of SiO_2 than that of upper Niutitang Formation shale, while that for the Al_2O_3 and CaO is contrary (Table 1).

Ferrum (Fe), calcium (Ca), sodium (Na) and phosphorus (P) present enrichment for the Niutitang Formation shale, potassium (K) and titanium (Ti) feature as relative enrichment, while magnesium (Mg) and manganese (Mn) show a certain deficit (Fig. 4). The higher EF_K is commonly related to the illite and talc in the shale (Yarincik et al. 2000; Ross and Bustin 2008; Chen et al. 2016). The lower EF_{Mg} indicates the lower concentration of Mg and K in the clay minerals, which is related to the lack of the kaolinite (Ross and Bustin 2008). The enrichment of Mg may also have a relationship with dolomite (Ross and Bustin 2008), and the lower EF_{Mg} also means the lower content of dolomite in the Niutitang Formation shale. Na features enrichment, and this is mainly due to the high content of feldspar, especially the anorthose (Wedepohl 1971; Ross and Bustin 2008; Liu et al. 2018). The enrichment of Fe and Ca indicates the possible high content of pyrite, siderite and carbonate minerals in the Niutitang Formation shale (Zeng et al. 2015; Liu et al. 2018). Ti is stable element in the sediments, the good relationship between Al_2O_3 and TiO_2 indicates that the Ti could both exist in the clay mineral crystal and the detrital influx (Ross and Bustin 2009a; Liu et al. 2018) (Fig. 5). The higher Mn concentration commonly accompanies with higher concentration of Al and Ca and lower concentration of silicon (Si), the EF_{Mn} of Niutitang Formation shale indicates that Mn may not come from the self-manganese carbonate (Ross and Bustin 2008) (Fig. 6).

Table 1 Major oxides, TOC and CIA of the Niutitang Formation shales

Sample	TOC /wt. %	Major oxides /%										CIA
		SiO_2	Al_2O_3	Fe_2O_3 + FeO	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	
Cn1	0.90	50.12	13.00	5.45	8.69	0.08	1.04	2.81	0.60	0.06	0.16	72.70
Cn2	1.95	63.68	13.23	4.58	1.68	0.07	2.29	2.66	0.58	0.05	0.14	72.76
Cn3	3.47	61.69	12.77	5.98	1.23	0.05	2.22	2.65	0.53	0.04	0.16	72.38
Cn4	3.58	62.34	10.77	6.00	1.86	0.05	1.46	2.37	0.45	0.04	0.60	73.77
Cn5	5.00	71.38	5.64	3.67	1.67	0.03	0.90	1.28	0.30	0.03	0.16	64.65
Cn6	5.54	69.87	7.44	4.09	1.80	0.03	1.31	1.69	0.40	0.03	0.50	71.30
Cn7	5.40	67.60	8.93	4.35	1.08	0.03	1.68	2.01	0.48	0.03	0.18	70.73
Cn8	5.18	57.99	8.88	4.02	1.58	0.05	1.23	1.90	0.55	0.04	0.18	73.93
Cn9	4.53	68.52	9.44	3.77	0.97	0.03	1.63	2.24	0.52	0.03	0.16	70.92

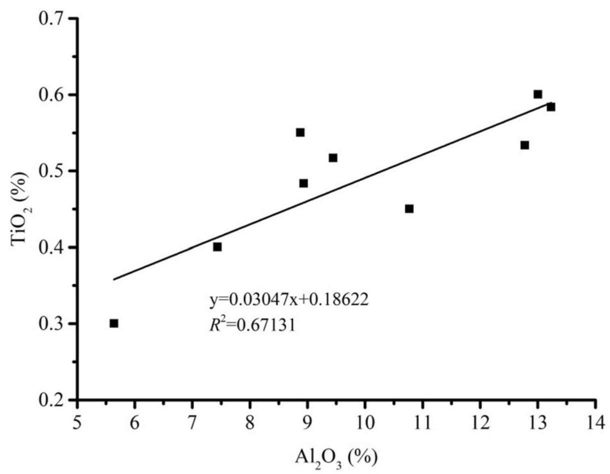


Fig. 5 Relationships between content of TiO_2 and Al_2O_3 in Niutitang Formation shale samples

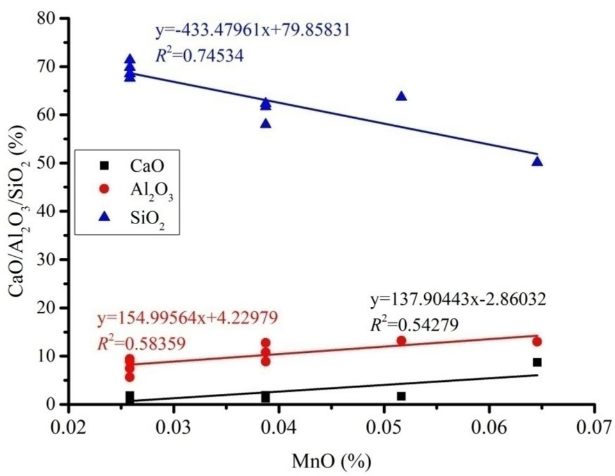


Fig. 6 Relationships between content of MnO and CaO, Al_2O_3, SiO_2 in Niutitang Formation shale samples

Trace elements geochemistry characteristics

The trace elements in the Niutitang Formation shale is not enrichment, while that for the vanadium (V), nickel (Ni), cuprum (Cu), zincum (Zn), lead (Pb), strontium (Sr), molybdenum (Mo), barium (Ba), uranium (U) and yttrium (Y) are enrichment (Table 2, Fig. 7).

Lithology characteristics

The inorganic minerals are quartz, feldspar, carbonate minerals, pyrite and illite in the Niutitang Formation shale. The dominant inorganic mineral is the quartz, the content of the quartz ranges from 31.30 to 63.30%; and the content of illite varies from 13.90 to 26.49%; the content of pyrite ranges from 7.70 to 17.10%; orthoclase and anorthose both exist in the Niutitang Formation shale, and the content of later is higher than that of former; the content of carbonate minerals varies from 5.40 to 22.10%, and the content of calcite and dolomite is almost equal (Table 3).

Pores characteristics

The intergranular pores are dominantly developed in the Niutitang Formation shale, and the intergranular pores distributed with various sizes (Fig. 8); the micro-fractures could be found developed in the mud-particles (Fig. 8b), and the intracrystalline pores are also developed (Fig. 8d). It can be found that the organic matters feature as disseminated for the upper Niutitang Formation shale samples, and the pyrite presents as scattered or framboid, and the content of the pyrite is also less (Fig. 8a–b). With the increase of burial depth, the distribution of the organic matters tends to be larger with disseminated or banded, and the organic matters commonly occur at the edge of the pores or micro-fractures, the content of pyrite also tends to be increased (Fig. 8c–g). When it comes to the bottom of the Niutitang Formation shale, the pyrite features surrounding the organic matters (Fig. 8h–i).

Discussion

The multi-geochemical indicators for the accumulation of organic matters

Paleoclimate

The paleoclimate determines the amounts of organisms, which will finally determine the enrichment of the organic matters. CIA and EF_{Sr} are effective indicators that could reflect the paleoclimate. With a range from 50 to 70 for CIA, the paleoclimate is commonly cold and dry, indicating a lower chemical weathering degree; if the CIA varies from 70 to 85, it indicates a warm and humid paleoclimate, and the chemical weathering is medium; once the CIA exceeds 85, the paleoclimate is hot and humid, and the chemical weathering is strong (Nesbitt and Young 1982). Sr could enter into the sediments in the warm and humid paleoclimate, which would lead to the enrichment of Sr in the shale.

The CIA of Niutitang Formation shale ranges from 64.65 to 74.41. The paleoclimate for the lower Niutitang Formation shale is stable, presents as cold and dry, while the paleoclimate for the upper Niutitang Formation shale is fluctuant, the cold and dry paleoclimate alternates with warm and humid paleoclimate. The distribution characteristics of Sr are similar to CIA, and Sr tends to be enrichment at the upper Niutitang Formation shale, which indicates the large

Table 2 Trace elements of Niutitang Formation shales

Sample	Trace elements /μg/g												
	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Pb	Rb	Sr
Cn1	16.00	1.98	18.40	122.00	69.00	17.00	37.00	43.30	138.00	19.60	21.00	92.00	980.00
Cn2	17.00	2.11	12.20	480.00	79.00	17.80	131.00	86.80	163.00	16.40	23.00	103.00	503.00
Cn3	22.00	2.23	12.10	276.00	72.00	21.10	90.00	97.10	151.00	16.80	23.00	99.00	305.00
Cn4	23.00	2.33	12.90	678.00	136.00	31.90	130.00	218.60	262.00	14.10	33.00	80.00	269.00
Cn5	20.00	2.01	9.90	1159.00	65.00	18.70	308.00	88.80	376.00	10.20	32.00	49.00	331.00
Cn6	24.00	2.10	12.20	250.00	52.00	15.20	127.00	62.80	108.00	10.40	31.00	56.00	240.00
Cn7	26.00	2.42	11.30	319.00	58.00	15.60	124.00	57.20	116.00	11.20	25.00	71.00	169.00
Cn8	17.00	2.05	14.70	571.00	84.00	20.30	119.00	103.30	304.00	12.20	22.00	56.00	689.00
Cn9	26.00	2.46	11.90	2366.00	131.00	17.80	179.00	103.10	930.00	16.10	29.00	69.00	114.00
Sample	Trace elements /μg/g												
	Zr	Nb	Mo	Cs	Ba	Hf	Ta	Th	U	La	Ce	Y	Ho
Cn1	141.21	12.21	9.60	8.27	5378.00	3.23	1.00	8.20	5.98	28.22	52.05	32.16	0.86
Cn2	145.26	10.42	58.60	7.43	5672.00	3.37	0.80	10.60	15.95	23.48	41.69	27.20	0.82
Cn3	132.03	13.63	68.80	6.75	10,604.00	3.04	0.70	9.90	29.52	26.37	48.18	26.72	0.81
Cn4	117.72	9.07	121.30	4.99	18,010.00	2.64	0.60	8.80	68.58	29.15	50.82	55.04	1.06
Cn5	73.84	5.79	268.60	2.96	23,513.00	1.52	0.40	5.70	122.76	21.84	33.77	50.56	0.78
Cn6	100.30	7.53	127.60	2.98	9576.00	2.29	0.50	6.10	100.80	28.53	45.43	57.12	0.83
Cn7	131.62	8.52	116.60	3.80	14,540.00	2.99	0.60	7.80	86.63	29.56	48.18	40.80	0.85
Cn8	145.26	9.04	75.30	2.69	84,410.00	3.40	0.60	6.10	56.63	26.78	43.12	55.52	0.96
Cn9	142.56	8.21	69.70	6.95	8461.00	3.14	0.70	6.80	42.32	28.22	40.70	60.96	1.32

Li-lithium, Be-beryllium, Sc-scandium, V-vanadium, Cr-chromium, Co-cobalt, Ni-nickel, Cu-cuprum, Zn-zincum, Ga-gallium, Pb-lead, Rb-rubidium, Sr-strontium, Zr-zirconium, Nb-niobium, Mo-molybdenum, Cs-cesium, Ba-barium, Hf-hafnium, Ta-tantalum, Th-thorium, U-uranium, La-lanthanum, Ce-cerium, Y-yttrium, Ho-holmium

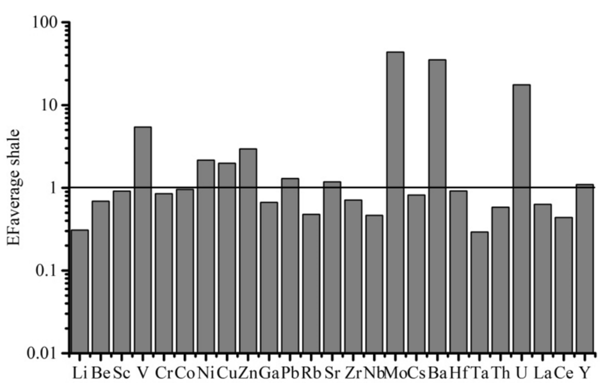


Fig. 7 Enrichment factors of trace elements in Niutitang Formation shale samples

amounts of detrital influx (Fig. 9). The content of TOC just features a faint increase for the lower Niutitang Formation shale under the cold and dry paleoclimate. Although there is a certain amount of terrigenous sediments, the organic matters may dominantly come from marine organisms. For the upper Niutitang Formation shale, the content of TOC tends to be decreased, the massive input of terrigenous sediments dilutes the concentration of organic matters in the shale. The relationships between CIA and content of TOC and EF_{Sr} and content of TOC are fluctuant, indicating that the paleoclimate is not the key factor that controls the accumulation of organic matters.

Detrital influx

The detrital influx presents two sides for the accumulation of the organic matters. For one thing, the detrital influx would dilute the concentration of the existed organic matters; for another thing, the organic matters contained in the detrital influx would increase the content of organic matters in the sediments. SiO_2/Al_2O_3, MnO/TiO_2 and Y/Ho are key indicators to distinguish the source of the sediments. For MnO/TiO_2, the value of MnO/TiO_2 below 0.5 means the sediments are mainly from the continental slope and marginal sea (Ryuichi et al. 1982). The value of SiO_2/Al_2O_3 for continental crust is approximately 3.6, if $SiO_2/Al_2O_3 > 3.6$, it indicates that the clastics not only come from the detrital influx, but also from the marine organisms or hydrothermal siliceous. Y/Ho could point out whether the sediments are

Table 3 The contents of various minerals in Niutitang Formation shales

Samples	Minerals /%								
	Quartz	Orthoclase	Anorthose	Calcite	Dolomite	Pyrite	Ankerite	I/S	Illite
Cn1	31.30	1.10	4.90	10.70	11.40	7.70	/	12.50	20.40
Cn2	40.40	1.90	10.70	1.80	5.60	8.80	/	4.31	26.49
Cn3	38.40	2.90	10.10	2.50	5.30	13.20	/	9.70	18.01
Cn4	43.70	4.00	7.00	3.50	4.10	17.10	/	/	20.70
Cn5	63.30	2.30	5.10	2.00	3.40	8.00	/	/	15.90
Cn6	53.40	3.50	7.30	4.50	5.40	10.30	/	/	15.50
Cn7	52.60	4.40	10.10	3.20	3.40	10.60	/	/	15.80
Cn8	46.40	6.00	7.90	11.30	0.00	10.50	4.00	/	13.90
Cn9	49.10	4.90	11.00	4.40	3.80	9.70	/	/	17.20

contaminated by the detrital influx, and it ranges from 44 to 77 for the marine shale (Webb and Kamber 2000).

SiO_2/Al_2O_3 exceeds 3.6 for Niutitang Formation shale, and MnO/TiO_2 is significantly less than 0.5, indicating the multi-sources of siliceous in the Niutitang Formation shale. Y/Ho indicates the lower Niutitang Formation shale is typical marine shale, while that for the upper Niutitang Formation shale is below 44, meaning there is a certain amounts of detrital influx enter into the upper Niutitang Formation shale. The similar distribution characteristics of SiO_2/Al_2O_3 and content of TOC and Y/Ho and content of TOC also make clear that the accumulation of organic matters in the Niutitang Formation shale is significantly influenced by the marine organisms and the hydrothermal activity (Fig. 10).

The chemical property of Al, Ti, Zr and Th is stable, and these elements could also indicate the detrital influx. Al commonly occurs in the clay minerals of shale, Zr and Th are the composition of the aluminosilicate, Ti could exist in the clay minerals, ilmenite and rutile (Liu et al. 2018). The positive relationship between content of TOC and SiO_2/Al_2O_3 indicates the enrichment of organic matter relates to the biogenetic silicon, especially that for the lower Niutitang Formation shale. EF_{Th} presents the similar distribution with the content of TOC, while the content of Al features contrary, meaning the detrital influx dilutes the concentration of organic matters in the upper Niutitang Formation shale (Fig. 10).

Redox of the water

The redox environment of water not only influences the enrichment of organic matters, but also the difference accumulation of the elements. According to the study the enrichment characteristics of various elements, the water environment could be recovered (Meyer et al. 2012; Maslov and Pldkovyrov 2018). V/(V + Ni), V/Cr, Ni/Co, EF_{Mo}, EF_U, EF_V, EF_{Ni}, U/Th and Cu/Zn are commonly used (Algeo and Maynard 2004; Ross and Bustin 2009b; Pi et al. 2014; Zhu et al. 2018). Ni and V could enter into the sediments under the reducing environment (Lewan and Maynard 1982; Breit and Wanty 1991), Co and Cr dominantly comes from the detrital influx. With the continuous decrease of oxygen in the water, the content of Ni and V would increase, leading to the increase of Ni/Co and V/Cr in the sediments. V/Cr could indicate the oxidation–reduction quality commendably. V/Cr exceeds 2 means the oxygen-deficient environment; V/Cr ranges from 1 to 2 indicate the weak oxidation environment; and V/Cr < 1 means the oxidation environment (Jones and Manning 1994). Taking the value of 7 as the inflection point, Ni/Co < 7 features an oxidation environment. Th is an inert element under the marine temperature, and it can enrich in the clay minerals. Under the reducing environment, U/Th is greater than 1.25; when it is below 0.75, the environment tends to be oxidative (Pattan et al. 2005). For the quiet marine environment, V/(V + Ni) ranges from 0.83 to 1, and V/(V + Ni) < 0.57 indicates the oxidation environment of water (Lewan and Maynard 1982). Cu/Zn < 0.2 commonly means an oxidation environment; conversely, it is a reducing environment.

Ni/Co ranges from 2.18 to 16.47 for the Niutitang Formation shale, V/Cr varies from 1.77 to 18.06, U/Th changes between 0.73 and 21.54, V/(V + Ni) and Cu/Zn range from 0.66 to 0.93 and 0.11 to 0.83, respectively. These indicators suggest that the water environment of the Niutitang Formation shale is dominantly reductive, which favors the preservation of the organic matters. The distribution of Ni/Co, V/Cr, U/Th and Cu/Zn is approximately similar, only the Cn5 sample features as abnormal. Although the water environment presents reductive totally, it increases firstly and then decrease, and this is similar to the distribution of content of TOC, indicating that the redox environment contributes dominantly to the accumulation of the organic matters. For the lower Niutitang Formation shale, V/(V + Ni) features continuously decrease, which is contrary to content of TOC, indicating some other accidents that may influence the preservation of the organic matters (Fig. 11).

U exists as $UO_2(CO_3)_3^{4-}$ in the oxidable marine and features high solubility, and when the marine changes to

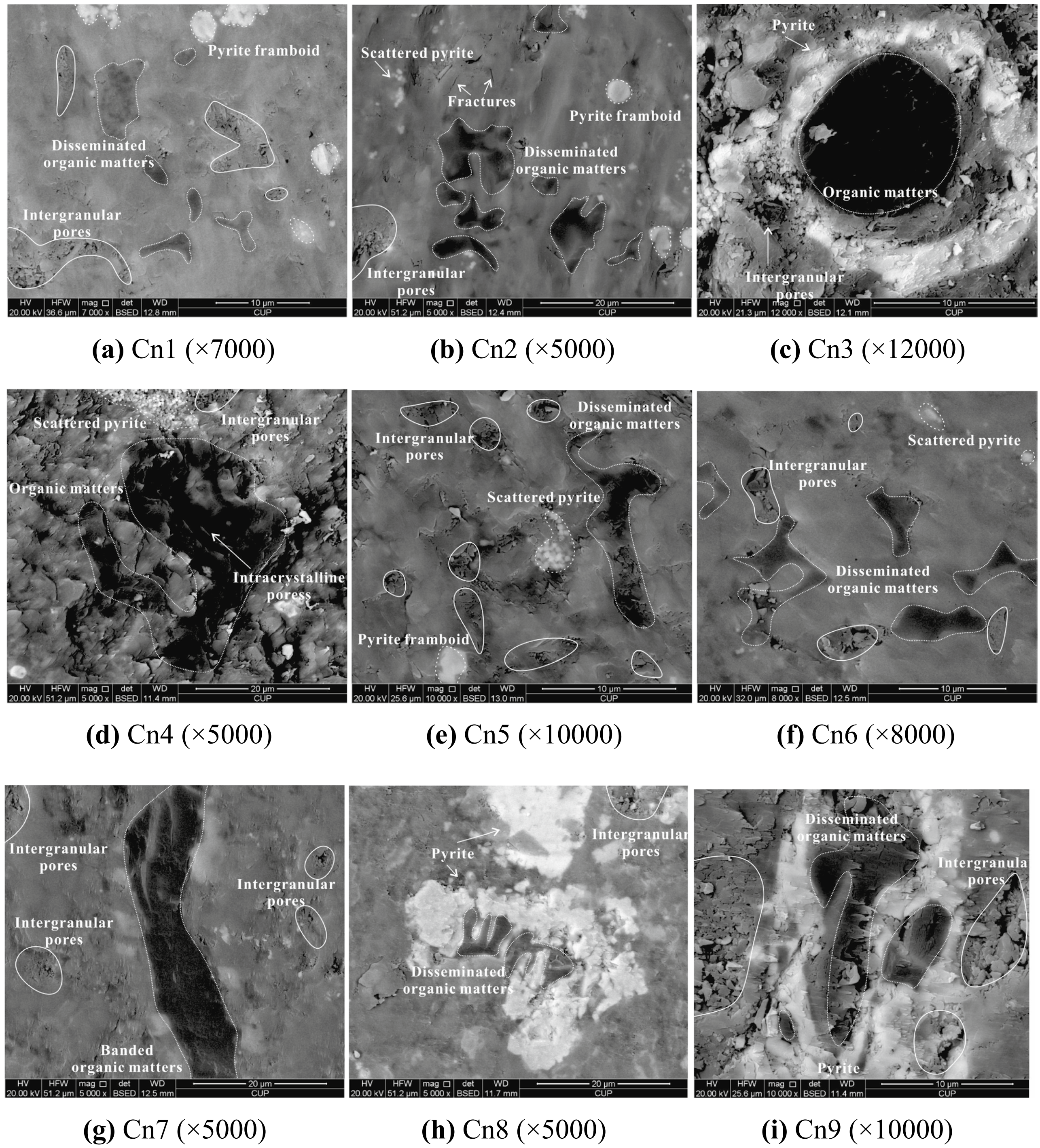


Fig. 8 The SEM of shale samples in Niutitang Formation

reductive, $UO_2(CO_3)_3^{4-}$ would be reduced to UO_2, U_3O_7 and U_3O_8 and fixed into the sediments, leading to the enrichment of U (Tribovillard et al. 2006). The phyrin compound separated from chlorophyll contains large amount of V and Ni. At the acidic reducing environment, V^{4+} is stable, and Ni could form sulfide precipitation (Lewan and Maynard 1982). At the non-sulfide reducing environment, the organic matters can adsorb and catch U and V in the water, then U and V enrich in the organic matters (Algeo and Maynard 2004). When it comes to the sulfide reducing environment, the content of H_2S is high in the water, U and V enter into the sediments in the form of sulfide or hydroxide, leading to indistinctive relationship between U/Al and content of TOC and V/Al and content of TOC (Ross and Bustin 2009b). The

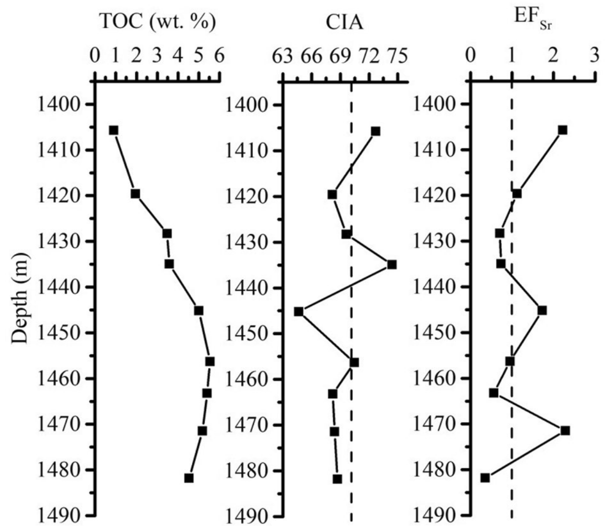


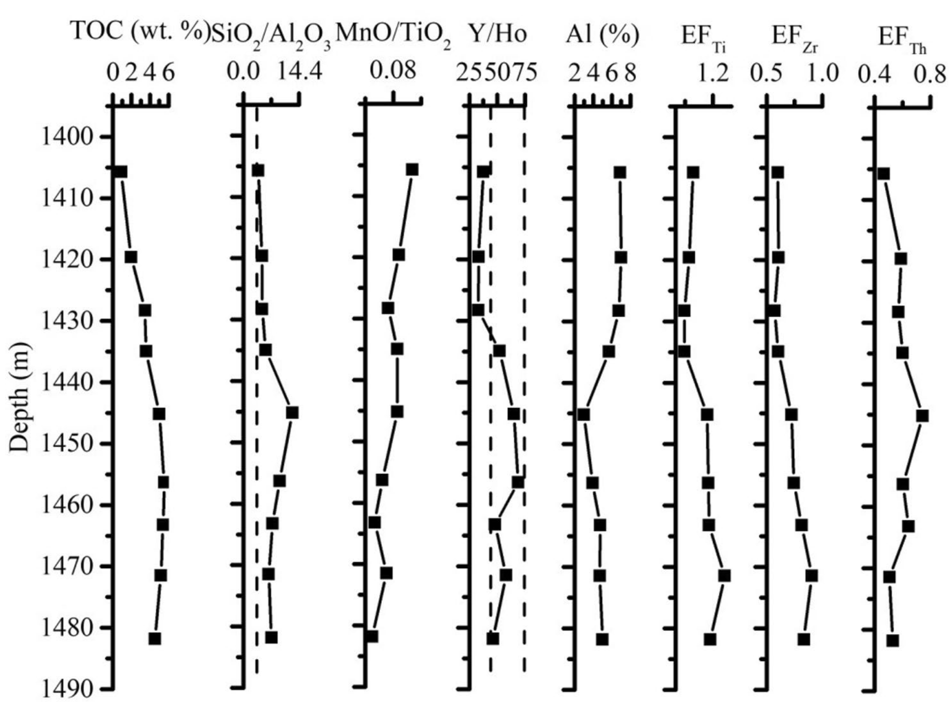
Fig. 9 The vertical distribution characteristics of detrital influx proxies indexes in Niutitang Formation

abnormal characteristics of Ce could also reflect the environment of water (German and Elderfield 1990; Schijf et al. 1991; Wilde et al. 1996). At the oxidative environment, Ce is easily adsorbed by the Fe oxides and Mn oxidex, leading to the positive anomaly or no obvious negative anomaly in the sediments; similarly, in the weak oxidation or reducing environment, Fe oxides would be dissolved, and Ce would enter into the water, leading to the positive anomaly in the water (Wilde et al. 1996; Yang et al. 2008). The distribution of U, V, Mo, U/Th and Ce is coincident with content of TOC, indicating that the reducibility of the water for Niutitang Formation increases firstly and then decreases (Fig. 11). The relationships between U/Al and content of TOC and V/Al and content of TOC are insignificant, especially for the later, indicating that the U and V enrich in the shale with two forms, organic matters and sulfide or hydroxide, respectively (Fig. 12), and this is identical with the distribution of V/(V/Ni).

The enrichment of V, Cr, Ni, Cu, Zn, Mo, Cd and Sb and loss of Sr, Re and Zr are commonly related to the hydrothermal activity in the deep water (Steiner et al. 2001). In the marine shale, the ratio of content Sr and Ba (Sr/Ba) is greater than 1, while in the sediments of modern seafloor, it is below 1, the smaller Sr/Ba indicates strong hydrothermal activity (Guo et al. 2007). The ratio of content Co and Zn (Co/Zn) is an impressible parameter to indicate the hydrothermal activity (Toth 1980). Influenced by the hydrothermal activity, Co/Zn is less than 0.15 in average (Toth 1980). Sr/Ba ranges from 0.01 to 0.18, and Co/Zn is below 0.15, indicating that the Niutitang Formation shale is influenced by the hydrothermal activity, especially that for the lower shale (Table 2). Due to the hydrothermal activity, the content of flint in the Niutitang Formation shale is high, and the rapidly sedimentary hydrothermal silica fluid provides a good preservation environment for the organic matters (Xie et al. 2021).

The locally closed sea basin leads to the difference accumulation of trace elements due to the obtained cycle of circulation of the bottom water. Algeo and Lyons (2006)

Fig. 10 The vertical distribution characteristics of TOC, SiO_2/Al_2O_3, MnO/TiO_2, Y/Ho, Al, EF_{Ti}, EF_{Zr} and EF_{Th} in Niutitang Formation



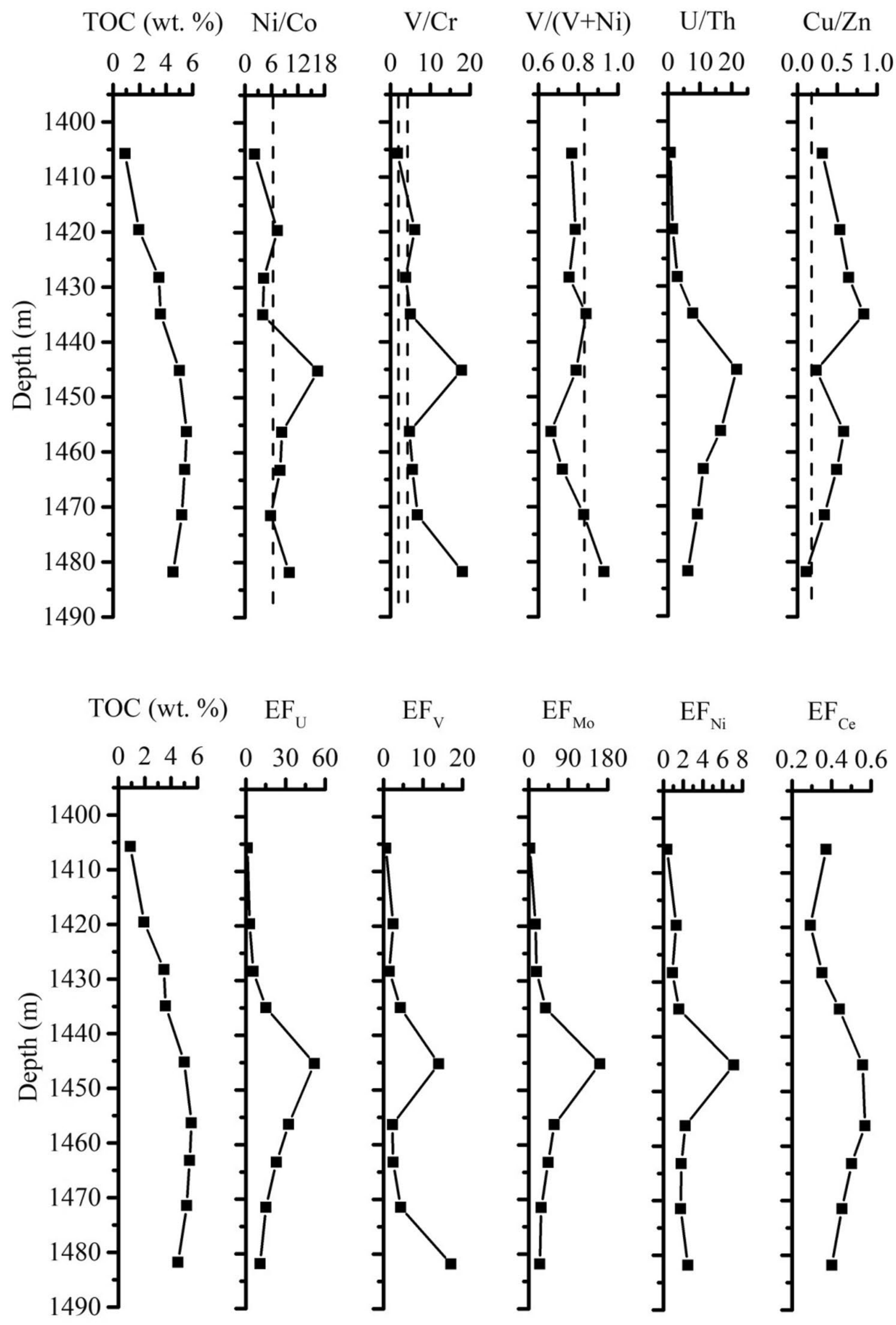


Fig. 11 The vertical distribution characteristics of various redox proxies indexes in Niutitang Formation

reported the Mo-TOC model to define the retention degree of basin water. Mo is a sensitive element in reflecting the redox environment. It can be enriched at the reducing environment, while it is easily influenced by the organic matters in the sediments, and there is a coupling relationship between the ratio of content Mo and TOC (Mo/TOC) and Mo concentration in the sea water. In the open sea, Mo in the sea water is enough, it can enter into the sediments largely, leading to a high Mo/TOC; in the locally closed water, the supplement of Mo is slow or inactive, leading to a low Mo concentration in the bottom water, especially the reducing water environment, Mo/TOC is comparatively low (Tribovillard et al. 2012). For the Niutitang Formation shale, the water environment features as moderate retention, and it reaches to maximum in the medium term (Fig. 13).

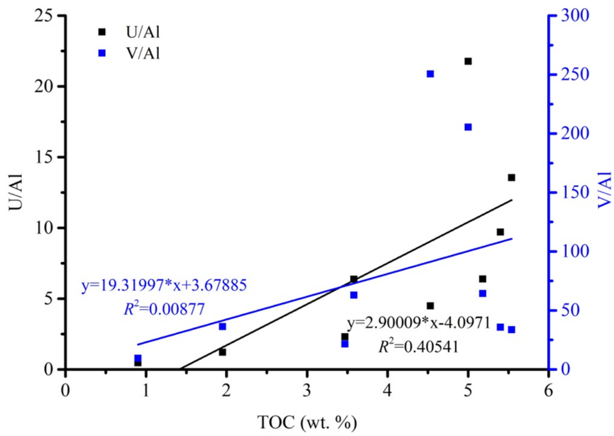


Fig. 12 The relationship between TOC and U/Al and V/Al in Niutitang Formation

Paleoproductivity

P and Ba are indicators to evaluate the paleoproductivity of the marine, while these elements could be diluted by the clastics, and P/Ti and Ba/Al are replaced (Dean et al. 1997; Algeo et al. 2011; Liu et al. 2018).

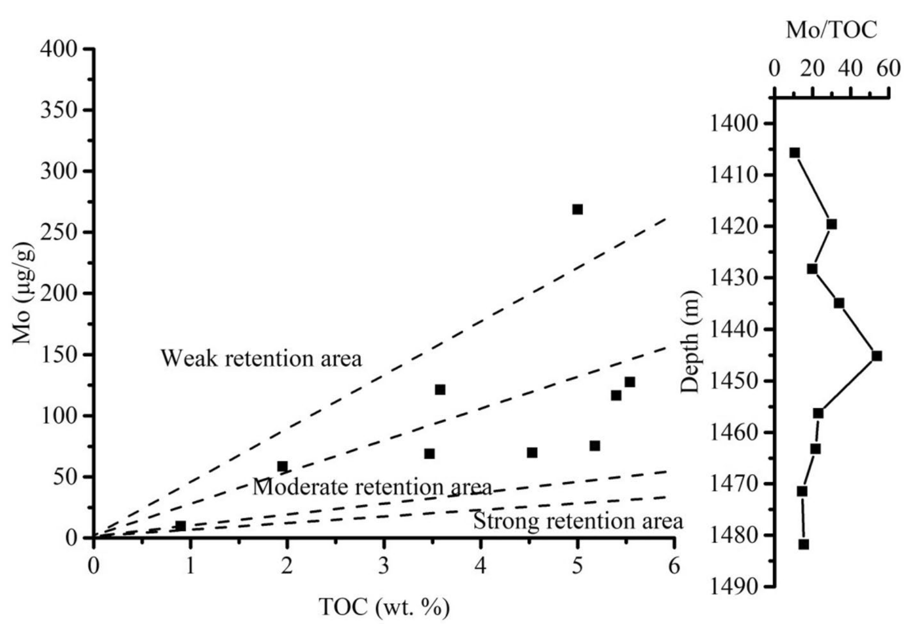
P/Ti ranges from 0.17 to 0.96 for the Niutitang Formation shale, and it is higher than that of the marine shale, indicating relative high productivity (Murray et al. 1993). P/Ti features as increase firstly and then decrease from the bottom to the top, and the lower Niutitang Formation shale presents higher P/Ti than that of the upper Niutitang Formation shale, which is similar to the distribution of content of TOC (Fig. 14). However, it should notice that the Cn6 and Cn4 shale samples present high P/Ti, while the content of TOC has not reached to the maximum, and this may relate to the redox environment of water. The reducibility of water for Cn4 sample is still strong, the high content of Fe in the water may adsorb P, leading to greater P/Ti and lower content of TOC (Algeo and Ingall 2007; Westermann et al. 2013).

Ba/Al varies from 782.82×10^{-4} to $17{,}997.87\times10^{-4}$ for Niutitang Formation shale, this is higher than the paleoproductivity of the layer sediments at continental margin of central California (Dean et al. 1997), indicating high paleoproductivity of Niutitang Formation shale. The distribution of Ba/Al and content of TOC presents high uniformity (Fig. 14). However, Ba/Al of Cn8 sample is maximum, while the water is reducibility (Chen et al. 2016), this may be related to the hydrothermal activity, which leads to the positive anomaly of Ba concentration.

The accumulation model of organic matters

The accumulation of organic matters for the Niutitang Formation shale is dominantly influenced by the redox environment. The paleoclimate is dominantly dry and cold during the sedimentary of Niutitang Formation shale, which does not favor the preservation of the organic matter. With the paleoclimate changes to warm and humid, the content of organic matters even decreases (Fig. 15). The relationships between Si and content of TOC, U and content of TOC, P/Ti and content of TOC and Ba and content of TOC present positive correlation, especially that for the Si and U, indicating that the deep water reducing environment favors the preservation of the organic matters and biogenic siliceous (Fig. 15). However, due to the hydrothermal activity and

Fig. 13 The relationship between TOC and Mo in Niutitang Formation



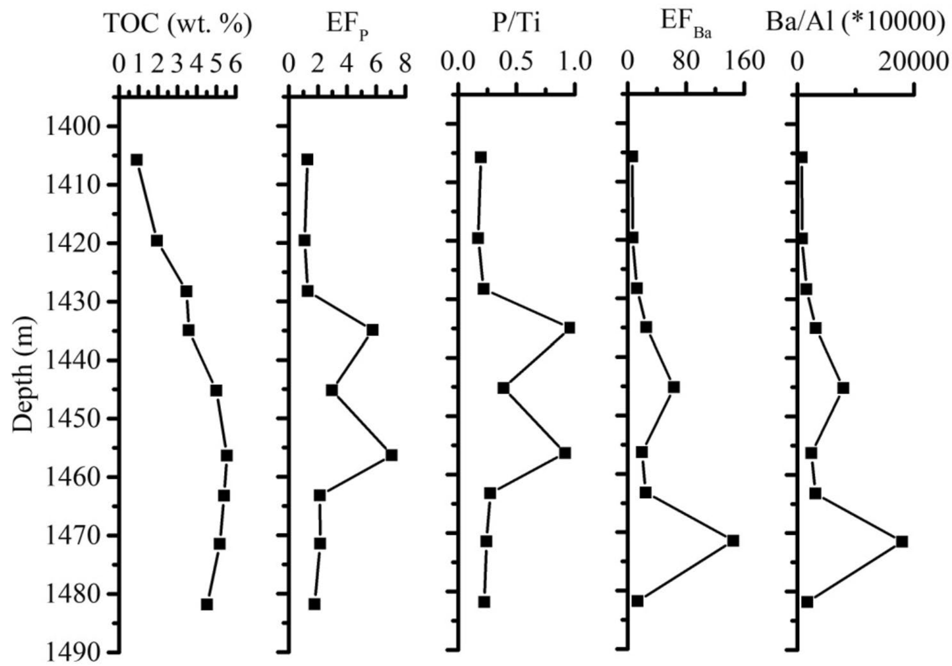


Fig. 14 The vertical distribution characteristics of various paleo-productivity proxies indexes in Niutitang Formation

the paleoclimate, the contribution of paleoproductivity to the accumulation of organic matters is not significant when it compares with the redox environment of water. Besides, the detrital influx from the continental slope or marginal sea has diluted the concentration of organic matters in the upper Niutitang Formation shale (Fig. 15).

The control of accumulation of organic matters on pore structure

The relationship between accumulation of organic matters and lithology characteristics

The quartz, pyrite, feldspar, clay minerals and carbonate minerals are dominant inorganic minerals in the Niutitang Formation shale. The distribution of the content of quartz and pyrite is approximately coincident with that of the TOC, while it is contrary with the content of clay minerals, and the distribution of the content of feldspar and carbonate minerals is mussy (Fig. 16). Due to the reducing water environment, both the organic matters and the biogenic siliceous are preserved; combined with the hydrothermal activity, massive hydrothermal silica fluid and sulfide enter into the Niutitang Formation shale, which finally promotes the content of quartz and pyrite. The clay minerals mainly come from the detrital influx, which dilutes the concentration of the organic matters, leading to a negative relationship between the content of TOC and clay minerals. The contents of feldspar and carbonate minerals show faint influence on the content of organic matters due to the limited amounts.

Characteristics of pore structure

The low-pressure nitrogen adsorption (LP-N_2A) curves of the Niutitang Formation shale samples show as IV type, and these curves could be divided into two different types according to the shape of the hysteresis loop. The hysteresis loops of Cn4 and Cn5 samples feature as H_3 type, while that for the other shale samples present as H_4 type, these mean the different shapes of pores in the Niutitang Formation shale (Fig. 17). The H_3 type hysteresis loop indicates the pores in the shale are dominant slit and wedge shape lamellar pores, while the H_4 type hysteresis loop means the parallel plate-shaped pores are dominant.

The distribution of pore aperture could also be distinguished into two types. The Cn4 and Cn5 samples feature two peaks for the distribution of the pore apertures, the left peak of the pore aperture ranges from 3 to 4 nm, and the right peak of the pore aperture varies from 5 to 30 nm. As for the other shale samples, the pore aperture only features one peak, ranging from 3 to 4 nm (Fig. 18). The location of the Cn4 and Cn5 samples is the deep water reducing environment, which favors the preservation of the organic matters and biogenic siliceous. Corresponding to the lithology characteristics, the content of quartz and pyrite is high, while that for the clay minerals are low. As the rigid minerals, the quartz and pyrite could preserve the shape and space of the pores, which contributes to the greater pore aperture in the Niutitang Formation shale. Besides, the minor amount of the plastic minerals would also not fill into the pores. The relationships between the pore specific surface area and content of TOC and the

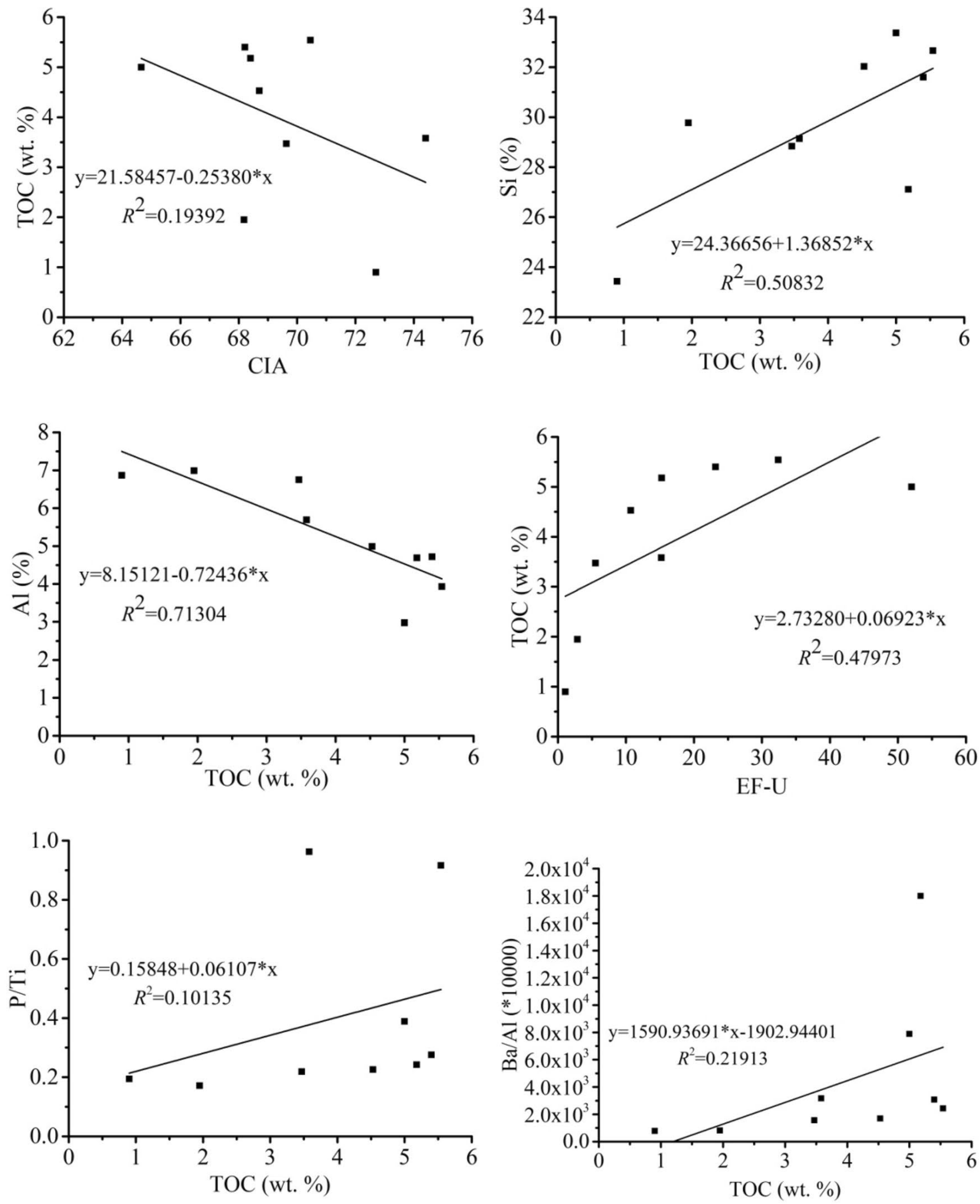


Fig. 15 The relationship between TOC and CIA, Si, Al, EF_U, P/Ti and Ba/Al in Niutitang Formation

pore specific surface area and the quartz also indicate that the new-born nanoscale pores also contribute to development of pores during the thermal evolution procedures. The cleats and intracrystalline pores developed in the clay minerals are compacted, and the dissolved pores are not developed in the feldspar and carbonate minerals, which do not favor the development of the pores (Fig. 19).

Conclusions

1) The content of organic matters in the Niutitang Formation shale is high, especially that for the lower Niutitang Formation shale. As the major elements, Mg and Mn show a certain deficit, while the other features as enrichment. The trace elements in the Niutitang Formation

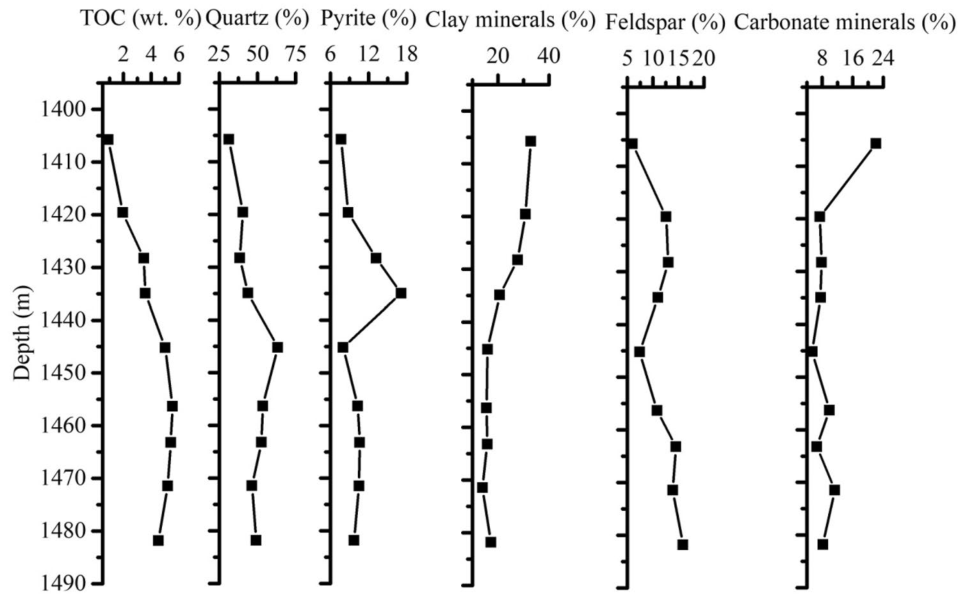


Fig. 16 The relationship between TOC and content of minerals in Niutitang Formation

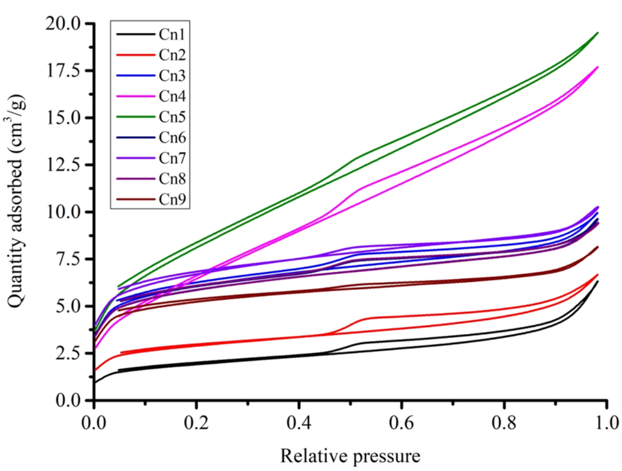


Fig. 17 The LP-N_2A curves of shales in Niutitang Formation

shale presents dominantly deficit. The minerals in the Niutitang Formation shale are dominantly quartz, clay minerals, pyrite, feldspar and carbonate minerals, and the Niutitang Formation shale features as enrichment of siliceous.

2) The paleoclimate of Niutitang period features cold and dry, it tends to be warm and humid at the later Niutitang period, while there is no obvious relationship between the content of organic matters and paleoclimate. The siliceous in the Niutitang Formation shale presents as multi-sources, it is biogenetic siliceous in the lower Niutitang Formation shale, and it is dominantly detrital siliceous for the upper Niutitang Formation shale, and this leads to the decrease of the content of organic matters. The water environment is reductive, which dominantly controls the accumulation of organic matters, the paleo-

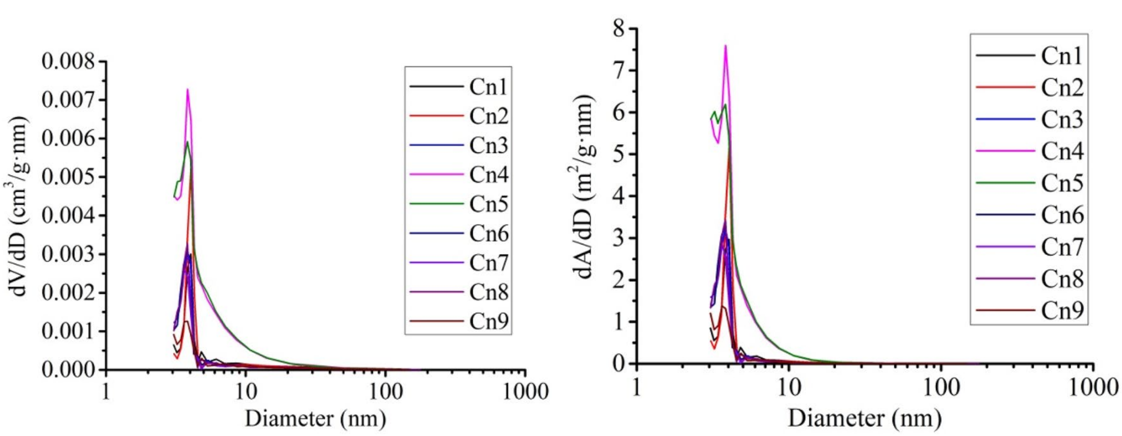


Fig. 18 The incremental pore volume and pore specific surface area curves of shales in Niutitang Formation

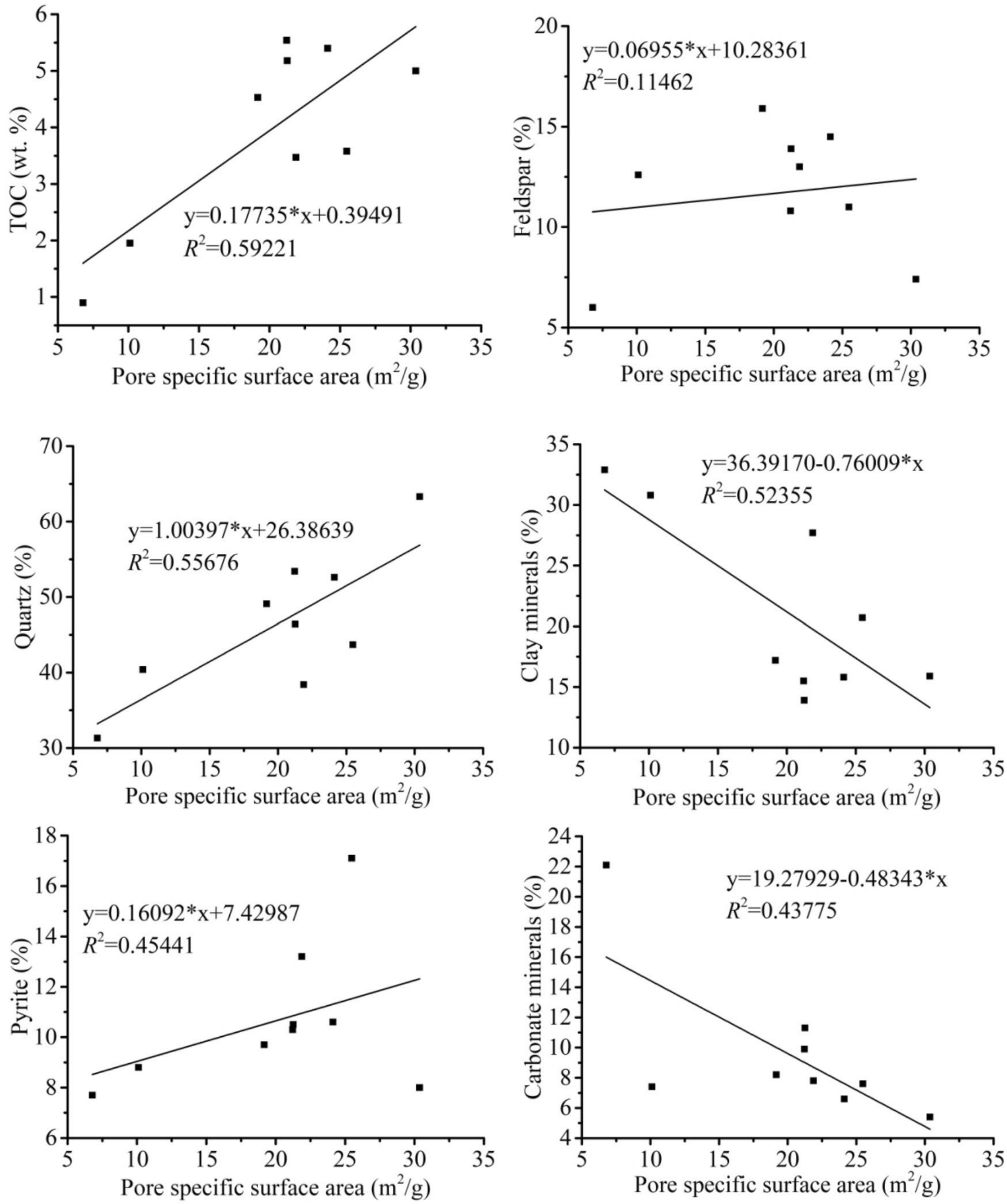


Fig. 19 The relationships of pores and minerals for shales in Niutitang Formation

productivity and hydrothermal activity contribute to the difference enrichment of organic matters.

3) Influenced by the accumulation of the organic matters, the pore structure in the Niutitang Formation shale could be divided into two different types. In the middle of the Niutitang Formation shale, the pores distribute into two sections, 3 nm to 4 nm and 5 nm to 30 nm, respectively, and this is mainly due to the strong reducing environment, hydrothermal activity and the productivity. The pore structure parameters show highly consistence with the content of TOC, quartz and pyrite, it indicates the sedimentary environment not only influences the accumulation of the organic matters, but also the lithology characteristics, and this finally controls the development of the pores in the shale.
4) The characteristics of enrichment of organic matters and pore structure indicate the Niutitang Formation shale is favorable for the development of shale gas, and the

lower Niutitang Formation shale would be the sweet spot stratum.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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