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Trace Element Geochemistry of Black Shales in Singhbhum Mobile Belt, Eastern India: Implications For Source Rock and Paleoredox Conditions

Geology

KEYWORDS : Black shales; paleoredox conditions; Singhbhum craton

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ABSTRACT

Studied black shales from Singhbhum Mobile Belt (SMB), eastern India are enriched in chalcophile elements such as Cu, Ni, Co, V and Cr and radioactive elements such as Th and U relative to North American Shale Composite (NASC). Their chondrite normalized light rare earth element (LREE) enrichment and heavy rare earth element (HREE) depletion indicates that the rare earth element (REE) concentrations decreased gradually from Gd to Lu rather than severely affected by the diagenesis and weathering processes. The comparison of immobile element ratios (Th/Sc, Th/Co, Th/Cr, Cr/Th, and La/Sc) of studied samples with those of sediments derived from felsic rocks, basic rocks, Upper Continental Crust (UCC) and Post Archean Australian Shale (PAAS) showed that the source of studied shales were generally felsic in nature. High U (0.39 to 11) content, significant negative Ce anomaly and ratios [Ni/Co, V/Cr and V/(V+Ni)] supports in favour of their reducing depositional environment.

Introduction

In the present study trace element geochemical data has been interpreted with an aim to decipher source rock characteristics and paleo-redox conditions of the Proterozoic shales from the Singhbhum Mobile Belt (SMB), eastern India. Geochemical data of terrigeneous clastic rocks has been widely used to work out the composition of source area (Wronkiewicz and Condie, 1989; Chakrabarti *et al.,* 2007), to evaluate weathering processes, post-depositional metasomatism and paleoclimate (Fedo *et al.,* 1997), and to reconstruct the tectonic setting of a depositional basin (McLennan *et al.,* 1989). Proterozoic shales have been studied in various parts of the world in order to understand the composition of the upper continental crust (Taylor and McLennan, 1985) as they represent the most abundant type of sediments in worldwide sedimentary basins and are considered to represent the average crustal composition of the provenance much better than any other detrital sedimentary rocks.

Brief Geological Setup

The Singhbhum Mobile Belt (SMB), almost 200km long, is nearly E-W striking geological province in the Eastern Indian Shield (Fig. 1, after Saha, 1994). This belt comprises the Dhanjori, Chaibasa, Dhalbhum, Dalma and Chandil Formations (Acharyya, 2003). The Dhanjori Formation is made up of lower and upper members. The lower member contains phyllites, quartzites, and thin conglomerates, whereas, volcanic and volcaniclastic rocks along with some quartzites and phyllites are important components of the upper member (Mazumder, 2005). The Chaibasa Formation is made up of interbedded sandstones, shales, and a heterolithic (very fine sandstone/siltstone–mudstone) facies with minor basic volcanic rocks. The 6 to 8 km thick siliciclastic Chaibasa Formation rests conformably on the granitic basement. The 2 to 4 km thick Dhalbhum Formation unconformably overlies the Chaibasa Formation, and it is composed of alternating phyllites and quartzites with ferruginous shale towards the base of the unit (Mazumder, 2005). The Dhalbhum Formation is conformably overlain by a thick sequence of mafic–ultramafic volcanic rocks with lenses of basic agglomerates know as the Dalma Formation. The Chandil Formation is of Mesoproterozoic age (~1500 Ma, Rb–Sr whole rock isochron age) (Sengupta and Mukhopadhaya, 2000), and it is made up of quartzites, mica schists, carbonaceous phyllite, weakly metamorphosed acidic volcanic and volcaniclastic rocks (including vitric and lithic tuffs), and amphibolites. The metasedimentary and metavolcanic Chandil Formation lies between the Dalma volcanic belt and the Chotanagpur Granite Gneiss Complex. The shale section outcropping (near Chandil, where NH-33 crosses NH-32) along the road is several hundred metres thick. The carbonaceous rich shales occur sporadically and repeatedly within the thick dark grey to greenish grey shale section.

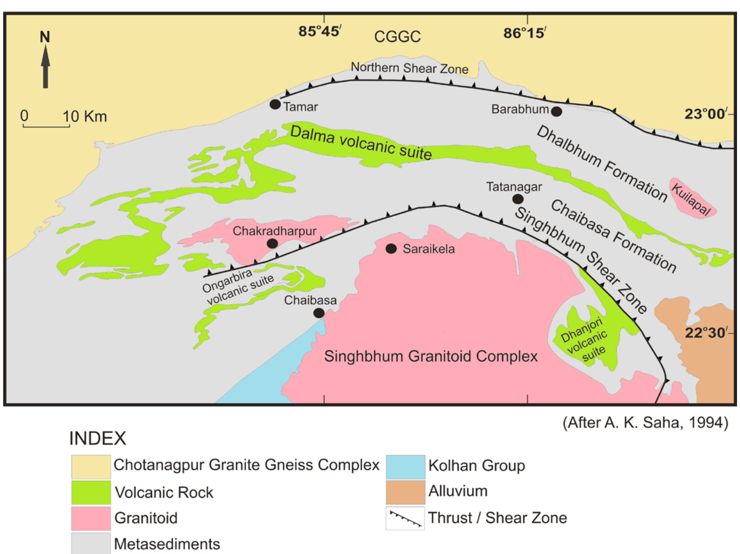

Fig. 1. Simplified geological map of the Singhbhum Mobile Belt,

eastern India (after Saha, 1994) showing major stratigraphic units.

Materials and methods

Studied black shale samples were powdered to -200mesh size in agate vessel. A solution of each sample was prepared for the determination of trace elements using inductively coupled plasma-mass spectrometry techniques (ICP-MS) at National Geophysical Research Institute (NGRI), Hyderabad following the open acid digestion method given by Balaram and Gnaneshwara 2003. The instrumental and data acquisition parameters are the same as given in Balaram and Gnaneshwara, 2003. The precision of ICP-MS data is better than ±6% RSD for all the REE and was obtained in all cases with comparable accuracy.

Results and discussion

General characteristics

Trace element data (including REE) of the black shale samples from Singhbhum Mobile Belt is given in Table 1. As per this data, studied samples are enriched in chalcophile elements relative to NASC such as Cu (avg. 44ppm), Ni (avg. 45ppm), Co (avg. 38 ppm), V (avg. 300 ppm) and Cr (avg. 142 ppm). Radioactive element distributions (Th and U) in these shales are also enriched relative to the NASC. The average Th/U ratio (3.1) indicates enrichment of uranium compared to the NASC. The total REE content of present shales varies from 14 to 270ppm, with an average value of 113ppm (Table 1). The chondrite normalized REE plots of these shales are given in Fig. 2. These samples show moderate fractionation of LREEs [avg. $(La/Sm)_N$ = 3.52], while the HREEs are very slightly fractionated [avg. $(Gd/Yb)_N$ = 1.24] compare to NASC (=1.39) and Proterozoic Shale Standard (=1.62) (Condie 1993). Their pronounced negative Eu anomalies <0.85 and [Gd/Yb_N ratios (0.77-1.60)<2.0] are characteristic of the rocks from the Post–Archean period (Taylor and McLennan 1985; Mishra and Sen 2012). The results show a HREE depletion with a $(Gd/Lu)_N$ ratio in a range of 1.60–0.72, indicating that the REE concentrations decrease gradually from Gd to Lu. Such depletion widely exists in the black shales, suggesting that the depletion was not severely affected by the diagenesis and weathering of the rocks.

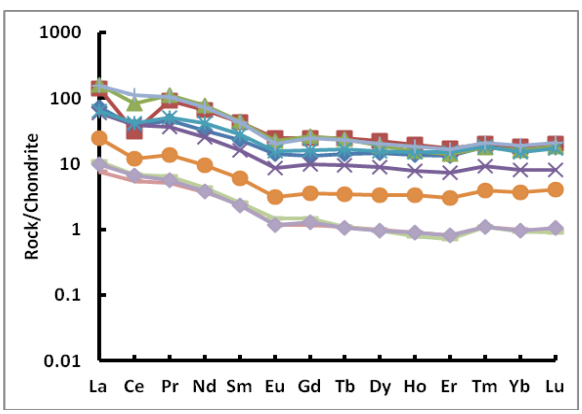

Fig. 2. Chondrite normalized REE pattern of black shale samples. Normalized values are taken from Taylor and Mclannen, 1985.

Source rock characteristics

The Th/Sc ratio is a good indicator of bulk composition of the provenance (Taylor and McLennan 1985). A Th/Sc >1 indicates a felsic (continental crust) source, i.e., enriched in an incompatible element source, whereas, a Th/Sc <0.5 is found in more mafic sources, i.e., enriched in compatible elements. In case of present shales Th/Sc ratios are >0.5 suggesting intermediate to felsic source (Fig.3a). Felsic source of present samples is also supported by diagram Th/Co vs. La/Sc (Fig. 3b), high LREE/HREE ratios (3.70 to 11.80) and negative europium anomalies (Eu/Eu*= 0.63 to 0.82) (Cullers, 2002). The ratios between relatively immobile elements such as La/Sc, Th/Sc, Th/Co, and Th/Cr are significantly different in felsic and basic rocks and may allow constraints on the average provenance composition (Cox *et al.,* 1995) because these elements have very short residence time in the water column, and thus are mostly transferred quantitatively into the sedimentary record. Hence, such parameters of studied shales are compared with those of sediments derived from felsic rocks, basic rocks, UCC and PAAS (Table 2). This comparison also suggests that these ratios are within the range of felsic rocks.

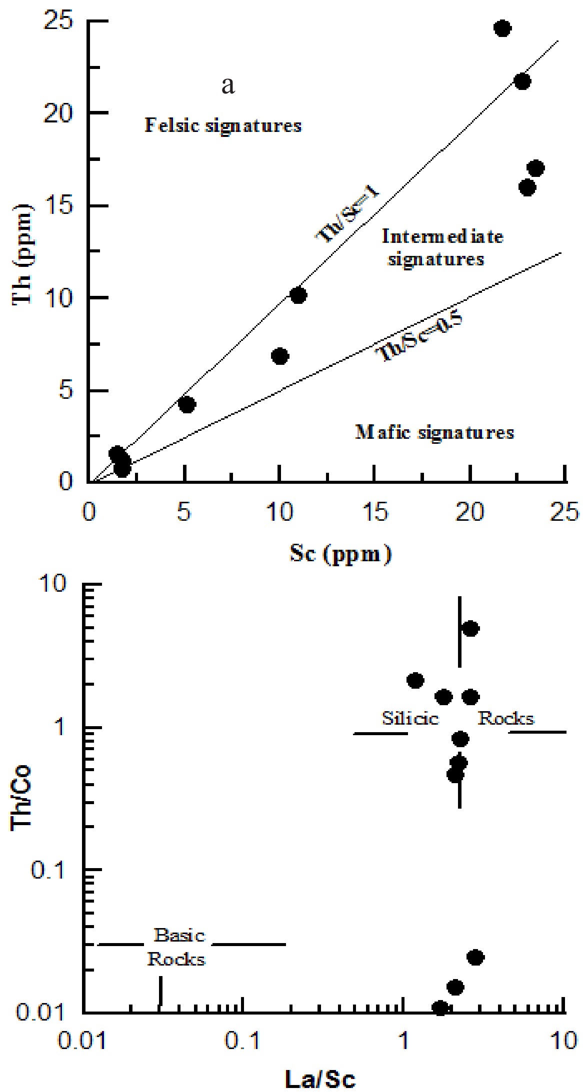

Fig. 3. (a) Sc vs Th plot of black shales in Singhbhum mobile belt; (b) La/Sc vs Th/Cu plot for black shales in Singhbhum mobile belt (after Cullers, 2002).

Table. 1. Trace and rare earth element data of black shales in Singhbhum mobile belt, Eastern India

Samples / Elements	SK-6	SK-2	SM-3	SM-8	SC-3	SC-6	SM-1	SP-7	SC-8	SK-8
Sc	23.03	23.40	22.70	9.96	10.95	5.14	21.69	1.69	1.44	1.75
V	260.51	147.31	248.03	113.82	1154.57	86.69	105.75	13.05	15.89	16.20

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Cr	293.05	152.69	126.78	102.48	198.32	26.76	147.75	84.73	48.36	85.35
Co	7.48	20.24	13.16	12.24	21.94	2.65	4.95	108.79	62.31	51.54
Ni	48.03	63.45	33.76	67.49	56.26	19.11	17.76	38.40	54.96	31.32
Cu	69.44	74.11	41.41	37.14	79.37	27.59	17.80	16.30	19.53	18.29
Zn	83.78	96.88	118.49	94.04	224.25	56.11	38.18	34.15	34.65	133.23
Ga	23.91	23.17	26.66	9.32	15.12	3.15	27.28	1.45	2.13	1.72
Rb	217.50	229.79	214.89	107.53	171.47	32.78	151.44	7.63	8.59	10.58
Sr	52.02	24.79	31.71	159.27	38.32	13.90	16.96	9.23	7.64	11.05
Y	30.55	42.81	31.07	18.81	44.89	8.21	37.82	2.06	1.74	2.18
Zr	242.88	282.94	231.83	94.12	146.48	31.97	242.89	14.98	14.80	6.18
Nb	22.72	19.92	17.45	4.52	5.92	2.22	19.03	3.66	1.79	2.79
Cs	11.50	14.00	6.55	8.85	11.08	2.27	5.11	0.33	0.23	0.82
Ba b	390.73	432.15	399.80	145.35	443.61	102.06	633.10	41.29	55.17	39.34
Hf	7.115	8.53	7.08	2.665	3.785	0.858	7.496	0.456	0.437	0.19
Ta	1.461	0.685	0.373	0.508	0.094	0.258	2.227	2.949	0.902	2.487
Pb	6.515	5.74	5.924	5.685	5.964	3.898	5.916	3.082	3.012	3.573
Th	16.037	17.102	21.736	6.894	10.219	4.3	24.634	1.198	1.533	0.798
U	5.522	3.754	7.802	2.95	11.056	1.34	2.831	0.528	1.239	0.386
La	26.99	52.45	59.56	21.73	23.14	9.18	56.03	2.84	3.98	3.68
Ce	36.30	30.29	79.68	37.66	39.83	11.66	107.26	5.33	6.64	6.31
Pr	6.24	12.47	15.28	4.98	7.00	1.90	14.28	0.72	0.89	0.78
Nd	22.83	47.48	55.78	18.11	30.00	6.86	52.13	2.64	3.11	2.73
Sm	5.45	9.98	10.35	3.78	6.56	1.40	10.04	0.58	0.59	0.54
Eu	1.25	2.14	1.97	0.75	1.36	0.27	1.80	0.10	0.13	0.10
Gd	4.01	7.65	7.96	3.06	4.96	1.10	7.62	0.36	0.45	0.40
Tb	0.82	1.46	1.38	0.56	0.95	0.20	1.33	0.06	0.06	0.06
Dy	5.67	8.57	7.17	3.37	5.99	1.26	7.66	0.38	0.36	0.37
Ho	1.18	1.65	1.35	0.67	1.30	0.29	1.58	0.08	0.07	0.08
Er	3.34	4.24	3.56	1.83	3.72	0.76	4.22	0.21	0.18	0.21
Tm	0.65	0.74	0.63	0.33	0.65	0.14	0.76	0.04	0.04	0.04
Yb	4.20	4.63	4.04	2.05	3.76	0.91	4.71	0.25	0.23	0.24
Lu	0.70	0.77	0.70	0.31	0.65	0.15	0.79	0.04	0.04	0.04
Total REE	120	184	249	99	130	36	270	14	17	16
Ratios										
V/Cr	0.89	0.96	1.96	1.11	5.82	3.24	0.72	0.15	0.33	0.19
Th/Cr	0.05	0.11	0.17	0.07	0.05	0.16	0.17	0.01	0.03	0.01
Cr/Th	18.27	8.93	5.83	14.87	19.41	6.22	6.00	70.72	31.54	106.95
La/Sc	1.17	2.24	2.62	2.18	2.11	1.79	2.58	1.68	2.76	2.10
La/Ce	0.74	1.73	0.75	0.58	0.58	0.79	0.52	0.53	0.60	0.58
Ni/Co	6.42	3.14	2.56	5.52	2.56	7.20	3.58	0.35	0.88	0.61
Cr/Ni	6.10	2.41	3.75	1.52	3.52	1.40	8.32	2.21	0.88	2.73
Th/Co	2.14	0.85	1.65	0.56	0.47	1.62	4.97	0.01	0.02	0.02

Table 2. Range of elemental ratios of studied black shales compared to the ratios from felsic rocks, mafic rocks, upper continental crust, and Post-Archaean Australian shale.

Elemental ratio	Range of black shale Samples from SMB	Range of Sediments (Felsic rocks) [10]	Range of Sediments (Mafic rocks) [10]	Upper Continental Crust [29]	Post-Archaean Australian average shale [29]
Th/Sc	0.46-1.14	0.84 - 20.5	0.05 - 0.22	0.79	0.9
Th/Co	0.01-4.97	0.67 - 19.4	0.04 - 1.4	0.63	0.63
Th/Cr	0.01-0.17	0.13 - 2.7	0.018 - 0.046	0.13	0.13
Cr/Th	5.83-106.95	4.00 - 15	25 - 500	7.76	7.53
La/Sc	1.17-2.76	2.5 - 16.3	0.43 - 0.86	2.21	2.4

Paleo-redox conditions

Trace-element ratios such as Ni/Co, V/Cr, and V/(V + Ni) have been used to evaluate paleoredox conditions by various workers (e.g., Jones and Manning, 1994; Nagarajan *et al.,* 2007). In the studied samples Ni/Co ratio varies from 0.35 to 7.20, V/Cr from 0.15 to 5.82 and V/(V+Ni) varies from 0.22 to 0.95. All these values indicate almost anoxic condition for the studied black shale samples (Jones and Manning, 1994). High U concentration and negative Ce anomaly (<–0.10) of studied black shales are likely result of the reducing sedimentary environment under which present studied black shales were formed (Wilde *et al.,* 1996; Nagarajan *et al.,* 2007; Yang *et al.,* 2011).

Conclusions

On the bases of immobile element ratios [like Th/Sc (>0.5 and <1), and La/Th and Th/Sc (more or less close to the PAAS values), high LREE/HREE ratios (3.70 to 11.80)] and negative europium anomalies (Eu/Eu*= 0.63 to 0.82), it is concluded that the source of studied shales is felsic in nature. Further, parameters such as Ni/Co ranging from 0.35 to 7.20, V/Cr ranging from 0.15 to 5.82 and V/(V+Ni) varies from 0.22 to 0.95, high concentration of U (0.39 to 11) and prominent Ce anomalies (<–0.10) are good indicators to support or conclude the reducing (anoxic) sedimentary environment under which present studied black shales were formed.

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