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ORIGINAL ARTICLE

Rare earth element geochemistry of Post- to Neo-archean shales from Singhbhum mobile belt, Eastern India: implications for tectonic setting and paleo-oxidation conditions

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Abstract In the present study, trace element (including rare earth element) chemical data has been interpreted with the aim to decipher the tectonic setting and paleo-redox conditions of the Post- to Neo-archean shales from the Singhbhum Mobile Belt, eastern India. The data show moderate enrichment of compatible elements [such as Cu (avg. 59.28 ppm), Ni (avg. 59.49 ppm), V (avg. 234.24 ppm) and Cr (avg. 181.23 ppm)] relative to the Post-Archean Australian Shale. Their chondrite normalized light rare earth elements are moderately fractionated [$(La/Sm)_N$ ranges from 2.21 to 5.78], whereas heavy rare earth elements show a nearly flat pattern [$(Gd/Lu)_N$ ranges from 0.74 to 1.68]; this indicates that the rare earth element (REE) concentrations, rather than being severely affected by the diagenesis and weathering processes, decreased gradually from Gd to Lu. The Post-Archean Australian Shale normalized multi-element diagram shows the slight enrichment of Cr, V, Zr, Y, U and Sc, whereas Sr, Pb, Hf and Th are depleted. The notable negative anomaly of Sr indicates the least accumulation of plagioclase, which is also supported by the negative Eu-anomaly in these rocks. The La–Th–Sc and Th–Zr–Sc tectonic setting diagrams indicate their continental arc setting. The geochemical parameters, such as U/Th, V/Cr, Ni/Co, and Cu/Zn, indicate that these shales were deposited under oxic to anoxic environmental conditions.

Keywords Geochemistry · Shales · Singhbhum craton · Tectonic setting

1 Introduction

Among the clastic sedimentary rocks, shales are considered the most abundant and well homogenized types of sediments in sedimentary basins (Pettijohn 1975). Shales provide the average crustal composition of the provenance much better than any other detrital rock can (McCulloch and Wasserburg 1978; Rudnick and Gao 2004). Various geochemical studies throughout the world have been carried out on Proterozoic shales in order to better understand their provenance characteristics, weathering processes, palaeoclimate, tectonic settings and paleoredox conditions (Taylor and McLennan 1985; Condie and Wronkiewicz 1990; Raza et al. 2002; Cullers 2002; Nagarajan et al. 2007; Absar et al. 2009). The shales of the Singhbhum Mobile Belt (SMB) occur in the Dhalbhum Formation of the Singhbhum Group. The carbonaceous phyllite bands in the western part are not very persistent, either pinching out or changing to purple phyllite or normal phyllite along the strike length. In the eastern part, a parallel range of hills consisting almost entirely of Black shale is exposed in the east and west of Chandil, north of the Dalma metavolcanic suite. Shales also crop out just south of the Dalma metavolcanic suite near Bansa. Ferruginous black shale occurs along the margins of the Dalma metavolcanic suite. The present study stands on trace elements {including rare earth elements (REEs)} because these elements are not seriously affected by secondary processes like diagenesis, metamorphism and heavy mineral fractionation (Condie 1993; Rudnick and Gao 2004), thus preserving a record of average upper crustal elemental abundances. It is well know that Archean and post-Archean sedimentary rocks show different REE patterns: Post-Archean sedimentary rocks are characterized by a well developed negative Eu anomaly, whereas the Archean sedimentary rocks generally

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have a lower total REE abundance, commonly less fractionated patterns (i.e. lower La/Yb) and an almost insignificant negative Eu-anomaly (Naqvi and Hussain 1972; Condie 1993). In this study, an attempt is made to classify the present samples as Post-Neo-Archean shales, on the basis of their trace element characteristics (discussed below in geochemistry section). REEs are not easily fractionated during sedimentation and their patterns may provide a key to discovering average provenance compositions (Taylor and McLennan 1985; Condie and Wronkiewicz 1990; Wani and Mondal 2011). Due to their wide distribution on Earth, they are useful for explaining the sedimentary environment processes and the structural setting of depositional basins (Su 2005; Chen 2011; Yang et al. 2011). The main aim of the present study is to understand the tectonic setting and paleo-oxygenation conditions of shales from SMB, eastern India. This study would add to the existing knowledge of the crustal evolution of Singhbhum craton.

2 Geology of study area

The Eastern Indian Shield is bounded by Mahanadi Graben and Sukinda thrust in the west and in the south by the granulite terrain of Eastern Ghats and recent coastal alluvium. In the north and east, it is masked by the vast Gangetic alluvium and Quaternary sediments of the Bengal Basin (Fig. 1). It has received adequate attention from geoscientists and almost all aspects of its geology have been discussed (Mukhopadhyay 2001; Mahadevan 2002). The Chotanagpur Granite Gneiss Complex, Singhbhum Mobile Belt (SMB) and Singhbhum Craton are three geological provinces in the Eastern Indian Shield from North to South (Fig. 1b). The Chotanagpur Granite Gneiss Complex covers an area of about 80,000 km^2 in parts of West Bengal and almost the entire Jharkhand state, except the Singhbhum region. It is a composite mass consisting mainly of granite-gneisses, migmatites and massive granites with enclaves of para-and ortho-metamorphics, dolerite dykes and innumerable veins of pegmatite, aplite and quartz (Naqvi and Rogers 1987). The Singhbhum craton, which lays south of SMB, records a long history of crustal evolution from the Mesoarchaean to Mesoproterozoic. It is an extensive terrain of granite and gneissic complex, with subordinate metabasic and minor metasedimentary rocks. A major part of this province is covered by the Singhbhum Granitoid Complex, which is made up of at least twelve separate magmatic bodies, which have been emplaced during the two major phases of magmatism (Saha 1994). The early phase of Singhbhum Granite has an age of 3.25 ± 0.05 Ga, based on an eight point Pb/Pb whole rock isochron (Moorbath et al. 1986). Available radiometric ages for the later phase of the Singhbhum Granitoid Complex are 3.06 Ga (Pb/Pb whole rock) and 2.9 Ga (Rb/Sr whole rock) as compiled by Saha (1994).

The formations occurring between the Singhbhum Granitoid Complex and the Chotanagpur Granite Gneiss Complex are collectively recognized either as the Singhbhum Mobile Belt (SMB) or the Singhbhum Group, despite the different opinions regarding the tectono-stratigraphic relationship between the rocks of this belt and those lying across the well known Singhbhum Shear Zone in the belt's southern side (e.g., Dunn 1929, 1940, 1966; Dunn and Dey 1942; Iyengar and Murthy 1982; Banerji 1984; Saha 1994) (Fig. 1c). The SMB has been divided into five litho-stratigraphic domains (Gupta and Basu 2000): (i) Low to medium grade volcano-sedimentary belt, between the Dalma metavolcanic suite and the CGGC in the north, (ii) Dalma metavolcanic belt, (iii) the metamorphic belt comprising of the schistose and high metamorphic grade Chaibasa and Dhalbhum Formations, between the SSZ and the Dalma metavolcanic belt, (iv) the rocks occurring in the SSZ and (v) the volcano-sedimentary formations, including the disputed Dhanjori and/or the Ongarbira metavolcanic rocks. The low to medium grade volcano-sedimentary belt, between the Dalma metavolcanic rocks and the CGGC in the north, has been variously referred to as the 'Dhalbhum Formation' (Saha 1994), the 'outer wild flysch belt' (Sarkar 1982) and the 'Iron Ore Stage' (Dunn 1929, 1966; Dunn and Dey 1942). This sequence of predominantly less-altered tuffaceous shaly phyllites passes into schists. The Dalma metavolcanic suite extends about 200 km long as an arcuate belt and forms a number of fold closures in the east and west Singhbhum districts. The shale section outcropping (near Chandil, where NH-33 crosses NH-32) along the road was several hundred metres thick. The carbonaceous rich shales sporadically and repeatedly occured within the thick dark-grey to greenish-grey shale section. The Dalma metavolcanic rocks comprise of both schistose and the relatively less deformed dominantly mafic to ultramafic volcanic rocks. The Paleoproterozoic age has been considered the period of emplacement of Dalma metavolcanic rocks (Misra 2006). The metasedimentary sequence, north of the SSZ, is composed of mica schists, often garnetiferous with numerous bands of amphibolite facies, and has variously been named as the 'Chaibasa Stage' (Dunn 1929), 'Chaibasa Formation' (Saha 1994), 'Ghatshila Group' (Iyengar and Murthy 1982) and central metaflysch belt (Sarkar 1982). These rocks have generally preserved primary sedimentary structures; such as cross bedding, convolute laminations, graded bedding and current ripple laminations. An arcuate belt about 200 km long in the southern part of the SMB is well known as the "Copper Thrust Belt" (Dunn 1929; Dunn and Dey 1942) or Singhbhum Thrust or Singhbhum Shear Zone (Sarkar 1982). The rocks occurring in the SSZ are mainly phyllonite,

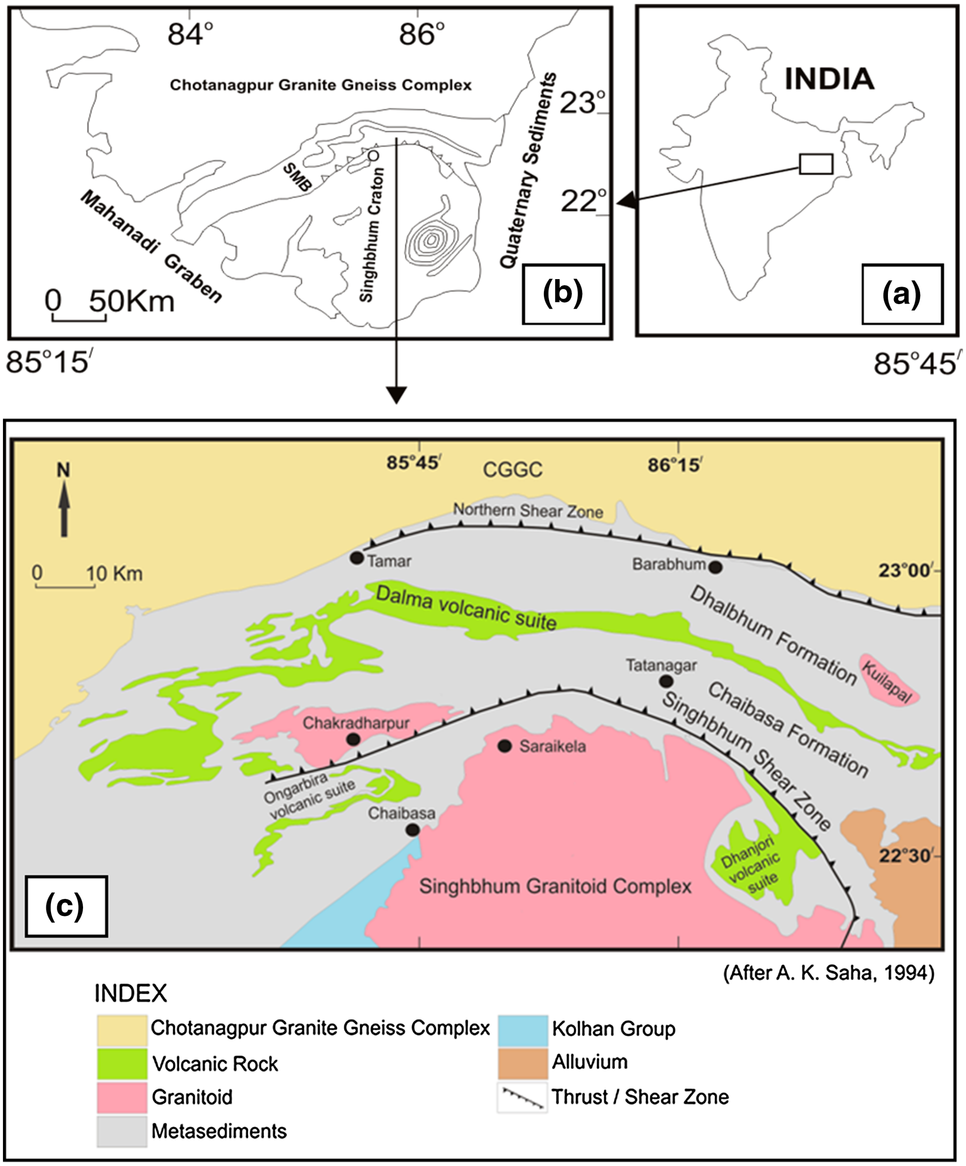


Fig. 1 **a** Map of India, showing location of eastern India shield; **b** showing three geological provinces of eastern Indian shield viz Chotanagpur Granite Gneiss Complex (CGGC), Singhbhum Mobile Belt (SMB) and Singhbhum Craton and **c** showing geological units in and around Singhbhum Mobile Belt (SMB) (after, Saha 1994)

chlorite sericite schist and sheared granite-gneiss, along with some lenticular bodies of sheared conglomerate and sandstone. The Ongarbira metvolcanic suite has a general ENE-WSW trend, which is discordant to the regional NNE-SSE strike of the Chaibasa metasedimentary rocks (Sarkar and Chakraborti 1982). The ultramafics, basalts and gabbro-pyroxinites with the subordinate tuffaceous members show intricate inter-fingering among them, in addition to the underlying metasediments with which they are co-folded (Gupta et al. 1981). Raza et al. (1995) suggested these volcanic rocks as typical arc-tholeiites. The Dhanjori metavolcanic suite contains a variety of rocks, from ultramafic to mafic, and the rarely acid lava flows, tuff and agglomerate are inter layered with the ortho-quartzite and phyllite and underlain by quartzite conglomerate, forming a group called the Dhanjori Group (Singh and Nim 1998).

3 Materials and methods

The studied black shale samples were powdered to −200 mesh size in an agate vessel. A solution of each sample was prepared to determine the REE at the National Geophysical Research Institute (NGRI), Hyderabad following the open acid digestion method given by Balaram and Gnaneshwara 2003. Fifty mg of the powdered rock sample was placed in a clean, dried PTFE Teflon beaker. Each sample was moistened with a few drops of ultra-pure water. Then, 10 ml of an acid mixture (containing 7:3:1 HF:HNO3:HClO4) was added to each sample. Samples were swirled until completely moist. The beakers were covered with lids and then kept overnight for digestion, after adding 1 ml of 5 g/ml Rh solution (to act as the internal standard). The next day, these beakers were heated

Table 1 Trace element (including rare earth elements) data of shales from SMB, eastern India

Sample	SK6	SC2	SK11	SM8D	SK8	SC9	SC6	SU5	SP2
Sc	20.99	23.41	24.43	20.14	20.90	21.43	46.97	27.85	15.82
V	243	118	263	263	303	195	275	129	251
Cr	148	81	154	149	142	228	158	153	303
Co	8.81	7.00	4.29	6.25	9.75	18.24	18.58	38.71	17.13
Ni	43.77	19.86	38.01	41.76	56.86	112.40	62.45	63.97	43.47
Cu	68.56	24.88	51.19	84.39	89.95	74.80	52.95	25.85	30.31
Zn	76.87	49.49	119.34	100.29	115.49	124.95	268.24	110.68	118.58
Ga	22.91	31.12	25.01	23.55	23.75	25.04	29.76	22.65	17.21
Rb	208	212	201	203	204	222	256	209	132
Sr	42.34	9.46	38.18	34.72	35.66	21.52	39.51	27.73	99.13
Y	28.07	74.34	34.63	31.41	52.00	26.97	33.14	43.18	19.63
Zr	224	793	269	218	221	214	278	221	185
Nb	22.24	29.38	17.36	16.98	18.88	16.29	22.42	40.93	12.81
Cs	11.36	4.92	6.14	8.29	10.50	11.21	8.39	4.56	7.42
Ba	394	528	389	407	391	398	536	436	292
Hf	7.12	8.53	7.08	2.67	3.79	0.86	7.50	0.46	0.44
Ta	1.46	0.69	0.37	0.51	0.09	0.26	2.23	2.95	0.90
Pb	6.52	5.74	5.92	5.69	5.96	3.90	5.92	3.08	3.01
Th	16.04	17.10	21.74	6.89	10.22	4.30	24.63	1.20	1.53
U	5.52	3.75	7.80	2.95	11.06	1.34	2.83	0.53	1.24
La	36.55	59.00	34.06	39.36	30.56	54.48	65.84	60.50	40.77
Ce	33.09	144.00	37.57	29.17	27.05	83.52	105.23	89.77	71.23
Pr	5.59	20.12	8.17	6.12	10.26	12.46	13.94	11.23	8.60
Nd	20.02	79.91	28.62	19.88	40.20	46.30	49.45	39.13	30.30
Sm	4.83	16.82	6.25	4.28	8.59	8.68	9.33	7.51	5.67
Eu	1.13	2.27	1.39	1.08	1.85	1.74	1.95	1.53	1.18
Gd	3.90	11.00	4.52	3.77	6.55	6.14	6.97	6.50	4.48
Tb	0.83	2.03	0.91	0.83	1.40	0.99	1.24	1.26	0.75
Dy	5.44	12.43	6.07	5.71	9.24	5.00	6.73	8.10	4.04
Ho	1.11	2.66	1.34	1.24	1.99	0.97	1.30	1.72	0.75
Er	3.13	8.12	3.75	3.42	5.35	2.73	3.43	4.65	2.01
Tm	0.62	1.62	0.73	0.65	0.99	0.47	0.58	0.86	0.35
Yb	4.02	10.92	4.84	4.10	5.99	2.97	3.71	5.16	2.27
Lu	0.65	1.98	0.82	0.69	0.96	0.53	0.64	0.89	0.37
Total REE	121	373	139	120	151	227	270	239	173
Th/U	2.90	4.56	2.79	2.34	0.92	3.21	8.70	2.27	1.24
Th/Sc	0.76	0.73	0.89	0.34	0.49	0.20	0.52	0.04	0.10
Th/Co	1.82	2.44	5.06	1.10	1.05	0.24	1.33	0.03	0.09
Th/Cr	0.11	0.21	0.14	0.05	0.07	0.02	0.16	0.01	0.01
Cr/Th	8.84	4.72	7.08	21.58	13.87	53.05	6.42	128	198
La/Sc	1.74	2.52	1.39	1.95	1.46	2.54	1.40	2.17	2.58
U/Th	0.34	0.22	0.36	0.43	1.08	0.31	0.11	0.44	0.81
Ni/Co	4.97	2.84	8.85	6.68	5.83	6.16	3.36	1.65	2.54
Cr/Ni	3.24	4.06	4.05	3.56	2.49	2.03	2.53	2.39	6.97
Th/Co	2.14	0.85	1.65	0.56	0.47	1.62	4.97	0.01	0.02
Gd/Lu	0.75	0.69	0.68	0.68	0.85	1.44	1.36	0.91	1.49
La/Sm	4.76	2.21	3.43	5.78	2.24	3.95	4.44	5.07	4.53
Gd/Yb	0.79	0.82	0.76	0.74	0.89	1.68	1.52	1.02	1.60
La/Lu	5.85	3.10	4.30	5.91	3.29	10.63	10.73	7.07	11.32
Eu/Eu*	0.80	0.51	0.80	0.82	0.75	0.73	0.74	0.67	0.72
Ce/Ce*	0.54	0.98	0.53	0.44	0.36	0.75	0.81	0.81	0.89

on a hot plate at ~200 °C for about 1 h; then, the contents were evaporated to incipient dryness until a crystalline paste was obtained. Ten ml of a 1:1 HNO3 solution was added to dissolve the residual material in the beakers. Again, the beakers were placed on a hot plate for 10 min with gentle heating (70 °C) to dissolve all suspended particles. Finally, the volume was diluted to 250 ml with double distilled water (purified water) (18 MΩ) and the liquid was stored in polyethene bottles. This solution was used for the estimation of REE elements, using inductively coupled plasma-mass spectrometry techniques (ICP-MS). The instrumental and data acquisition parameters are the same as those given in Balaram and Gnaneshwara 2003. The precision of the ICP-MS data is better than ±6 % RSD for all the REE data and in all cases, was obtained with comparable accuracy.

4 Results

4.1 Trace elements

Trace element data is given in Table 1. High field strength elements (HFSEs) (such as Zr, Hf, Nb, Ti) prefer to be in melt phase during the crystallization of magma or partial melting of rocks (Feng and Kerrich 1990). As a result, they have higher concentrations in felsic rocks than in mafic rocks. Their immobile geochemical characteristics make them useful, in addition to REEs, for provenance studies (Taylor and McLennan 1985). In the present samples, Zr varied from 185 to 793 ppm and Nb varied from 13 to 41 and Y from 20 to 74. Large ion lithophile elements (LILEs) (such as Rb, Ba, Sr, Th, U, Cs) are considered to be mobile during post magmatic alterations. In the studied shales, Rb ranged from 132 to 256 ppm, Ba varied from 292 to 536, Sr from 9 to 99, Th from 1 to 25, U from 0.53 to 11 and Cs from 5 to11. Transitional elements such as Ni, Cr, Co, V and Sc are compatible elements and they prefer being in solid phases during crystallization or partial melting. Generally, they have higher concentration in mafic rocks than in felsic rocks. In studied the samples, Ni varies from 20 to 112 ppm, Cr from 80 to 103 ppm, Co from 4 to 39 ppm, V from 118-303 ppm and Sc from 16 to 47 ppm. Higher Ni and Cr concentrations relative to PAAS confirm these shales to be Post-archaean to Neo-archaean clastic sedimentary rocks (Fig. 2). The Post-Archaean Australian Shale (PAAS) normalized multi-element diagram showed slight enrichment of Cr, V, Zr, Y, U and Sc whereas Ni, Rb, Nb and Cu were of same magnitude as PAAS. Sr, Pb, Hf and Th were depleted (Fig. 3). A noteworthy sharp negative anomaly of Sr indicated that the accumulation of plagioclase was the least, which is also supported by the negative Eu-anomaly in these rocks.

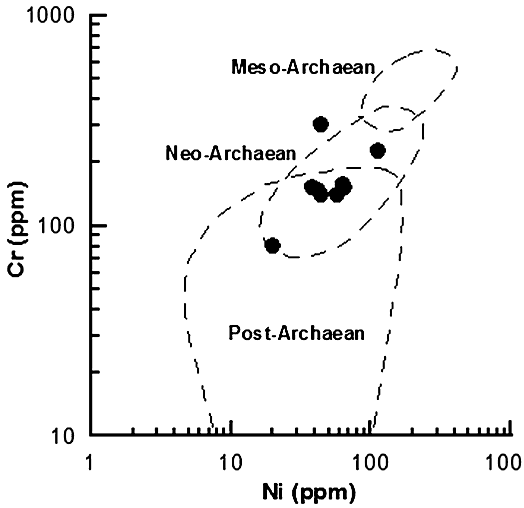


Fig. 2 Distribution of Ni and Cr in the shales of SMB. Different fields are after Condie (1993)

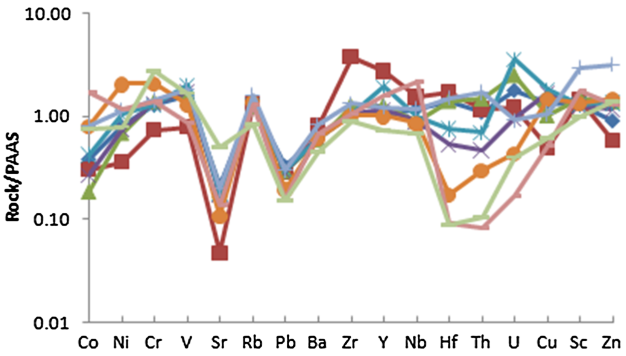


Fig. 3 PAAS normalized multi-element diagram for shales of SMB. Normalization values are taken from Taylor and Mclennan (1985)

4.2 Rare earth elements

Rare earth element (REE) data is given in Table 1. The chondrite-normalized REE diagram reflects that the LREEs are inclined whereas the HREEs show a nearly flat pattern (Fig. 4). These samples show the moderate fractionation of LREEs [$(La/Sm)_N$ varies from 2.21 to 5.78 avg. = 4.05], while the HREEs are very slightly fractionated [$(Gd/Yb)_N$ varies from 0.74 to 1.68 avg. = 1.09] compared to the NASC (=1.39) and Proterozoic Shale Standard (=1.62) (Condie 1993). These shales contain Eu/Eu* values less than 0.85, which is a characteristic of sediments recycled from the upper continental crust. Their pronounced negative Eu anomalies <0.85 and Gd/Yb_N ratios (0.74–1.68) < 2.0 are characteristic of clastic sedimentary rocks of the Post–Archean period (Taylor and McLennan 1985). The negative Eu-anomalies also indicate that the intra-crustal differentiation, such as partial melting or fractional crystallization involving the separation of plagioclase, had affected the source rocks. The results show a HREE depletion with a

$(Gd/Lu)_N$ ratio ranging from 1.49–0.68, indicating that the REE concentrations decreased 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.

5 Discussions

5.1 Tectonic setting

A number of studies have concluded that the chemical compositions of clastic sedimentary rocks are significantly controlled by the plate tectonic settings of their provenance. To visualize the tectonic settings of old sedimentary basins from the geochemical data, it is presumed that the nature of the source terrain is intimately related to tectonic processes controlling the origin and evolution of the adjacently lying sedimentary basin (Bhatia and Crook 1986). Relatively immobile trace elements (like La, Th, Sc, Zr) have been successfully used to interpret the tectonic settings of sedimentary rocks. For the current study, La–Th–Sc and Zr–Th–Sc triangular systematics were tested, as these plots are considered strong indicators to discriminant various tectonic settings (Bhatia 1983; Bhatia and Crook 1986). In these diagrams (Fig. 5), some of the studied shales were plotted in the continental arc setting while some of the other samples scattered outside the field.

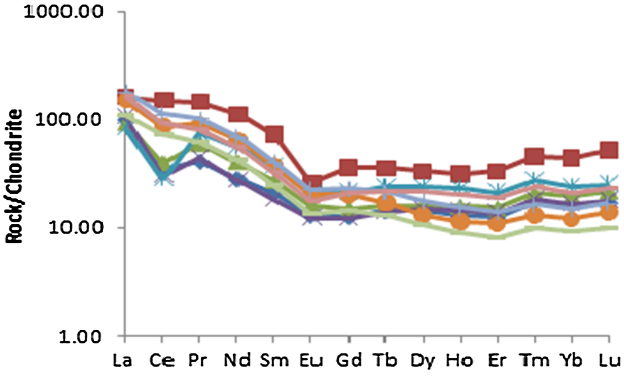
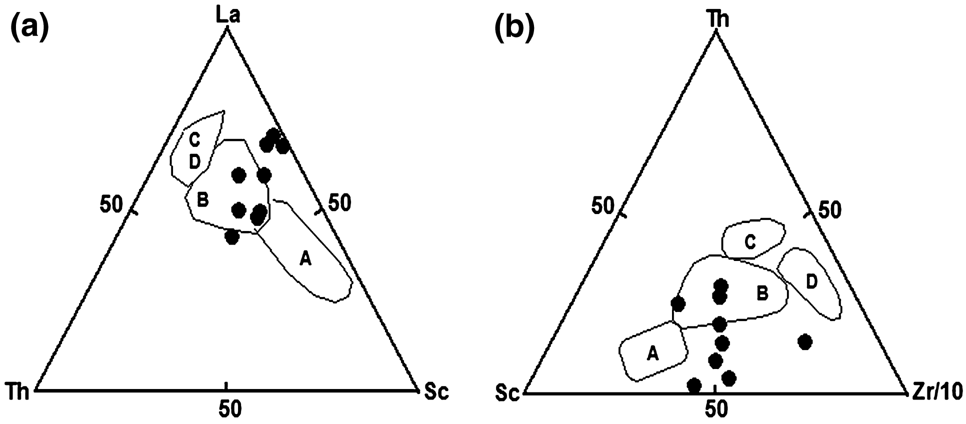


Fig. 4 Chondrite-normalized rare earth element (REE) patterns of shales of SMB. Normalization *values* are taken from Taylor and Mclennan (1985)

5.2 Paleo-oxidation conditions

In the past, trace-element ratios such as Ni/Co, V/Cr and V/(V + Ni) have been used to evaluate the paleoredox conditions by various workers (e.g., Jones and Manning 1994; Rimmer 2004; Nagarajan et al. 2007). Jones and Manning (1994) suggested that Ni/Co ratios <5 inferred oxic conditions, 5–7 dysoxic conditions and >7 suboxic to anoxic conditions. Vanadium, which is generally found in sediments deposited in reducing environments, may be bound to organic matter by the incorporation of V^{4+} into porphyrins (Nagarajan et al. 2007). V also may occur when adsorbed onto clay minerals, an association that probably results following its burial (Breit and Wanty 1991). Cr is thought to be associated only with the detrital faction (Dill 1986) and is not influenced by redox conditions, thus high V/Cr values (>2) are thought to indicate anoxic conditions. According to Jones and Manning 1994, V/Cr ratios <2 infer oxic conditions, 2–4.25 indicate dysoxic conditions and >4.25 infer suboxic to anoxic conditions; in addition, V/(V + Ni) ratios greater than 0.84 suggest euxinic conditions, 0.54–0.82 represent anoxic conditions and 0.46–0.60 represent dysoxic conditions. In the present study, the Ni/Co and V/Cr values match the oxic to dysoxic conditions (Fig. 6a), whereas the V/(V + Ni) predicts the anoxic to euxinic redox conditions (Fig. 6b). Further, the U/Th and Cu/Zn parameters were used to check redox conditions. Low contents of U are generally found in sediments deposited in oxygenated conditions in marine environment, whereas high U contents are found in sediments from the oxygen minimum zone (Somayajulu et al.

Fig. 5 **a** La–Th–Sc and **b** Th–Zr–Sc triangular tectonic setting discriminant diagrams (after Bhatia 1983) showing continental arc setting for shales of SMB. A=Oceanic island arc, B=Continental island arc, C=Active continental margin and D=Passive margin



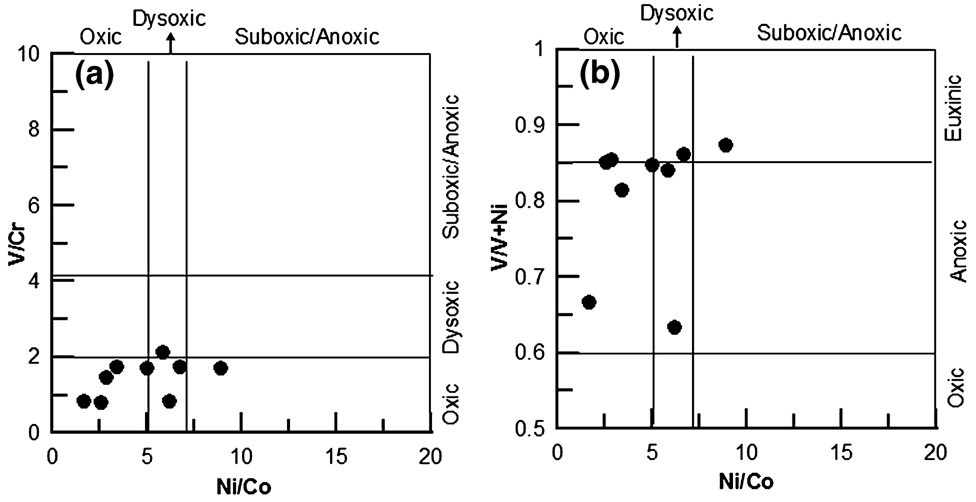


Fig. 6 **a** Ni/Co versus V/Cr and **b** Ni/Co versus V/(V + Ni) binary plots (after Rimmer 2004) for shales of SMB

1994; Nagarajan et al. 2007); thus, the U/Th ratio may be used as a redox indicator (Jones and Manning 1994). U/Th ratios below 1.25 suggest oxic conditions of deposition, whereas values above 1.25 indicate suboxic and anoxic conditions (Nath et al. 1997). High Cu/Zn values indicate reducing depositional conditions, whereas low Cu/Zn values support oxidizing conditions (Hallberg 1976; Nagarajan et al. 2007). Therefore, low U/Th (0.11–1.08) and Cu/Zn (0.20–0.89) ratios in the studied shales favored their oxic conditions of deposition. In addition, the Ce anomaly was used as an important indicator of Ce ion exchange in an oxidation stage, which is therefore sensitive to the variation of the redox condition (Wilde et al. 1996; Yang et al. 2011). Present seawater is characterized by Ce/Ce* values of 0.4–0.7 (Elderfield and Greaves 1982), whereas the average shales typically yield Ce/Ce* values of ~ 1.0 (Cox et al. 1995; Cullers and Berendsen 1998). Under an oxidized condition, Ce is more easily oxidized to Ce^{4+}, which is less soluble than its reduced compartment Ce^{3+} and therefore remains in the sediment, causing a positive Ce anomaly (>0.10). On the contrary, an anoxic environment will cause a negative Ce anomaly (<0.10). In the present samples, the Ce anomaly ranged from 0.36 to 0.98, which is greater than (0.10), a redox threshold value revealing the depositional environment of these samples to be oxic. Therefore, all these parameters suggest that the depositional conditions for the studied shales were oxic to anoxic.

6 Conclusions

On the basis of the Ni and Cr concentrations the studied shales were treated as Post-archaean to Neo-archaean clastic sedimentary rocks. The Post-Archaean Australian Shale normalized multi-element diagram showed a slight enrichment of Cr, V, Zr, Y, U and Sc and depletion of Sr, Pb, Hf and Th. Their negative Sr and Eu anomalies indicate the accumulation of plagioclase to be the least in these rocks, which may be due to a smaller concentration of plagioclase-feldspars in their provenance. A continental arc setting is suggested for these rocks on the basis of the La–Th–Sc and Zr–Th–Sc tectonic setting discriminant diagrams. The geochemical parameters, such as the Ni/Co, V/Cr and U/Th ratios, favor an oxic to dysoxic conditions of deposition, and their V/(V + Ni) values matches with anoxic to euxinic redox conditions. While observing their Ce anomaly (>0.10) in addition to Cu/Zn values (0.20–0.89) it has been concluded that the depositional environment for these shales was fluctuating between oxidizing and reducing conditions, probably due to the sea-level changes during Post-archean Era.

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