

## Geochemistry of Neoproterozoic shales of the Rabanpalli Formation, Bhima Basin, Northern Karnataka, southern India: implications for provenance and paleoredox conditions

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### ABSTRACT

The Rabanpalli Formation exhibits two types of shales, viz. grey and calcareous shales. These shales (grey and calcareous) have been analysed for major, trace, and rare earth elements to find out their source rocks characteristics and paleo-oxygenation conditions. The grey shales have higher concentration of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Zr, Th, U, V, Cr, La, Ce, and Y than calcareous shales, whereas calcareous shales are enriched in CaO, Mn, Sr, Ba, Cu, and Zn, which indicate that the carbonate phase minerals are higher in calcareous shales. The positive correlation of K<sub>2</sub>O with other elements, and abundance of Al<sub>2</sub>O<sub>3</sub>, Ba, Th, and Rb suggest that these elements are primarily controlled by the dominant clay minerals. La/Sc, Th/Sc, Th/Co, Th/Cr, and Cr/Th ratios of shales were compared with those of sediments derived from felsic and basic rocks (fine fraction), upper continental crust (UCC) and post-Archean Australian average shale (PAAS) ratios, which reveal that these ratios are within the range of felsic rocks. The La/Sc vs. Th/Co plot also suggests the felsic nature of the source rocks. The shales show slightly light rare earth element (LREE) enriched and flat heavy rare earth element (HREE) patterns with negative Eu anomaly, and are similar to the granitoids from Dharwar Craton, which suggest that the Archean Dharwar Craton contributed the sediments to the Bhima basin. The geochemical parameters such as U, authigenic U, U/Th, V/Cr, Ni/Co, and Cu/Zn ratios indicate that these shales were deposited under oxic environment.

Key words: geochemistry, shale, provenance, paleo-oxygenation conditions, Rabanpalli Formation, Bhima Basin, India.

### RESUMEN

La Formación Rabanpalli incluye dos tipos de pizarras: grises y calcáreas. Esas pizarras fueron analizadas por elementos mayores y traza para establecer las características de las rocas fuente y las condiciones de paleo-oxigenación. Las pizarras grises tienen concentraciones más altas de SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Zr, Th, U, V, Cr, La, Ce, e Y que las pizarras calcáreas, mientras que las pizarras calcáreas están enriquecidas en CaO, Mn, Sr, Ba, Cu y Zn, lo cual indica una mayor abundancia de fases carbonatadas en las pizarras calcáreas. La correlación positiva de K<sub>2</sub>O con otros elementos y la abundancia de Al<sub>2</sub>O<sub>3</sub>, Ba, Th y Rb sugieren que esos elementos están principalmente controlados por los

*minerales arcillosos dominantes. Las comparación de las relaciones La/Sc, Th/Sc, Th/Co, Th/Cr y Cr/Th de las pizarras con las relaciones que exhiben los sedimentos derivados de rocas básicas y félsicas (fracción fina), la corteza continental superior y la lutita australiana postarqueana (post-Archean Australian average shale, PAAS) reveló que esas relaciones se encuentran en el rango de las rocas félsicas. Un gráfico de La/Sc vs. Th/Co también sugiere una naturaleza félsica para las rocas fuente. Las pizarras presentan patrones ligeramente enriquecidos en tierras raras ligeras y un patrón plano para las tierras raras pesadas, así como anomalías negativas de Eu; estos patrones son similares a los granitoides del cratón Dharwar sugiriendo que este cratón arqueano aportó los sedimentos a la cuenca Bhima. Parámetros geoquímicos como U, U autógeno, y las relaciones U/Th, V/Cr, Ni/Co y Cu/Zn indican que las pizarras fueron depositadas en un ambiente oxidante.*

*Palabras clave: geoquímica, pizarra, proveniencia, condiciones de paleo-oxigenación, Formación Rabanpalli, Cuenca Bhima, India.*

## INTRODUCTION

Shales represent the most abundant type of sediments in sedimentary basins worldwide (Pettijohn, 1975) and are considered to represent the average crustal composition of the provenance much better than any other detrital sedimentary rocks (McCulloch and Wasserburg, 1978). 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; Condie and Wronkiewicz, 1990; Manikyamba *et al.*, 1997; Panahi and Young, 1997). Some researchers emphasized that major element geochemistry of the sedimentary rocks are more useful in discriminating the tectonic setting (Bhatia, 1983; Roser and Korsch, 1986). However, Armstrong-Altrin and Verma (2005) have warned against an indiscriminate use of discrimination diagrams for provenance studies using major element geochemistry.

The trace elements such as La, Y, Sc, Cr, Th, Zr, Hf, Nb, and particularly TiO<sub>2</sub> among other major elements are best suited for provenance and tectonic setting determination studies, because of their relatively low mobility during sedimentary processes (McLennan *et al.*, 1983). In addition, the relative distribution of the immobile elements that differ in concentration in felsic and basic rocks such as La and Th (enriched in felsic rocks) and Sc, Cr, and Co (enriched in basic rocks relative to felsic rocks) has been used to infer the relative contribution of felsic and basic sources in shales from different tectonic environments (Wronkiewicz and Condie, 1990). Similarly, geochemical parameters have been used by various authors to understand the paleo-oxygenation condition of ancient sediments (Calvert and Pedersen, 1993; Jones and Manning, 1994; Nath *et al.*, 1997; Madhavaraju and Ramasamy, 1999; Cullers, 2002; Armstrong-Altrin *et al.*, 2003; Dobrzinski *et al.*, 2004). The purpose of the present study is to identify the source rock characteristics as well as the paleo-oxygenation conditions by using major, trace, and rare earth elements geochemistry of the Rabanpalli Formation exposed in the Bhima basin, southern India.

## GEOLOGY AND STRATIGRAPHY

Bhima basin is an S-shaped Neoproterozoic, epicratonic, extensional basin (Figure 1), which formed due to gravity faulting. The epicratonic Mesoproterozoic Kaladgi supergroup and Neoproterozoic Bhima Group overlie the Archean granite-greenstone basement in Karnataka, southern India. The Archean granite-greenstone terrain mainly consists of TTG (tonalite-trondhjemite-gneiss) popularly known as Peninsular gneisses (Dharwar greenstone belts). The cratonization of the Archean province occurred ~ 2.5 Ga ago accompanied by the emplacement of K-rich granitoids (Closepet granite; Jayananda *et al.*, 1995). The Mesoproterozoic sedimentary rocks of Kaladgi supergroup and Neoproterozoic Bhima Group were deposited on the eroded edges of the Dharwar Craton (Senthil Kumar and Srinivasan, 2002). The sedimentary rocks of Bhima basin and the granitoids have been affected by intense faulting. Major faults across the basin define the structural boundaries of the different sectors (Kale and Peshwa, 1995). They are (1) East-West trending Tirth, Gogi and Mogalavadi kavagu faults, and (2) NW-SE trending Wadi fault. Due to the effect of the E-W trend faults, the limestone of the middle part of the basin directly rests on granites.

King (1872) coined the term Bhima Series and he divided the sedimentary rocks into Muddebihal Sandstones and Talikote Limestone. Mahadevan (1947) proposed a new three fold classification: 1) Lower Bhima Series, 2) Middle Bhima Series, and 3) Upper Bhima Series. The Lower Bhima Series includes the basal conglomerate-sandstones and shales. The Middle Bhima Series is dominantly made up of limestones. The Upper Bhima Series includes sandstones, shales, and limestones. Janardhana Rao *et al.* (1975) assigned the Group status to the Neoproterozoic sedimentary rocks of Bhima basin. They classified the Bhima Group into five distinct formations: 1) Rabanpalli Formation, 2) Shahabad Formation, 3) Halkal Shale, 4) Katamadevarhalli Formation, and 5) Harwal Shale. Mishra *et al.* (1987) subdivided the Bhima Group into Sedam Subgroup (Rabanpalli and Shahabad Formations) and Andola Subgroup (Halkal

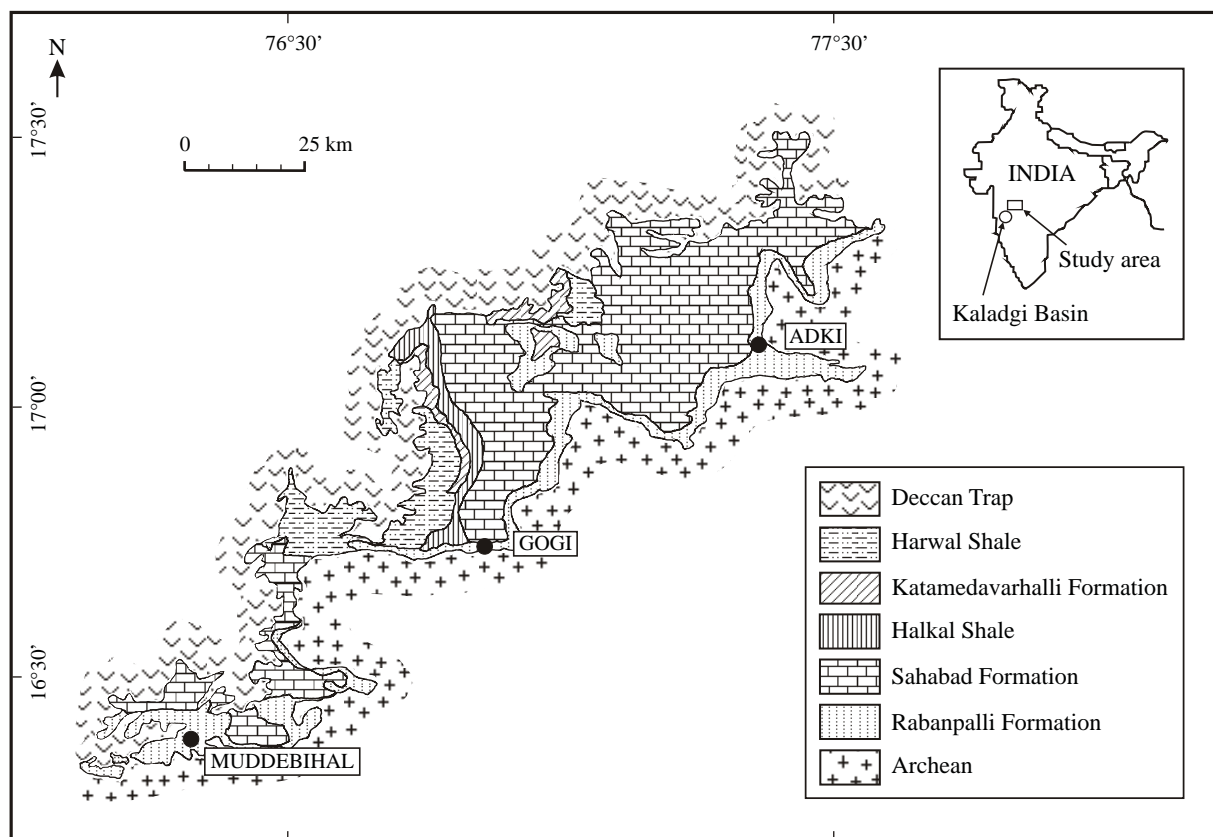


Figure 1. Geological map of the Bhima basin showing the study area. The shale samples were collected from Adki, Gogi, and Muddebihal areas, which belong to the Rabanpalli Formation (modified after Janardhana Rao *et al.*, 1975).

Shale, Katamedavarhalli Formation, and Harwal-Gogi Shale). They identified the sedimentation break between Sedam and Andola Subgroup, and interpreted as paraconformity. Later, Malur and Nagendra (1994) introduced a new name for Shahabad Formation as Kurkunta Formation. The classification proposed by Janardhana Rao *et al.* (1975) and Malur and Nagendra (1994) has been followed in this study.

The sedimentary rocks are trending in the NE-SW direction, and exhibit a total thickness of about 300 m (Misra *et al.*, 1987). These sedimentary rocks mainly comprise an alternating sequence of clastic and carbonate rocks (Janardhana Rao *et al.* 1975; Misra *et al.*, 1987; Kale, 1990; Kale *et al.*, 1990). In the clastic rocks, fine-grained sediments dominate over the coarse clastics. The Rabanpalli Formation has been considered as the oldest sedimentary rocks in the Bhima basin that deposited over the Archean basement. Harwal shale is the youngest formation of the Bhima Group, which is overlain by Deccan Trap with intratrappean sediments. The Rabanpalli Formation is placed under the lower series of Bhima Basin. Quartz arenites, arkoses, siltstones, and shale are the dominant members of this Formation. The exposures of this formation are seen all along the southern boundary of the Bhima basin. Except the conglomerate member, all the other members of the

Rabanpalli Formation are well exposed toward the north of Rabanpalli village. The conglomerate grades upward to coarse to fine-grained sandstones, siltstone, and shale. The calcareous and grey shales occur as discontinuous outcrops throughout the southern boundary of the Bhima basin. The calcareous shales are best-exposed member of the Rabanpalli Formation. These shales are fissile and very friable in nature. Toward the top, they become compact and slabby.

## MATERIALS AND METHODS

The calcareous and grey shales of the Rabanpalli Formation were collected from the outcrop sections. The collected samples were washed thoroughly in distilled water to remove the contamination. The samples were digested in a solution of  $\text{HNO}_3 + \text{HF}$ . The digested samples (ten calcareous and three grey shales) were analyzed for major and trace elements by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES-Jobin-Yvon Jy138 Ultrace). Replicate analyses of samples indicate that errors for major elements are better than 1%, whereas the precision for trace elements varies between 3 and 5%.

Seven representative shale samples (five calcareous

and two grey shales) were analyzed for rare earth elements. 0.2 g were digested with 4 ml HNO<sub>3</sub> and 1 ml of HClO<sub>4</sub> for 24 hours in a tightly closed Teflon vessel on a hot plate at temperature <150°C, and then digested with a mixture of 4 ml of HF and 1 ml of HClO<sub>4</sub>. Later, the solution was evaporated to dryness, and extracted with 10 ml of 1% HNO<sub>3</sub>. The digested samples were measured for rare earth elements by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, Plasma QUAD 3). The geochemical standard SPL - 29 was used for calibration. The precision of REE analyses are better than 5%. The REE data were normalized relative to the chondrite values (Taylor and McLennan, 1985).

## RESULTS

### Major elements

The major element data are given in Table 1. The calcareous shales show low content of SiO<sub>2</sub> whereas grey shales show high content of SiO<sub>2</sub>. The calcareous shales show large variations in Al<sub>2</sub>O<sub>3</sub> content (~4.84–12.4%) whereas grey shales show small variations (~8.39–12.10%). The distribution of Al<sub>2</sub>O<sub>3</sub> is reverse to that of SiO<sub>2</sub>. Aluminium concentration is a reasonably good measure of detrital flux, the positive correlations of K<sub>2</sub>O, TiO<sub>2</sub>, and Na<sub>2</sub>O, with Al<sub>2</sub>O<sub>3</sub> (statistically significant at a very strict significance level of 0.001; linear correlation coefficient  $r = 0.81, 0.89, \text{ and } 0.76$ , respectively, number of samples  $n = 13$ ) indicate that these elements are associated entirely with detrital phases. Many elements have clear positive linear correlation coefficients with K<sub>2</sub>O (*e.g.*,  $r = 0.81$  for Al<sub>2</sub>O<sub>3</sub>;  $0.82$  for Th;  $0.88$  for Rb)

suggesting that the absolute abundances of these elements are primarily controlled by illite.

The K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of sediments can be used as an indicator of the original composition of ancient sediments. The K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios for clay minerals and feldspars are different (0.0 to 0.3, 0.3 to 0.9, respectively; Cox *et al.*, 1995). The average K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio for calcareous shales vary from 0.21 to 0.30 (the mean with one standard deviation value being  $0.24 \pm 0.03$ ;  $n = 10$ ), and for grey shales it varies from 0.14 to 0.24 ( $0.20 \pm 0.05$ ;  $n = 3$ ). In most of the samples, the K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios are close to the upper limit of the clay mineral range, which suggest that the illite is the dominant clay mineral in these shales.

Titanium is mainly concentrated in phyllosilicates (Condie *et al.*, 1992) and is relatively immobile compared to other elements during various sedimentary processes and may strongly represent the source rocks (McLennan *et al.*, 1993). The calcareous and grey shales of Bhima basin show lower TiO<sub>2</sub> values than the post-Archean Australian average shale (PAAS; Taylor and McLennan, 1985), which suggests more evolved (felsic) material in the source rocks. Most of the samples have low P<sub>2</sub>O<sub>5</sub> contents. The depletion of P<sub>2</sub>O<sub>5</sub> may be explained by the lesser amount of accessory phases such as apatite and monazite compared to PAAS.

### Trace elements

All the trace elements were normalized using PAAS values (Taylor and McLennan, 1985) and are plotted in a multielement diagram (Figure 2). PAAS normalized patterns of trace elements of shales show a moderate depletion of Ni,

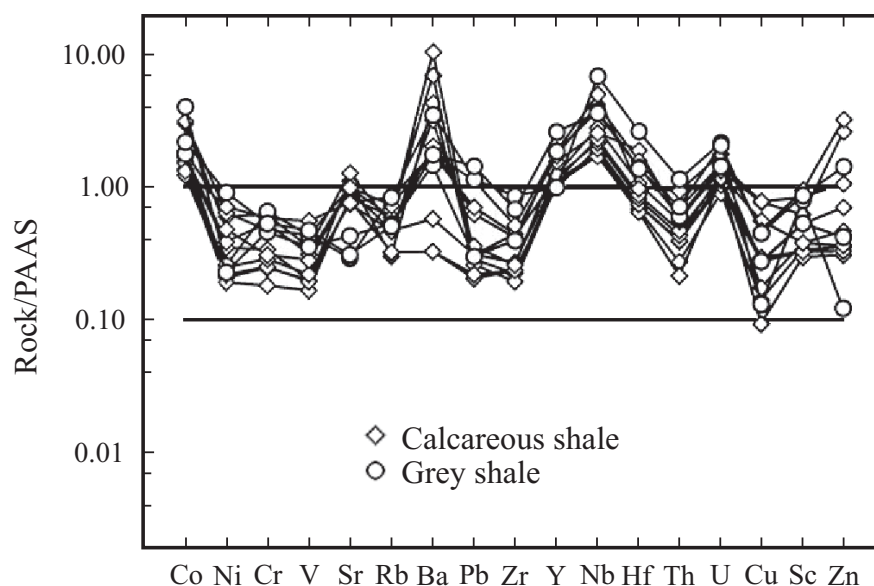


Figure 2. PAAS normalized trace elements distribution of shale samples from the Rabanpalli Formation. The two horizontal lines at rock/post-Archean Australian shale (PAAS) values of 1 and 0.1 are included for reference.

Table 1. Major (%) and trace (ppm) elements concentration for calcareous and grey shales of the Rabanpalli Formation, and for post-Archean Australian average shale (PAAS).

Rock type	Calcareous shale										Grey shale			PAAS
	S53	S51A	E117	S51B	S38E	S4	S23	C111	E121	C122	E49	C103	E189	
SiO <sub>2</sub>	33.70	26.80	30.80	20.60	27.60	27.80	28.10	38.10	40.90	23.80	76.60	64.90	52.60	62.40
TiO <sub>2</sub>	0.23	0.25	0.20	0.25	0.29	0.36	0.39	0.31	0.53	0.60	0.89	0.44	0.50	0.99
Al <sub>2</sub> O <sub>3</sub>	5.22	5.88	4.84	5.97	6.60	8.00	9.53	7.09	10.30	12.40	12.10	8.39	11.60	18.78
Fe <sub>2</sub> O <sub>3</sub>	2.51	2.01	2.26	2.04	2.60	3.46	4.66	2.39	4.36	6.41	2.79	1.99	10.60	7.18
MgO	0.87	0.84	0.65	0.83	1.00	0.89	0.87	0.97	1.29	1.59	0.64	0.64	2.07	2.19
CaO	32.60	33.70	34.60	33.90	30.50	24.50	22.60	27.70	21.10	15.20	0.43	0.34	1.29	1.29
Na <sub>2</sub> O	0.29	0.09	0.11	0.09	0.24	0.68	0.59	0.38	0.52	0.69	0.54	0.09	0.55	1.19
K <sub>2</sub> O	1.23	1.32	1.37	1.33	1.71	2.36	2.16	1.50	2.27	2.61	2.86	1.86	1.61	3.68
P <sub>2</sub> O <sub>5</sub>	0.13	0.18	0.15	0.18	0.11	0.15	0.10	0.12	0.11	0.13	0.12	0.13	0.23	0.16
LOI	22.88	26.87	23.41	32.14	28.79	31.15	29.49	20.98	17.83	34.84	2.64	19.00	16.42	-
Total	99.66	97.94	98.39	97.33	99.44	99.35	98.49	99.54	99.21	98.27	99.61	97.78	97.47	97.86
Rb	47.60	51	94	51.30	73.80	93.80	82.30	73.70	115	133	133	84	80.70	160
Sr	219	157	164	158	147	195	252	187	197	151	58	85	61	200
Ba	2755	212	4474	212	373	6718	1306	2046	1131	1149	2250	941	1128	650
Pb	5.73	4.07	5.21	4.40	6.19	6.16	12.50	7.21	14.10	22.30	22.80	5.99	28.70	20
Zr	47.20	49.80	40.90	49.80	56.90	92.90	87.90	54.50	93.50	109	180	83.60	143	210
Nb	3.46	3.72	3.29	3.76	4.14	4.45	5.41	4.93	8.03	9.62	13.30	7.17	6.97	1.90
Th	4.06	5.79	3.20	5.88	6.45	7.02	8.20	8.63	10.30	13.90	17.10	8.95	10.60	14.60
U	2.85	3.27	3.62	3.56	3.94	3.72	4.61	4.19	4.72	5.61	6.79	4.53	6.50	3.10
Sc	5.55	5.36	4.89	5.39	6.23	6.24	8.69	10.20	13.70	15.60	13.10	8.75	14.20	16
Hf	3.46	3.72	3.29	3.76	4.14	4.45	5.41	9.62	8.03	4.93	13.30	7.17	6.97	5
V	29.40	29.50	24.80	28.90	32.80	46.40	51.90	41.90	64.80	82.80	64.30	52.60	70.40	150
Cr	37	26.80	19.70	27.20	31.10	58.10	67.70	33.50	51.60	63.30	71.70	49.80	57.90	110
Ni	19	11.30	10.40	11.90	13.50	21	32.60	26.20	34.80	38.80	13.89	12.40	49.70	55
Co	37.90	35.80	31.20	27.90	34.40	40.40	43	68.20	71.50	30	91.80	40.70	49.60	23
Cu	7.28	14.10	4.81	15.10	28.50	8.97	13.90	39.40	40	24.10	6.72	14.10	23.10	50
Zn	31.10	28.90	26.80	28.90	31.90	40.90	61.50	227	92.70	280	10.80	36.80	124	85
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	6.46	4.56	6.36	3.45	4.18	3.48	2.95	5.37	3.97	1.92	6.33	7.74	4.53	3.32
K <sub>2</sub> O/Na <sub>2</sub> O	4.24	14.67	12.45	14.78	7.13	3.47	3.66	3.95	4.37	3.78	5.30	20.67	2.93	3.09
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0.24	0.22	0.28	0.22	0.26	0.30	0.23	0.21	0.22	0.21	0.24	0.22	0.14	
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	23	24	24	24	23	22	24	23	19	21	14	19	23	19
La/Sc	2.25	2.30	-	-	2.35	-	-	-	1.92	2.03	-	3.41	2.13	2.40
Th/Sc	0.73	1.08	0.65	1.09	1.04	1.13	0.94	0.85	0.75	0.89	1.31	1.02	0.75	0.90
La/Th	3.08	2.13	-	-	2.27	-	-	-	2.55	2.28	-	3.33	2.86	2.60
Zr/Hf	13.64	13.39	12.43	13.24	13.74	20.88	16.25	5.67	11.64	22.11	13.53	11.66	20.52	42
Cr/Ni	1.95	2.37	1.89	2.29	2.30	2.77	2.08	1.28	1.48	1.64	5.16	4.02	1.16	2.00
Cr/Th	9.11	4.63	6.16	4.63	4.82	8.28	8.26	3.88	5.01	4.55	4.19	5.56	5.46	7.53
Th/Co	0.11	0.16	0.10	0.21	0.19	0.17	0.19	0.13	0.14	0.46	0.19	0.22	0.21	0.63
Th/Cr	0.11	0.22	0.16	0.02	0.21	0.12	0.12	0.26	0.20	0.22	0.24	0.18	0.18	0.13
U/Th	0.70	0.56	1.13	0.61	0.61	0.53	0.56	0.49	0.46	0.40	0.40	0.51	0.61	0.21
V/Cr	0.79	1.10	1.26	1.06	1.05	0.80	0.77	1.25	1.26	1.31	0.90	1.06	1.22	1.36
Ni/Co	0.50	0.32	0.33	0.43	0.39	0.52	0.76	0.38	0.49	1.29	0.15	0.30	1.00	2.39
Cu/Zn	0.23	0.49	0.18	0.52	0.89	0.22	0.23	0.17	0.43	0.09	0.62	0.38	0.19	0.59

Cr, V, Sr, Rb, Zr, and Sc whereas Co, Nb, and U contents are enriched with respect to those of PAAS. Grey shales have higher abundances in Co, Ba, Y, Hf, and U than PAAS. The calcareous shales are enriched in Sr (~147–252 ppm), whereas a marked depletion is noticed in the grey shales (~58–85 ppm; Figure 2). The high Sr content in calcareous shales indicates that Sr may be associated with calcite minerals. Similarly, calcareous shales have higher content of Ba (~212–6,718 ppm) than grey shales (~941–2,250 ppm) as well as to PAAS. Ba enrichment in sedimentary rocks can be considered as an indicator of detrital flux. The calcareous and grey shales were deposited in a shallow marine environment and hence may be enriched by adsorbed Ba. The high content of Ba concentration in Rabanpalli shales indicates the presence of barite crystals of syn-sedimentary origin (Jayaprakash, 1985). Some trace elements such as Cr, Sc, Ni, and V are positively correlated with  $Al_2O_3$  ( $r = 0.89$ ,  $r = 0.93$ ,  $r = 0.68$ ,  $r = 0.97$ , respectively), which suggest that these elements may be bound in clay minerals and concentrated during weathering (e.g., Fedo *et al.*, 1996).

### Rare earth elements

The concentrations of rare earth elements (REE) are listed in Table 2. In  $\Sigma$ REE content, large variations are observed between calcareous (58.75 to 151.10) and grey shales (117.39 to 133.14). The bulk REE normally reside

in the fine fraction (silt or clay) and it has also been inferred that trivalent REE readily accommodated in most clay minerals enriched with alumina and ferric iron (Cullers *et al.*, 1987, 1988). In a chondrite-normalized REE plot (Figure 3), the shale samples from the Rabanpalli Formation show slightly LREE enriched and flat HREE pattern with negative Eu anomaly. The calcareous and grey shales show less fractionation of REE ( $La_N/Yb_N = 6.26$  to  $10.20$  and  $8.05$  to  $8.53$ , respectively). These ratios are slightly lower than the PAAS [ $(La/Yb)_{PAAS} = 9.5$ , Taylor and McLennan, 1985], except C122.

## DISCUSSION

### Provenance

The geochemical signatures of clastic sediments have been used to find out the provenance characteristics (Taylor and McLennan, 1985; Condie *et al.*, 1992; Cullers, 1995; Madhavaraju and Ramasamy, 2002; Armstrong-Altrin *et al.*, 2004).  $Al_2O_3/TiO_2$  ratios of most clastic rocks are essentially used to infer the source rock compositions, because the  $Al_2O_3/TiO_2$  ratio increases from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks, and from 21 to 70 for felsic igneous rocks (Hayashi *et al.*, 1997). In the calcareous shales, the  $Al_2O_3/TiO_2$  ratio ranges from 19.40 to 24.25 and in grey shales it varies between 13.60 and 23.34.

Table 2. Rare earth element concentrations (ppm) for calcareous and grey shales of the Rabanpalli Formation and average values of granitic gneisses, granitoids, and post-Archean Australian shale (PAAS) for comparison. \*

Rock Type Sample #	Calcareous shale					Grey shale		Shale <sup>1</sup>	Granitic gneisses <sup>2</sup>	Granitoids <sup>3</sup>	PAAS <sup>4</sup>
	S53	S51A	S38E	E121	C122	C103	E189				
La	12.5	12.3	14.7	26.3	31.7	29.8	30.3	22.51	69.00	100.03	38.20
Ce	21.4	18.5	22.5	48.9	59.2	37.3	46.5	36.32	67.00	195.73	79.60
Pr	3.70	3.50	4.10	7.40	8.70	6.72	7.00	5.87	-	18.14	8.83
Nd	13.8	14.1	14.8	22.6	26.9	20.7	25.5	19.75	27.60	69.31	33.90
Sm	3.30	2.50	2.60	4.90	5.84	4.80	5.40	4.19	5.60	11.07	5.55
Eu	0.56	0.48	0.51	1.10	1.06	0.63	1.30	0.80	1.40	1.57	1.08
Gd	2.90	2.40	2.97	4.70	5.40	4.97	5.10	4.06	6.40	7.75	4.66
Tb	0.40	0.32	0.45	0.70	0.82	0.80	0.80	0.61	-	1.07	0.77
Dy	2.60	1.90	2.68	4.40	5.20	4.91	4.60	3.76	3.20	5.76	4.68
Ho	0.50	0.41	0.50	0.90	1.00	0.88	0.90	0.73	-	1.11	0.99
Er	1.30	1.00	1.40	2.40	2.60	2.65	2.62	2.00	0.80	3.09	2.85
Tm	0.20	0.15	0.18	0.34	0.31	0.37	0.35	0.27	-	0.45	0.41
Yb	1.35	1.02	1.30	2.33	2.10	2.50	2.40	1.86	0.80	2.73	2.82
Lu	0.20	0.16	0.20	0.34	0.29	0.37	0.36	0.27	-	0.39	0.43
$\Sigma$ REE	64.7	58.8	68.8	127.3	151.1	117.4	133.1	103.02	181.80	418.20	184.77
Eu/Eu*	0.54	0.59	0.56	0.69	0.57	0.40	0.75	0.59	0.71	0.49	0.63
$(La/Yb)_n$	6.26	8.18	7.62	7.63	10.20	8.05	8.53	8.18	58.28	24.76	9.15
$(La/Sm)_n$	2.38	3.11	3.55	3.38	3.42	3.91	3.53	3.37	7.76	5.69	4.33
$(Gd/Yb)_n$	1.74	1.91	1.85	1.63	2.08	1.61	1.72	1.77	6.48	2.30	1.34

<sup>1</sup> Average value of this study, <sup>2</sup>Jayaram *et al.* (1983), <sup>3</sup>Jayananda *et al.* (2000), <sup>4</sup>Taylor and McLennan (1985). Subscript <sub>n</sub> refers to chondrite-normalized values. \* Before data presentation in the Table, an attempt was made to round the data to the number of significant digits as suggested by Verma (2005).

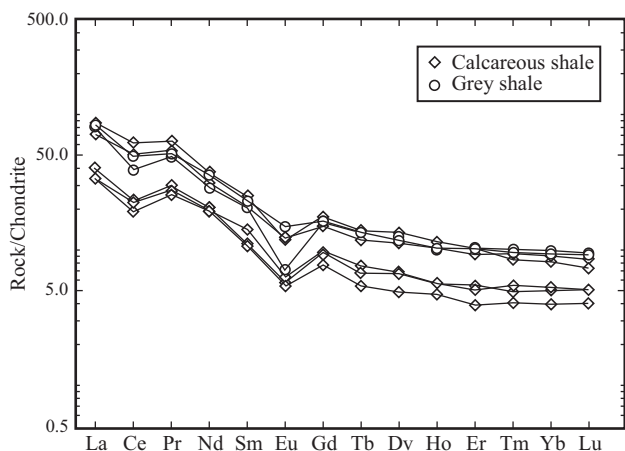


Figure 3. Chondrite normalized rare earth element plot for shale samples from the Rabanpalli Formation. Chondrite normalization values are from Taylor and McLennan (1985).

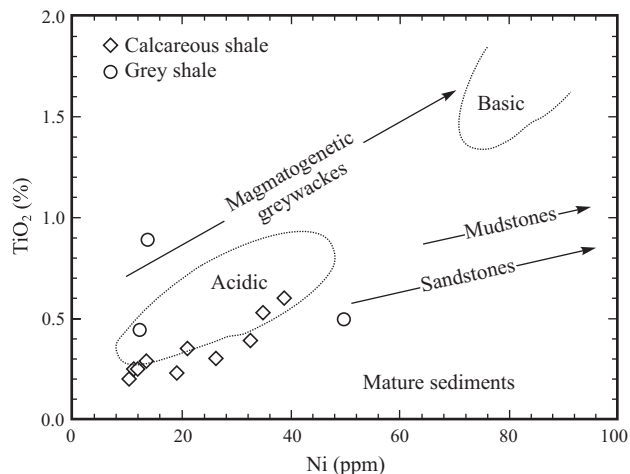


Figure 4.  $TiO_2$  versus Ni bivariate plot for shale samples from the Rabanpalli Formation (fields after Floyd *et al.*, 1989).

The  $Al_2O_3/TiO_2$  ratio is essentially identical and range between 15 and 25 for shales and sandstones of Precambrian age reported from Egypt (Willies *et al.*, 1988). Thus, the  $Al_2O_3/TiO_2$  ratio of this study suggests that intermediate to felsic granitoid rocks must be the probable source rocks for the shales of the Rabanpalli Formation. This interpretation is further supported by the  $TiO_2$  vs. Ni bivariate plot (Figure 4; Floyd *et al.*, 1989), which also indicate that these shales were mainly derived from felsic source rocks.

The abundance of Cr and Ni in siliciclastic sediments are considered as a useful indicator in provenance studies. Chromium and Ni concentrations are low in the calcareous and grey shales (Table 1). According to Wrafter and Graham (1989) a low concentration of Cr indicates a felsic provenance, and high contents of Cr and Ni are mainly found in sediments derived from ultramafic rocks (Armstrong-Altrin *et al.*, 2004). The Cr/Ni ratios are low in both grey (~1.16–5.16) and calcareous (~1.28–2.77) shales. However, the Th/Cr ratio in both grey (~0.18–0.24) and calcareous shales (~0.12–0.26) is higher than in PAAS (Th/Cr = 0.13;

Taylor and McLennan, 1985).

Ratios 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 (Wronkiewicz and Condie, 1990; Cox *et al.*, 1995; Cullers, 1995). Th/Sc, Th/Co, Th/Cr, Cr/Th, and La/Sc ratios of shales from this study are compared with those of sediments derived from felsic and basic rocks (fine fraction) as well as to upper continental crust (UCC) and PAAS values (Table 3). This comparison also suggests that these ratios are within the range of felsic rocks. In addition, the La/Th and Th/Sc ratios are fairly constant in sedimentary rocks (2.4 and 0.9, respectively; Taylor and McLennan, 1985). The La/Th and Th/Sc ratios of the shales in the present study are more or less close to PAAS (Table 1), which suggest a felsic nature of the source rocks. Furthermore, the Th/Co vs. La/Sc plot (Figure 5; Cullers, 2002) also suggests that the shales of the Rabanpalli Formation were derived from felsic source rocks.

The REE pattern and europium anomaly in the sedi-

Table 3. Range of elemental ratios of calcareous and grey shales in this study compared to the ratios in similar fractions derived from felsic rocks, mafic rocks, upper continental crust, and Post-Archean Australian shale.

Elemental ratio	Range of shales from the Rabanpalli Formation <sup>1</sup>		Range of sediments <sup>2</sup>		Upper continental crust <sup>3</sup>	Post-Archean Australian average shale <sup>3</sup>
	Calcareous shale (n = 10)	Grey shale (n = 3)	Felsic rocks	Mafic rocks		
Th/Sc	0.65 - 1.13	0.75 - 1.31	0.84 - 20.5	0.05 - 0.22	0.79	0.9
Th/Co	0.10 - 0.46	0.19 - 0.22	0.67 - 19.4	0.04 - 1.4	0.63	0.63
Th/Cr	0.11 - 0.26	0.18 - 0.24	0.13 - 2.7	0.018 - 0.046	0.13	0.13
Cr/Th	3.88 - 9.11	4.19 - 5.56	4.00 - 15	25 - 500	7.76	7.53
La/Sc	1.92 - 2.35 <sup>a</sup>	2.13 - 3.41 <sup>b</sup>	2.5 - 16.3	0.43 - 0.86	2.21	2.4

<sup>1</sup> This study; <sup>2</sup> Cullers (1994, 2000); Cullers and Podkovyrov (2000); Cullers *et al.* (1988); <sup>3</sup> Taylor and McLennan (1985). n = number of samples; <sup>a</sup> number of samples = 5; <sup>b</sup> number of samples = 2.

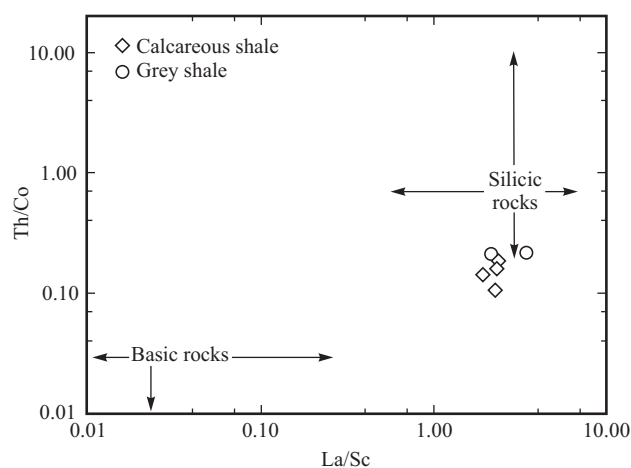


Figure 5. Th/Co versus La/Sc diagram for shale samples from the Rabanpalli Formation (fields after Cullers, 2002).

mentary rocks will provide important clues regarding the source rock characteristics (Taylor and McLennan, 1985). Higher LREE/HREE ratios and negative Eu anomalies are generally found in felsic rocks, whereas the mafic rocks exhibit lower LREE/HREE ratios and no or small Eu anomalies (Cullers, 1994). The positive Eu anomalies are generally found in Precambrian rocks [tonalite-tronjhemitgneiss (TTG), granodiorite, and quartz diorite]. The TTG rocks exhibit very high LREE/HREE ratios and no or small positive Eu anomalies, and the positive anomaly resulted from hornblende-melt equilibria (Cullers and Graf, 1984). The Rabanpalli shales show slightly LREE enriched and flat HREE patterns with negative Eu anomalies (Figure 3). However, the Rabanpalli shales show high LREE/HREE ratios ( $6.49 \pm 0.66$ ,  $n = 7$ ) and negative europium anomaly (avg. 0.93,  $n = 4$ ), which suggest that these sedimentary rocks were mainly derived from the felsic source rocks. The  $(\text{Gd}/\text{Yb})_N$  ratios ( $1.79 \pm 0.17$ ,  $n = 7$ ) of Rabanpalli shales are less than 2, which suggest that these shales were derived from the less HREE depleted source rocks.

The paleocurrent current data of Akhtar (1977) suggest that the Archean Dharwar Craton, exposed in an area adjoining this basin, was the source rocks for the Bhima Group. Hence, the REE data of this study are compared with granitic gneisses (tonalitic and granitic gneisses, average of 22 samples from Dharwar Craton; Jayaram *et al.*, 1983) and granitoids (granites and granodiorites, average of 11 samples from Dharwar Craton; Jayananda *et al.*, 2000) to find out the source rocks (Figure 6). The REE patterns and Eu anomaly of the Rabanpalli shales are similar to granitoids from Dharwar Craton, which suggests that these shales were predominantly derived from the Archean Dharwar Craton. This interpretation is further supported by the  $\text{Eu}/\text{Eu}^*$  vs.  $(\text{Gd}/\text{Yb})_N$  plot (Figure 7). The  $(\text{Gd}/\text{Yb})_N$  ratio also document the nature of source rocks and the composition of the continental crust (Taylor and McLennan, 1985). Archean crust generally has higher  $(\text{Gd}/\text{Yb})_N$  ratio, recording typically

values above 2.0 in sedimentary rocks, whereas the Post-Archean rocks have  $(\text{Gd}/\text{Yb})_N$  values commonly between 1.0 and 2.0 (McLennan, 1989; McLennan and Taylor, 1991). In a  $\text{Eu}/\text{Eu}^*$  vs.  $(\text{Gd}/\text{Yb})_N$  plot (Figure 7), samples fall below the  $(\text{Gd}/\text{Yb})_N = 2.0$  boundary, except one sample, which fall above this line. All samples fall below the  $\text{Eu}/\text{Eu}^* = 0.85$  line. The  $\text{Eu}/\text{Eu}^*$  and  $(\text{Gd}/\text{Yb})_N$  ratios of the Rabanpalli shales fall more or less near to granitoids from the Dharwar Craton, which suggest that the Archean rocks from Dharwar Craton could be the source rocks for Rabanpalli Formation. The HREE depletion [ $(\text{Gd}/\text{Yb})_N > 2.0$ ] is common in the Archean rocks and is essentially absent in the post-Archean rocks (Taylor and McLennan, 1985). The  $(\text{Gd}/\text{Yb})_N$  vs.  $\text{Eu}/\text{Eu}^*$  plot suggests that the Rabanpalli shales fall between PAAS and granitoids, and have REE patterns (Figure 3) somewhat similar to PAAS. It suggests that intracrustal differentiation processes occurred on a local scale in the Archean crust of Dharwar Craton (*e.g.*, Gibbs *et al.*, 1986; Taylor *et al.*, 1986; McLennan, 1989).

### Paleo-oxygenation condition

The oxidation of uranium exerts a strong control on the marine geochemistry (Barnes and Cochran, 1990). In oxic conditions, uranium is present in high concentrations as uranyl tricarbonate species, whereas in reducing condition U(VI) will be converted into U(IV) species, which can be easily removed from the seawater and precipitated onto particle surfaces (Barnes and Cochran, 1990; Nath *et al.*, 1997). Calcareous and grey shales show moderate to high content of U ( $\sim 2.85$ – $5.61$ ,  $\sim 4.53$ – $6.79$ , respectively). Low contents of U are generally found in sediments deposited in oxygenated conditions in marine environment (Somayajulu *et al.*, 1994; Madhavaraju and Ramasamy, 1999), whereas

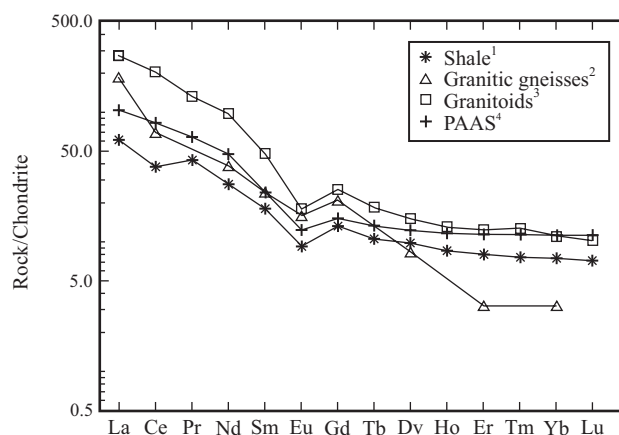


Figure 6. The chondrite normalized rare earth element pattern of Rabanpalli shales (average value) is compared with granitic gneisses and granitoids from Dharwar Craton to find out the source rock composition. <sup>1</sup>This study; <sup>2</sup>Jayaram *et al.* (1983); <sup>3</sup>Jayananda *et al.* (2000); <sup>4</sup>Taylor and McLennan (1985).



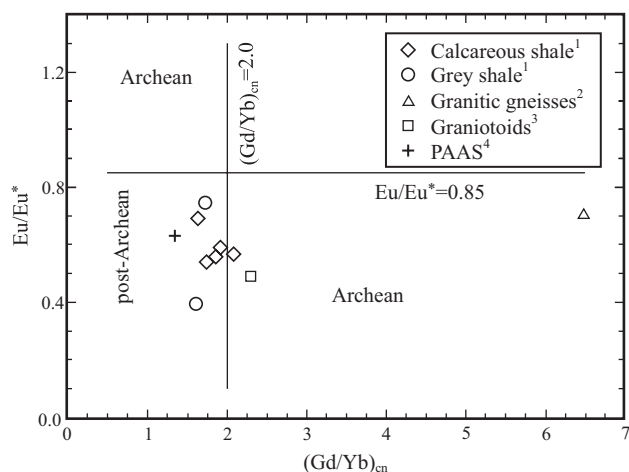


Figure 7. Plot of  $\text{Eu}/\text{Eu}^*$  versus  $(\text{Gd}/\text{Yb})_{\text{cn}}$  for the Rabanpalli shales. Fields after McLennan and Taylor (1991). The symbols are the same as in Figure 6.

high U contents are found in sediments from the oxygen minimum zone (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Sarkar *et al.*, 1993; Somayajulu *et al.*, 1994; Nath *et al.*, 1997).

The Late Archean granitoids, *i.e.*, the basement rocks of Bhima basin, exhibit high content of U (3–21 ppm with an average of 8 ppm; Senthil Kumar and Srinivasan, 2002). These granitoids have been altered as result of hydrothermal activity, which leached out uranium from the accessory minerals and concentrated them along the fault zones (Senthil Kumar and Srinivasan, 2002). The observed moderate to high content of U in both calcareous and grey shales are mainly due to enrichment of U in the source rocks, which contributed more U to these shales. Furthermore, the calcareous and grey shales do not show significant variation in U content. The ratio of uranium to thorium may be used as a redox indicator with U/Th ratio being higher in organic rich mudstones (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). In the Arabian Sea, sediments below the oxygen minimum zone (OMZ) show high U/Th (>1.25) ratios, whereas the sediments above the OMZ exhibit low U/Th (<1.25) ratios. The calcareous and grey shales of this study show low U/Th ratios (~0.40–1.13, ~0.40–0.61, respectively), which indicate that these shales were deposited in an oxic environment.

The authigenic uranium content is also considered as an index of bottom water condition in ancient sedimentary sequences (Wignall and Myers, 1988). The authigenic uranium content is calculated as: (authigenic U) = (total U) – Th/3. Values of authigenic U below 5 are thought to represent oxic depositional conditions, while values above 5 are indicative of suboxic and anoxic conditions. In this study, authigenic U contents are low in both calcareous (~0.98–2.55 ppm) and grey shales (~1.09–2.97 ppm). If the

observed high content of U in these shales resulted from uranium mobilization (removed from seawater and precipitated on particles surfaces) then it should also be reflected in the U/Th ratios and authigenic uranium contents. Thus, the observed low U/Th ratio and low authigenic U content in calcareous and grey shales indicate that these shales were deposited in an oxic environment.

The V/Cr ratio has been used as an index of paleo-oxygenation in many studies (Ernst, 1970; Bjorlykke, 1974; Dill, 1986; Dill *et al.*, 1988). Cr is mainly incorporated in the detrital fraction of sediments and it may substitute for Al in the clay structure (Bjorlykke, 1974). Vanadium may be bound to organic matter by the incorporation of  $\text{V}^{4+}$  into porphyrins, and is generally found in sediments deposited in reducing environments (Shaw *et al.*, 1990). Ratios above 2 indicate anoxic conditions, whereas values below 2 suggest more oxidizing conditions (Jones and Manning, 1994). In the present study, the V/Cr ratios of all samples (calcareous and grey shales) varies between 0.77 and 1.31, which imply that these shales were deposited in an oxic depositional environment.

Dypvik (1984) and Dill (1986) used the Ni/Co ratio as a redox indicator. Jones and Manning (1994) suggested that Ni/Co ratios below 5 indicate oxic environments, whereas ratios above 5 suggest suboxic and anoxic environments. The calcareous and grey shales show low Ni/Co ratio (~0.32–1.30, ~0.15–1.00, respectively), which suggest that these sediments were deposited in a well oxygenated environment. In addition, the Cu/Zn ratio is also used as a redox parameter (Hallberg, 1976). According to Hallberg (1976) high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions. Thus, the low Cu/Zn ratios for calcareous (~0.09–0.89) and grey shales (~0.19–0.62) indicate that the Rapanpalli shales were deposited under well oxidizing conditions.

## CONCLUSIONS

The Proterozoic shales of the Rabanpalli Formation show considerable variations in major, trace, and rare earth elements. Higher concentration of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , Zr, Th, U, V, Cr, La, Ce, and Y are observed in the grey shales than the calcareous shales, whereas the calcareous shales are enriched with CaO, Mn, Sr, Ba, Cu, and Zn contents. The REE pattern, as well as other geochemical parameters like La/Sc, Th/Sc, Th/Co, Th/Cr, and Cr/Th ratios, and La/Sc vs. Th/Co plot suggests that these sediments were mainly derived from felsic source rocks. The REE patterns and Eu anomaly indicate that a derivation of these sedimentary rocks from the Archean Dharwar Craton, which was exposed during the Proterozoic time. The geochemical parameters like U, authigenic U, U/Th, V/Cr, Ni/Co, and Cu/Zn ratios strongly imply that these shales were deposited in an oxic environment.

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