

## SPECIAL REPORT

## Trace element geochemistry of the Lower Cambrian black rock series from northwestern Hunan, South China<sup>\*</sup>

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**Abstract** Samples of black rock series collected from the Lower Cambrian Niutitang Formation, northwestern Hunan Province, China, were analyzed for trace elements. The trace element geochemical characteristics of the ore layer (high enrichments of Ni, Mo, V, U, Cu, Pb, Zn, Cd, Tl and Ba; high U/Th ratios and LREE-enriched patterns with positive Eu and Y anomalies) support the assumption that the Ni-Mo polymetallic layer is of submarine hydrothermal origin. High field strength elements (HFSE) and lithophile elements such as Nb, Ta, Zr, Hf, Li, Be, Rb, Cs, Th and Sc are remarkably higher in the upper unit than those in the lower unit of the Niutitang Formation. These features may reflect that hydrothermal contributions were diminished, and terrigenous constituents were increased in the sediments of the upper unit of the Niutitang Formation.

**Keywords:** black rock series, Early Cambrian, trace elements, northwestern Hunan, China

The seemingly abrupt mass appearance of metazoan phyla during the Early Cambrian, which is called the “Cambrian Explosion”, is one of the most important bio-events in the Earth’s history. The replacement of Ediacaran biota by an emerging diversity of metazoans, which happened in the relatively short period of the Precambrian-Cambrian transitional interval, has aroused great interest of paleontologists, geochemists and geologists for its causes. A lot of progress has been made based on multidisciplinary and systematical studies, but the real cause for such a bio-event is still disputable and remains a topic of general interest<sup>[1~5]</sup>.

Numerous discoveries of metazoans in black shales of Early Cambrian age worldwide have made the studies on the origin of black shales and their formational environments of special significance. The geochemistry of black shales is commonly supposed to be able to reflect the geochemical characteristics of sediment sources and oceanic waters. Thus, study on the trace element (including rare earth elements) concentrations and their relative distribution in these black shales will provide evidence of their origins, and help understand the paleo-oceanic environments in

which the metazoan developed during the Early Cambrian<sup>[6, 7]</sup>.

### 1 Geological setting

In South China, the Early Cambrian strata are mainly composed of black shales, cherts and mudstones, which are distributed along the southeastern margin of the Yangtze Platform, forming a black-rock-series belt with a total coverage around 500 000 km<sup>2</sup><sup>[8]</sup>. Detailed stratigraphic information and measured sections of the terminal Neoproterozoic to Cambrian boundary interval in Sancha profile, 5 km SE of Zhangjiajie, Hunan, and Zunyi profile, 25 km W of Zunyi, Guizhou, can be found in Steiner et al. (2001) and Mao et al. (2002)<sup>[6, 9]</sup>.

In this paper, systematical sampling for trace elemental concentrations was made along the geological profiles at Ganziping, 10 km NW of Zhangjiajie City. The Ganziping section is 15 km NW of the Sancha section, geological settings of both sections are similar.

The black rock series of Niutitang Formation in the Ganziping section, unconformably overlying

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dolomite of Sinian Dengying Formation, may lithologically be divided into two parts; lower unit and upper unit. The lower unit consists of ascending sequence of siliceous shale intercalated with lenses of phosphorite or phosphate nodules with a 90 cm thick-

ness, a Ni-Mo-PGE-Au-bearing sulfide ore bed with a 15 cm thickness, and carbonaceous and siliceous shale with a 5 m thickness. The upper unit consists of carbonaceous hydromica claystone-shale with a thickness of >60 m (Fig. 1).

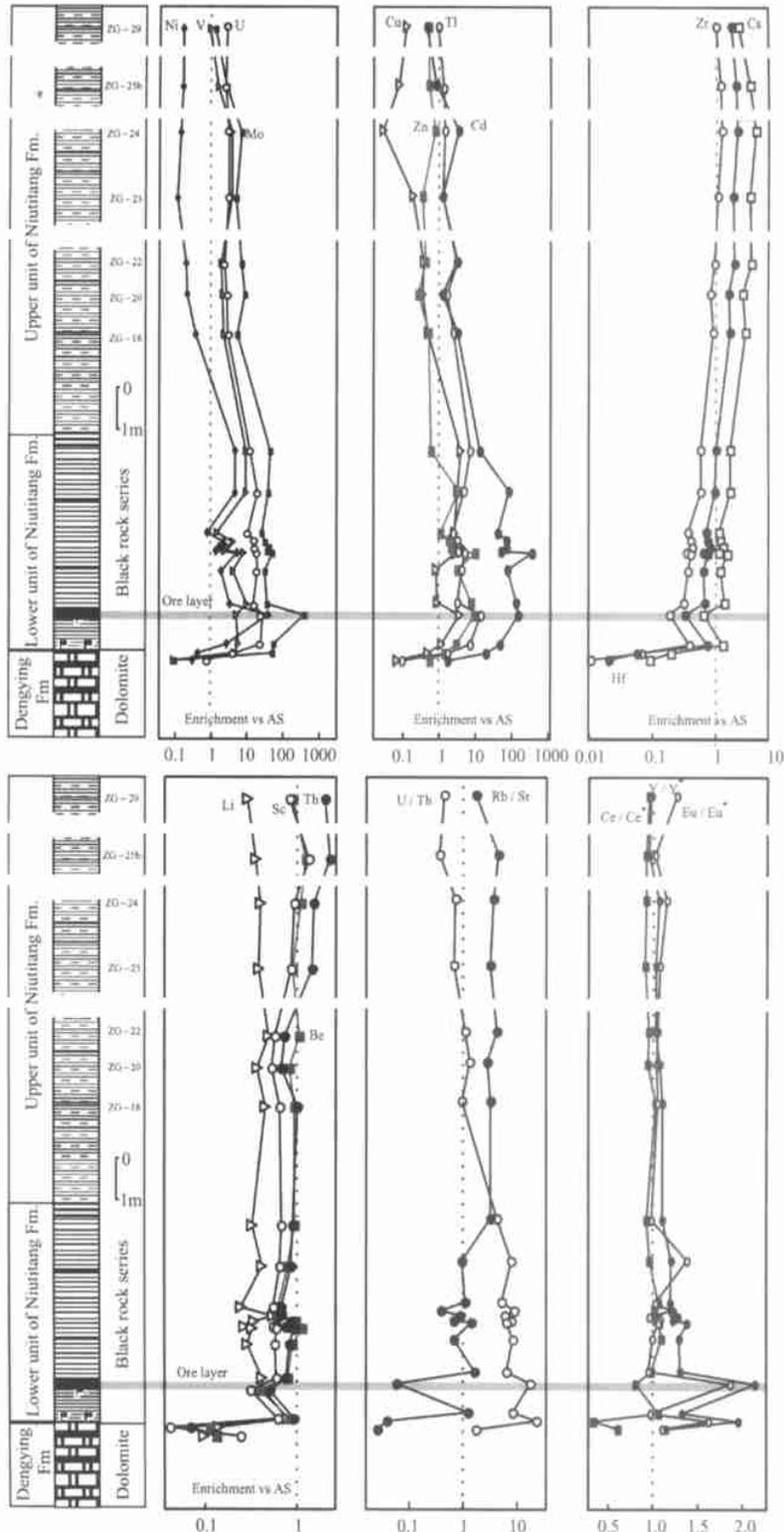


Fig. 1. Trace element distribution in the Niutitang Formation at the Gangziping section, NW Hunan; enrichment of trace elements to an average shale is shown at the lower axis.

## 2 Methods and result

### 2.1 Sampling and method

Of 37 rock samples were collected along the Ganziping section and 20 fresh rock samples selected were used for trace element analysis. The data of the sampling locations were calculated based on measurement of profile and with a 0m definition of boundary of the Dengying Formation and the Niutitang Formation.

Fresh rock samples were powered in an agate mortar with a pestle. 0.05 g powered rock samples were digested with 1 mL HF and 0.6 mL HNO<sub>3</sub> mixed acids in a tightly sealed Teflon PFA screw-cap beakers, heated for 96 h on a hot plate under 190 °C, then evaporated nearly to dryness. The residues were dissolved with 1.0 mL HNO<sub>3</sub> by heating for 3 ~ 5 h at a temperature of 140 °C. For organic carbon-enriched samples, repeated processes for dissolving the residues with 1.6 mL HNO<sub>3</sub> by heating were taken. The solutions were diluted to 1:1000 in mass. Concentrations of trace element and REE were determined using the inductively coupled plasma mass spectrometry (Finnigan Element II) at the State Key Lab for Mineral Deposits Research, Nanjing University. Analytical precision for the concentrations of trace elements and REEs is better than 5%. Analytical results are given in Table 1.

### 2.2 Trace elements

As shown in Table 1 and in Fig. 1, the concentrations of the transition elements and chalcophile elements such as Ni, Mo, V, U, Cu, Pb, Zn, Cd, Tl and Ba in the ore layer are extremely high compared with those of the average shales, with enrichment factors vs. average shale of 38.21, 383.20, 5.06, 27.26, 3.70, 1.84, 9.07, 145.17, 14.15 and 8.33 respectively. These elements are also strongly enriched in black rock series of the lower unit of the Niutitang Formation compared with those of the average shales and the upper unit of the Niutitang Formation, but Pb and Ba, which are also enriched in the upper unit of Niutitang Formation.

In striking contrast to the above-mentioned elements, most of high field strength elements (HFSE) and lithophile elements with large ionic radii such as Nb, Ta, Zr, Hf, Li, Be, Rb, Cs, Th and Sc, demonstrate much lower contents in the ore layer, with enrichment factors vs. average shale of 0.18,

0.09, 0.18, 0.33, 0.42, 0.40, 0.24, 0.64, 0.50 and 0.32 respectively, and in the black rock series of the lower unit of the Niutitang Formation, with enrichment factors vs. average shale of 0.03 ~ 0.46, 0.00 ~ 0.46, 0.07 ~ 0.56, 0.06 ~ 1.00, 0.14 ~ 0.79, 0.11 ~ 1.13, 0.04 ~ 0.53, 0.19 ~ 1.70, 0.07 ~ 0.94 and 0.04 ~ 0.71 respectively. Furthermore, their distributions in the Niutitang Formation exhibit obviously elevated concentrations of these elements in the upper unit compared with the lower unit (Fig. 1).

### 2.3 REEs compositions

Table 1 lists REE data of different samples from the Ganziping section. Eu/Eu\* was calculated by the formula:  $Eu/Eu^* = Eu_{NASC} / (1/2Sm_{NASC} + 1/2Gd_{NASC})$ , Ce/Ce\* and Y/Y\* were calculated in same manner with respect to La and Pr, Dy and Ho respectively.

The abundance level of  $\Sigma$ REE in ore layer (346.24 ppm) is much higher than those in the lower unit rocks (82.63 ~ 160.88 ppm) and those in the upper rocks (98.98 ~ 200.57 ppm). LREE/HREE ratios are much lower in ore layer (6.45) and in the lower unit (2.67 ~ 6.24) than those in the upper unit (8.96 ~ 11.77).

The REE curve of the ore bed shows a positive Eu anomaly ( $Eu/Eu^* = 1.87$ ), a positive Y anomaly ( $Y/Y^* = 2.14$ ) and a slightly negative Ce anomaly ( $Ce/Ce^* = 0.81$ ). REE curves of black rock series of all samples show no Ce anomalies ( $Ce/Ce^* = 0.91 \sim 1.10$ ) but a siliceous shale (ZG-2) with clear negative Ce anomaly ( $Ce/Ce^* = 0.34$ ).

Eu/Eu\* and Y/Y\* ratios of all samples range from 0.97 to 1.87 and from 0.95 to 2.14 respectively. Eu/Eu\* ratios are positively correlated with Y/Y\* ratios ( $r = 0.73$ ), whereas they are negatively correlated with Ce/Ce\* ratios ( $r = -0.59$ ).

## 3 Discussion

### 3.1 Origin of Ni-Mo ore layer

The origin of the Ni-Mo-V-U enriched Lower Cambrian "black rock series" in South China has attracted great attention of geologists from both China and abroad for many years, but it is still controversial. Several hypotheses based on geological investigations and analytical data have been put forward, of

Table 1. REEs compositions (ppm) and enrichment vs average shale of trace elements of rock samples from Dengying Fm. of Sinian and Niutitang Fm. of Early Cambrian in N. W. Hunan

Lithology	Upper unit of Niutitang Fm.												Lower unit of Niutitang Fm.												Dengying Fm. Dolomite	Average shale(10)
	Carbonaceous hydromica claystone-shale						Carbonaceous and siliceous shale						Ni-Mo ore layer		Siliceous shale with phosphorite											
	ZG-29	ZG-25h	ZG-24	ZG-23	ZG-22	ZG-20	ZG-18	ZG-16	ZG-15	ZG-13	ZG-11	ZG-9	ZG-7	ZG-6	ZG-5	ZG-4	ZG-3b	ZG-3	ZG-2							
No	62.31	32.87	24.77	23.18	9.57	8.80	7.86	5.00	4.00	3.00	2.80	2.65	2.55	2.50	2.10	1.30	1.00	0.30	0.10	ZG-0	-0.10					
Location (m)	0.16	0.16	0.14	0.12	0.20	0.21	0.37	4.47	4.46	0.76	2.17	1.64	1.38	5.15	1.89	3.32	38.21	2.65	0.43		0.30	56				
Ni	1.27	2.72	6.72	4.92	6.73	8.56	5.42	42.16	38.99	25.20	30.49	40.37	34.78	49.42	31.33	34.63	383.20	55.00	48.70		0.09	3				
Mo	0.88	1.58	3.66	3.64	1.87	2.05	2.17	9.33	8.92	1.43	4.04	2.82	2.39	8.13	4.10	9.52	5.06	5.79	4.16		0.09	99				
Mn	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0.04	0.21	0.13	0.23	0.26	0.36	0.57	0.16	0.08	1.19	0.14	0.03		0.12	927				
Co	0.03	0.06	0.04	0.04	0.06	0.04	0.06	0.84	0.89	0.78	0.78	1.40	1.27	1.76	1.11	0.95	1.00	1.53	0.19		0.14	15				
Zr	0.86	1.12	1.27	1.11	1.15	0.94	0.92	0.73	0.71	0.44	0.51	0.60	0.50	0.80	0.68	0.87	0.41	0.83	4.39		0.12	71				
W	0.02	0.94	0.90	0.89	1.22	1.23	1.20	1.52	2.10	1.20	7.31	2.58	1.64	1.20	1.00	0.68	0.94	0.75	0.21		1.15	2				
Cu	0.12	0.07	0.03	0.18	0.37	0.33	0.49	3.94	3.08	2.59	2.45	4.16	3.32	2.77	0.83	0.87	3.70	1.11	0.48		0.07	39				
Pb	3.58	2.50	4.59	2.48	3.46	2.31	2.34	3.37	6.12	2.28	1.75	3.08	2.80	2.12	2.87	2.40	1.84	3.54	0.26		1.60	18				
Zn	0.50	0.52	0.79	0.35	0.41	0.25	0.53	0.59	3.49	1.06	1.87	2.16	2.55	10.32	3.24	7.67	9.07	3.01	1.39		0.56	76				
Ga	1.14	1.62	1.42	1.23	1.29	1.05	1.06	0.71	0.65	0.50	0.54	0.66	0.53	0.65	0.57	0.59	0.41	0.66	0.07		0.08	16				
Tl	0.96	1.33	1.37	1.21	3.17	1.59	2.46	7.04	4.68	2.36	3.25	3.42	3.35	4.93	4.05	3.14	14.15	7.26	1.74		0.09	1.1				
Cd	0.43	0.83	3.43	1.26	2.87	1.26	3.09	12.74	82.57	40.17	69.43	73.70	49.83	353.09	77.13	133.96	145.17	48.04	19.91		1.70	0.23				
Ba	21.28	5.97	7.26	5.55	3.26	2.77	3.69	2.59	11.16	2.42	2.16	2.17	2.83	2.55	2.57	2.53	8.33	3.66	9.24		2.30	469				
Sr	0.16	0.09	0.10	0.09	0.06	0.07	0.08	0.05	0.17	0.10	0.32	0.18	0.19	0.10	0.20	0.09	1.27	0.13	0.29		0.53	342				
Li	0.28	0.35	0.39	0.38	0.48	0.36	0.45	0.32	0.41	0.24	0.56	0.33	0.26	0.32	0.28	0.42	0.42	0.79	0.14		0.09	50				
Be	0.87	1.21	1.08	0.89	1.05	0.83	0.93	0.94	0.80	0.60	0.66	0.97	0.79	1.13	0.87	0.80	0.40	0.83	0.11		0.13	2.2				
Rb	0.83	1.24	1.13	0.92	0.77	0.58	0.76	0.53	0.49	0.35	0.40	0.52	0.39	0.46	0.44	0.49	0.24	0.49	0.04		0.04	108				
Cs	2.21	3.49	4.11	3.44	3.66	2.59	2.98	1.70	1.70	1.11	1.18	1.32	1.13	1.48	1.19	1.38	0.64	1.31	0.19		0.09	3.7				
Nb	0.13	1.05	1.10	0.85	1.00	0.78	0.96	0.45	0.43	0.34	0.34	0.46	0.37	0.41	0.38	0.35	0.18	0.45	0.03		0.03	14				
Ta	0.05	0.19	0.28	0.13	0.63	0.12	0.35	0.29	0.46	0.23	0.23	0.27	0.11	0.23	0.06	0.07	0.09	0.29	0.00		0.12	1.6				
Zr	0.99	1.18	1.25	1.03	0.94	0.83	0.91	0.56	0.56	0.37	0.39	0.43	0.33	0.39	0.36	0.31	0.18	0.38	0.07		0.01	142				
Hf	1.74	2.05	2.18	1.87	1.94	1.59	1.64	1.00	0.95	0.72	0.74	0.80	0.62	0.72	0.64	0.66	0.33	0.75	0.06		0.02	2.5				
Sc	0.81	1.31	0.91	0.83	0.57	0.52	0.63	0.67	0.65	0.54	0.59	0.71	0.56	0.59	0.57	0.59	0.32	0.62	0.04		0.24	10				

To be continued

Lithology	Upper unit of Nunitang Fm.														Lower unit of Nunitang Fm.														Dengying Fm Dolomite	North American shale (NASC)
	Carbonaceous hydromica claystone-shale														Carbonaceous and siliceous shale															
	ZG-29	ZG-25b	ZG-24	ZG-23	ZG-22	ZG-20	ZG-18	ZG-16	ZG-15	ZG-13	ZG-11	ZG-9	ZG-7	ZG-6	ZG-5	ZG-4	ZG-3b	ZG-3	Siliceous shale with phosphinite	ZG-2	ZG-0									
No	62.31	2.66	1.96	0.44	1.68	33.11	39.21	36.38	31.12	24.74	19.7	22.14	18.48	21.49	14.11	13.22	19.75	15.34	23.25	15.99	18.85	63.03	15.75	11.99	38.68	31.1				
Location (m)	32.87	24.77	23.18	9.57	8.80	7.86	5.00	4.00	3.00	2.80	2.65	2.55	2.50	2.10	1.30	1.00	0.30	0.10	-0.10											
U	2.66	2.50	3.11	3.00	2.40	2.60	2.94	11.59	19.72	10.65	16.75	15.22	17.08	17.48	19.85	14.59	27.26	23.91	4.74	0.72										
Th	1.96	2.20	1.47	1.43	0.73	0.66	1.00	0.89	0.85	0.68	0.64	0.88	0.75	0.94	0.81	0.75	0.50	0.94	0.07	0.13										
U/Th	0.44	0.37	0.69	0.69	1.07	1.29	0.96	4.24	7.57	5.14	8.48	5.67	7.45	6.07	7.99	6.33	17.70	8.32	22.23	1.75										
Rb/Sr	4.36	3.60	3.16	4.12	2.75	3.21	3.08	0.92	1.09	0.39	0.89	0.66	1.40	0.69	1.66	0.06	1.21	0.04	0.03											
La	67.1	76.14	71.07	58.5	48.72	38.03	46.3	37.57	45.68	31.91	28.14	44.22	32.62	51.74	37.01	37.68	89.63	36.12	7.51	54.39	66.7									
Ce	8.25	9.53	8.95	7.36	5.78	4.52	4.97	4.83	5.8	3.56	3.19	4.84	3.62	5.52	3.92	4.3	10.07	4.04	2.18	11.05	7.9									
Pr	28.6	33.6	30.48	27.39	20.97	15.92	18.05	20.21	23.97	14.22	13.13	19.19	15.07	23.03	16.72	18.57	43.98	16.91	10.58	54.45	27.4									
Nd	4.15	5.07	4.31	4.14	2.67	2.27	2.64	4.19	4.55	2.63	2.48	3.56	2.96	4.26	3.17	3.54	7.57	3.07	2.07	10.03	5.59									
Sm	1.09	1.11	1.06	0.96	0.6	0.51	0.6	1.01	1.48	0.63	0.69	0.81	0.79	1.13	0.72	0.8	3.73	0.71	0.93	2.9	1.18									
Eu	3.75	4.84	4.06	3.95	2.54	2.19	2.61	5.07	5.26	2.97	2.74	4.02	3.66	5.33	3.46	4.05	10.56	3.56	3.12	13.67	5.2									
Tb	0.6	0.83	0.68	0.64	0.38	0.35	0.45	0.95	0.94	0.52	0.51	0.73	0.68	0.94	0.67	0.78	1.87	0.68	0.58	2.32	0.85									
Dy	3	4.28	3.66	3.13	1.98	1.84	2.48	5.04	4.71	2.85	2.82	3.86	3.58	4.74	3.4	3.75	9.13	3.49	3.43	9.72	5.8									
Y	13.69	19.02	18.13	17.01	10.7	10.22	14.54	28.71	29.98	17.63	18.07	25.29	22.5	33.57	20.86	23.61	94.44	22.13	34.17	55.22	28									
Ho	0.5	0.72	0.62	0.66	0.41	0.38	0.53	1.03	1	0.58	0.58	0.78	0.72	0.96	0.59	0.67	1.64	0.61	0.69	1.81	1.04									
Er	1.81	2.61	2.28	1.98	1.32	1.23	1.75	2.95	2.76	1.7	1.72	2.31	2.07	2.82	2.21	2.5	5.63	2.22	2.6	5.39	3.4									
Tm	0.31	0.46	0.38	0.39	0.28	0.24	0.36	0.53	0.49	0.31	0.32	0.43	0.4	0.52	0.36	0.39	0.8	0.38	0.39	0.86	0.5									
Yb	2	2.82	2.4	2.3	1.63	1.36	2.05	2.74	2.38	1.76	1.78	2.31	2.02	2.65	1.99	2.15	3.71	2.22	2.12	5.01	3.06									
Lu	0.25	0.35	0.31	0.36	0.25	0.23	0.34	0.45	0.38	0.29	0.29	0.38	0.34	0.42	0.27	0.28	0.46	0.28	0.27	0.8	0.46									
ΣREE	168.22	200.57	184.78	159.89	122.98	98.98	119.82	133.76	150.88	95.66	89.68	132.5	106.4	160.88	111.4	121.92	346.24	112.16	82.63	266.3	188.18									
L/H	11.64	9.74	10.58	9.65	11.77	10.35	8.96	4.6	5.74	6.11	5.66	6.24	5.23	5.92	5.99	5.75	6.45	5.7	2.67	4.33	6.89									
Ce/Ce*	0.95	0.93	0.93	0.91	0.96	0.95	1.03	0.93	0.96	1.06	1.02	1.06	1.03	1.02	1.07	1.1	0.98	0.81	1.06	0.34	0.62	0.95								
Eu/Eu*	1.26	1.02	1.16	1.08	1.06	1.04	1.05	0.99	1.38	1.03	1.2	0.97	1.08	1.07	0.99	0.95	1.87	0.97	1.62	1.11	1.26									
Y/Y*	0.98	0.95	1.06	1.04	1.03	1.07	1.11	1.1	1.2	1.2	1.23	1.28	1.22	1.38	1.29	1.31	2.14	1.33	1.95	1.15	0.98									

which, three are representative: (1) extra-terrestrial sources<sup>[8]</sup>, (2) submarine hydrothermal exhalative origin<sup>[9, 11]</sup>, and (3) syngenetic marine sedimentation<sup>[9]</sup>.

The trace element geochemical characteristics of the ore layer show as the following (Table 1, Fig. 1): (1) The high enrichments of Ni, Mo, V, U, Cu, Pb, Zn, Cd, Tl and Ba exceed the enrichment pattern of other Neoproterozoic to Early Cambrian metalliferous black shales<sup>[12, 13]</sup>. (2) The U/Th ratios of the samples from the ore layer and the lower unit of Niutitang Fm., ranging from 4.24 to 22.23, are much higher than those of the sample in the upper unit of Niutitang Fm., ranging from 0.44 to 1.29. (3) LREE-enriched patterns with positive Eu anomalies and positive Y anomalies are exhibited in the ore layer.

Ba and chalcophile elements such as As, Sb, Ag, Cu, Zn are strongly enriched in sulfide deposits associated with hydrothermal vent<sup>[14]</sup>. U/Th ratios are different between hydrothermal exhalative deposits ( $U/Th > 1$ ) and normal marine sediments ( $U/Th < 1$ )<sup>[15, 16]</sup>. All of REE patterns of acidic hydrothermal fluids exhibit LREE-enriched patterns with positive Eu and Y anomalies<sup>[17]</sup>. Positive Eu anomalies, which are very common in marine sediments near the spreading ocean ridges where the hydrothermal activities develop<sup>[17-20]</sup>, are the most persuasive evidence for the hydrothermal sources of the sulfide layer and cherts.

Similar trace elemental geochemical characteristics between the ore layer and hydrothermal deposits support that the sulfide layer is of a submarine hydrothermal origin. This hypothesis has further been confirmed by other scholars<sup>[9, 21]</sup>.

### 3.2 Trace elemental distribution patterns

The concentrations of trace elements show great variations with section. The lower unit, by comparison with upper one, is characterized by the enrichments of chalcophile elements and transition elements (Cr, Ni, Cu, Pb, Zn, V, Fe, W, Mo), dispersion elements (Cd and Tl) and radioactive element (U). Of these enriched elements, Ni, Mo, V and U are extremely high and, at some locations, become Ni-Mo-V-U ores with economic value (Fig. 1). Such distribution patterns of these elements in the Niutitang Formation are believed to result from hydrother-

mal activities, which probably occurred during the sedimentation of the lower unit. So most of the critical trace elements indicative of palaeoredox conditions (V/Ni; V/Cr; Ni/Co; U/Th) cannot be applied to the lower Niutitang Formation, due to the obvious hydrothermal input of Ni, Cr and U.

In contrast, high field strength elements (HFSE) and lithophile elements with large ionic radii such as Nb, Ta, Zr, Hf, Li, Be, Rb, Cs, Th and Sc are remarkably higher in the upper unit than those in the lower unit of the Niutitang Formation (Fig. 1). These elements are generally considered to be immobile during weathering and sedimentary processes. They are incorporated in detrital phases in sediments and sedimentary rocks<sup>[22, 23]</sup>. These features may reflect that hydrothermal contributions were diminished in the upper unit, in the course of terrestrial sources becoming more important during the forming period of upper unit. This inference is confirmed by the elevated content of argillaceous constituents in upper unit of the Niutitang Formation.

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