Geochemistry of Neoproterozoic Limestones of the Shahabad Formation, Bhima Basin, Karnataka, Southern India

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ABSTRACT: Major, trace and rare earth element (REE) geochemistry of carbonate rocks of the Neoproterozoic Shahabad Formation, southern India were studied in order to investigate the depositional environment and source for the REEs. The PAAS (Post Archaean Australian Shale) normalized REE+Y pattern of Shahabad limestones have consistent seawater-like pattern i.e. i) LREE depletion (average \((Nd/Yb)_{SN} = 0.64 \pm 0.08\)), ii) negative Ce anomaly, iii) positive Gd anomaly (average \((Gd_{SN}/Gd^*) = 1.05 \pm 0.16\)), iv) superchondritic Y/Ho ratio (average \(Y/Ho = 38.13 \pm 21.35\)). The depletion of LREE and enrichment of HREE are clearly indicated by the \((La/Yb)_{SN}\), \((Dy/Yb)_{SN}\) and \((Nd/Yb)_{SN}\) ratios, which suggest the retention of seawater characteristics in these limestones. The negative Ce anomaly reflects the incorporation of REE directly from seawater or from the pore water under oxic condition, and also reveals the mixing of two-component systems with terrigenous clay (detrital) in the marine sediments. The terrigenous input in these limestones is confirmed by positive correlation of \(\sum\)REE with \(Al_2O_3\), negative correlation of \(\sum\)REE with \(CaO\) and differences in \(Y/Ho\) ratios. \(V\), \(Cr\), and \(Sc\), are positively correlated with \(Ti\), and strong positive correlation of \(\sum\)REE with \(Fe_2O_3\), \(Ni\), \(Cr\), \(Sc\), and \(Y\) also indicate the presence of terrigenous materials in the Shahabad limestones.

Keywords: Rare earth elements, geochemistry, Neoproterozoic limestones, Paleo-redox conditions, Bhima Basin, South India
1. INTRODUCTION

Rare earth element (REE) concentrations in ancient carbonate rocks are useful to identify the marine versus non-marine sources of REE (Banner et al., 1988; Frimmel, 2009; Zhao et al., 2009). REE have low residence time and low solubility in seawater (Piper, 1974a). REEs are relatively immobile during the post-depositional processes like diagenesis (Chaudhuri and Cullers, 1979) and metamorphism (Muecke et al., 1979). Earlier studies mentioned that the carbonate rocks have low REE concentrations (Goldberg et al., 1963; Haskin and Haskin, 1966; Tlig and M’Rabet, 1985), and the REE patterns in carbonate rocks are mainly influenced by depositional environment (Murray et al., 1990, 1992, Madhavaraju and Ramasamy, 1999) and diagenetic processes (Armstrong-Altrin et al., 2003; Fu et al., 2011; Morad et al., 2010; Scherer and Seitz, 1980; Schieber, 1988). REEs are considered as an indicator to identify the depositional environmental system such as widespread marine anoxia (Liu et al., 1988; German and Elderfield, 1990; Murray et al., 1991b), oceanic palaeo-redox conditions (Wang et al., 1986; Elderfield and Pagett, 1986; Liu et al., 1988; Kato et al., 2002), variations in surface productivity (Toyoda et al., 1990), proximity to source area (Murray et al., 1991b), lithology and diagenesis (German and Elderfield, 1990; Murray et al., 1991b; Nath et al., 1992; Madhavaraju and Ramasamy, 1999; Armstrong-Altrin et al., 2003; Madhavaraju and Lee, 2009; Madhavaraju et al., 2010) and paleogeography and depositional models (e.g., Kamber and Webb, 2001; Kemp and Trueman, 2003). The study of REE, particularly LREE from the marine sediments/sedimentary rocks may reflect the original characteristic of seawater. Because, REE+Y in sedimentary carbonates can be affected by fluid mobilization during diagenesis and metamorphism and ancient sedimentary rocks were considered as reliable sources for REE.
proxies (Holser, 1997). According to Zhong and Mucci (1995), REE+Y are substituted for Ca\(^{2+}\) in the carbonate lattice and are expected to be more stable than oxygen or carbon isotopes within the carbonate lattice during diagenesis. In addition, REE+Y concentrations are low in diagenetic fluids (10\(^{-6}\) to 10\(^{-4}\) ppm) (Sholkovitz et al., 1989; Banner and Hanson, 1990). So, REE+Y concentrations in ancient carbonate rocks may be stable even during relatively intense diagenesis (Webb and Kamber, 2000; Frimmel, 200). REEs are not easily fractionated during sedimentation, and their patterns may provide a key to average provenance compositions (Taylor and McLennan, 1985; Wani and Mondal, 2010; Bakkiaraj et al., 2010). Marine chemical sediments reveal seawater REE+Y patterns that appears to be independent of Age of deposition (Shields and Webb, 2004; Bolhar and Kranendonk, 2007). They are characterized by a uniform LREE depletion; La enrichment, Ce depletion, slight Gd enrichment, and positive Y anomaly in shale normalized patterns (Zhang and Nozaki, 1996). No systematic study has yet been carried out on REE geochemistry of Neoproterozoic limestones of Shahabad Formation. In this study, we report new major, trace, and REE data, and its variations in different types of limestones. Our aims are to trace the depositional environment, to interpret the possible source of REEs, and to know the reason for the variations in Eu and Ce anomalies in the Neoproterozoic limestones of Shahabad Formation.

2. GEOLOGICAL SETTING

Bhima basin, south India is a NE-SW trending Neoproterozoic, epicratonic, extensional basin (Fig. 1), which formed due to gravity faulting. Sedimentary rocks of the Bhima Basin are exposed as an array of narrow, E-W stretching, sygmoideal strips arranged in an en-echelon
pattern. The epicratonic Mesoproterozoic Kaladgi Super Group and Neoproterozoic Bhima Group overlie the Archaean granite-greenstone basement in Karnataka, Southern India. This Basin is exposed on the northeastern margin of the Dharwar Craton and is the smallest of all the Purana Basins of the Indian Peninsula (Kale and Phansalkar, 1991). The Archaean granite-greenstone terrain mainly consists of TTG (Tonalite-Trondhjemite-Granodiorite) gneisses popularly known as peninsular gneisses (Dharwar greenstone belts). The Cratonization of Archaean 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 the Kaladgi Super Group and Neoproterozoic Bhima Groups were deposited on the eroded edges of the Dharwar Craton (Senthil kumar and Srinivasan, 2002). The Kaladgi sedimentary Basin is exposed EW for a length of ~160km, with a width varying from 40-65km, and covers an area of about 8000km² to the west of Bhima Basin. The Bhima Basin is younger than the Kaladgi Super Group and is well exposed in the Bijapur and Gulburga districts of northern Karnataka and Ranga Reddy district of Andhra Pradesh, India. Bhima exposures are sandwiched between Early Precambrian granite - greenstone terrain of the East Dharwar Craton in the south and the Late Cretaceous - Paleocene Deccan Trap volcanic Province in the north. The Bhima Basin sediments extended further towards north, which concealed under Deccan Traps. The sedimentary rocks of the Bhima Basin and the granitoids have been affected by intense faulting. The major structural faults and associated joint structures are associated by intense shearing, brecciation and silicification. Major faults across the basin define the structural boundaries of the different sectors (Kale and Peshwa 1995). They are i) East-West trending Tirth, Gogi, and Mogalavadikavagu faults and ii) 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 divided the sedimentary rocks into Muddebihal Sandstones and Talikote Limestone. Mahadevan (1947) proposed three fold classification viz. i) Lower Bhima Series [Basal conglomerate, sandstones and shales], ii) Middle Bhima Series [dominantly consists of limestones] and iii) Upper Bhima Series [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 that include, from base up, i) Rabanpalli Formation, ii) Shahabad Formation, iii) Halkal Shale, iv) Katamadevarhalli Formation, and v) Harwal Shale. Misra et al. (1987) subdivided the Bhima Group into Sedam Subgroup (Rabanpalli Formation and Shahabad Formation) and Andola Subgroup (Halkal Shale, Katamadevarhalli Formation and Harwal-Gogi Shale). They identified the sedimentation break between Sedam and Andola Subgroup and interpreted as paraconformity. The classification proposed by Janardhana Rao et al. (1975) has been followed in this study.

The sedimentary rocks of Bhima Basin are trending in the NE-SW direction, which exhibit total thickness of about 300m (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) and covering an area of 5,200 km$^2$. In the clastic rocks, fine-grained sediments (sandstone, siltstone, and shale) dominate over the coarse arenites and arkoses. The Rabanpalli Formation has been considered as the oldest sedimentary rocks in the Bhima Basin, which 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 (Nagarajan et al., 2007a, b). The limestone member is the dominant lithology of the Bhima Basin and is classified under Shahabad and Katamadevarahalli Formations.

The Shahabad Formation is exposed in the central and eastern parts of the Bhima Basin (lat. 16°15′ to 17°35′ N long. 76°15′ to 77°30′ E). Shahabad Formation was described by different names by different authors such as Talikote limestone by Newbold (1842), Upper Bhima Series by Foote (1876), Middle Bhimas by Mahadevan (1947) and subsequently Janardhana Rao et al. (1975) named this formation as Shahabad limestone formation. Later, Mathur (1977) changed the name Shahabad limestones to Kurkunta limestones to avoid confusions, since the name had been used for limestones exposed in Madhya Pradesh and Uttar Pradesh in India. However, Shahabad limestones famed as the “Shahabadi paving slabs”, which attracted geologists as well as cement and construction industries. Later, Misra et al. (1987) reintroduced the name Shahabad to this Formation. The limestones of Bhima Basin are the non-stromatolitic and non-dolomitic nature. These limestones occupy an area of 2,000 km² in the Bhima Basin. According to Kale et al. (1990) Shahabad Formation’s vertical thickness is less than 75m including exposures of the Katamadevarahalli limestone. These limestones are micritic in nature, petrographically cryptocrystalline in texture (Malur and Nagendra, 1994; Nagendra and Nagarajan, 2003) with number of macro and micro stylolites, which are filled with secondary minerals (Nagarajan et al., 2008). These limestones separated into five different varieties, representing microfacies in the carbonate platform of the Bhima Basin. The five varieties are (i) flaggy impure limestone; (ii) blocky micritic limestone; (iii) variegated limestone; (iv) blue-grey massive limestone; and (v) argillaceous micritic limestone. Flaggy
impure limestones are creamy brown to dusty bluish grey colour. These impure limestones often contain silty and clay parting laminations, which show wavy ripples and rippled undulating bedding planes. Blocky limestones display light grey shades with irregular bluish tinge. These limestones are characterized by their continuous, parallel bedding separated by mud or clay partings, which are profusely the nature of stylolites (Jayaprakash, 1986). Generally, these are micritic in nature, which has re-crystallized at some places. Variegated limestones exhibits grey and banded appearance imparted due to parallel continuous alternating siliceous and pure calcareous laminae. Blue grey massive limestones show dark blue and bluish grey shades accentuated by occasional dark black laminations. Within them disseminated pyrite grains are common. Some places the pyrites are altered to limonite. Argillaceous micritic limestones consist of alternate beds of pure and impure calcareous micritic composition and have puff creamy to pinkish brown colour. Quartz clasts with minor rock fragments are embedded within these impure micritic limestones (Kale and Peshwa, 1995). However, on the field it is difficult to identify the differences between the flaggy impure and argillaceous micritic limestones; or between the slabby/blocky limestones and the massive limestones. The petrographic classification of Bhima limestones is characterized by their colour and texture. The black to dark grey, grayish black to purple, fine grained, massive flaggy, siliceous, and argillaceous limestones are exposed with randomly distributed pyrite grains. The thinly bedded limestones are argillaceous in nature. Three limestone varieties (classification based on color) were selected in this study and the representative limestone samples were collected from Chincholi, Malkapur, Kurkunta, Gundgurti, Shahabad, Sedam, Malkhaid, Mubol, Gudur, Chitapur, Ravur, Wadi, Sirwal, Gogi, and other exposures of Shahabad Formation (Fig. 1).
3. METHODOLOGY

Samples were collected from the outcrops of Shahabad Formation, Bhima Basin. The collected samples were washed thoroughly in distilled water to remove the contamination. Eighteen representative samples were selected and analysed i.e., eight from the grey limestone (GL), six from the yellow limestone (YL) and four from the brown limestone (BL). Care was taken to remove the weathered portions from the surface of the limestone samples. The selected samples were washed with distilled water, air dried and grinded in an agate mortar and sieved through a 200 ASTM (American Society for Testing and Materials) mesh for chemical analysis. The samples were digested in of HNO₃ + HF solution. The digested samples 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%. 1 g of sample was heated to 1000°C for 1 hour to measure the Loss on ignition (LOI).

About 0.2 g of samples were digested with 4 ml HNO₃ and 1 ml of HClO₄ for 24 h in a tightly closed Teflon vessel on a hot plate at 150°C, heated to dryness, and then digested with a mixture of 4 ml of HF and 1 ml of HClO₄. Later, the solution was evaporated to dryness, and extracted with 10 ml of 1% HNO₃. The digested samples were measured for rare earth elements by ICPMS (Plasma QUAD 3). The geochemical standard SPL – 29 and GSR 5 were used for evaluation of the accuracy of analytical data. The analytical accuracy of La, Nd, Eu, Gd, Tb, Dy, Tm, Yb and Lu are better than ± 2%. The precision of Ce, Pr, Eu, Gd Ho, Er are better than ± 5%. The accuracy of Sm is better than ± 10%. For preparing REE normalized diagrams, Post
Archaean Australian Shale (PAAS) values listed by Taylor and McLennan (1985) are used. Based on the color, the limestones are classified as grey limestone (GL), yellowish limestone (YL), and brown limestone (BL).

4. RESULTS

The limestones are mostly micritic in nature. The major and trace element concentrations including rare earth elements are shown in Tables 1 and 2, respectively.

4.1. Major elements

Major element concentrations are listed in Table 1. Wide variations are observed in the SiO₂, CaO, and Fe₂O₃ contents in these limestones (GL = 9.60 to 22.56 wt.%, 33.8 to 49.2 wt.%, 0.27 to 1.59 wt.%, respectively; YL = 7.20 to 13.25 wt.%, 40.2 to 49.2 wt.%, 0.23 to 1.23 wt.%, respectively; BL = 12.10 to 25.50 wt.%, 34.5 to 42.3 wt.%, 0.98 to 1.95 wt.%, respectively). Smaller variation is observed in the Al₂O₃ contents in BL (2.13 to 4.42 wt.%) than GL (0.69 to 3.44 wt.%) and YL (0.78 to 4.11 wt.%). Low contents of MgO, Na₂O, K₂O, TiO₂, and P₂O₅ are observed in the GL, YL and BL (Table 1). SiO₂ vs CaO shows distinct negative correlation (statistically significant at a significance level of 0.001; linear correlation coefficient r = -0.86, n = 18), which probably suggests that these two elements exhibit different modes of origin.

4.2. Trace elements

Trace element concentrations are shown in Table 2. Trace elements were normalized using PAAS values (Taylor and McLennan, 1985) and are given in the spider diagram (Fig. 2).
Cr and Rb are highly depleted in comparison to PAAS, whereas Nb is more or less equal to PAAS. The PAAS normalized patterns of Shahabad limestones show a moderate depletion in V, Ni, Cu, Zn, Sc, Pb and Th, whereas Ba contents are higher than PAAS. Grey limestones show slight enrichment of Zn, Sr when compared to YL and BL. In general, all the limestone samples are higher in Ba and Pb contents than PAAS. However, some YL and BL samples are higher in Ba content (~ 2041, 2047, 5121 ppm) than the grey limestones (~ 747, 1229 ppm) (Fig. 2). The Sr content (~ 101 - 223 ppm; avg. 138 ± 34.74) is lower than the average value given for the lithosphere carbonates (Sr = 610 ppm; Turekian and Wedepohl, 1961). Mn may be incorporated and Sr may be expelled from the carbonate system (Brand and Veizer, 1980; Veizer, 1983). Hence, the diagenetic alteration of low Mg calcite will decrease the Sr content and increase the Mn content (Veizer, 1983). However, Mn does not show any perfect trend with Sr (Fig. 5a), suggesting that these limestones were not subjected to diagenetic alterations.

4.3. Rare earth elements

REE concentrations are shown in Table 2 and are normalized to PAAS values (Taylor and McLennan, 1985) in Figure 3. ΣREE content shows significant variation among the different limestone types (GL = 35.82 ± 16.20; YL = 25.55 ± 9.91; BL = 35.02 ± 9.79). The low ΣREE in YL is due to marine carbonate phases, which generally contain significantly lower REE content than detrital clays and heavy minerals (Piper, 1974b; Palmer, 1985).

PAAS-normalized REE+Y patterns of Shahabad limestones are given in Figure 3a, b, c. These limestones exhibits 1) seawater like REE+Y pattern with LREE depletion [average
(Nd/Yb)$_{SN}$ ($SN = \text{shale normalized}$) $= 0.64 \pm 0.08$; (Nd/Yb)$_{SN}$ ratio of modern shallow seawater $= \sim 0.205$ to 0.497 for 50m water depth; Zhang and Nozaki, 1996; De Baar et al., 1985 respectively]; 2. Consistent negative Ce$_{SN}$ and positive La$_{SN}$ anomalies (Fig. 4); 3. Positive Gd$_{SN}$ anomalies (avg. 1.05 $\pm$ 0.16; Gd$_{SN}$/Gd$^*$ ratio of modern shallow seawater is $\sim$ 1.30 to 1.05; De Baar et al., 1985 and Zhang and Nozaki, 1998); 4. Super chondritic Y/Ho ratio (avg. Y/Ho = 38.13 $\pm$ 21.35; Y/Ho of seawater is $\sim$ 44-74; Bau, 1996). Two samples from GL show Ce/ Ce$^*$ values (0.35 and 0.46) near to oceanic water (Ce/ Ce$^*$ values of oceanic water range from $<$ 0.1 to 0.4; Elderfield and Greaves, 1982; Piepgras and Jacobsen, 1992).

5. DISCUSSION

5.1. Possible source for REE in Shahabad Limestone

The enrichment and depletion of REE in limestones may be influenced by various factors, viz. i) addition of terrigenous particles from the continent (Piper, 1974a; McLennan, 1989), ii) biogenic sedimentation from the overlying seawater (Murphy and Dymond, 1984), and iii) scavenging process related to depth, salinity and oxygen levels (Elderfield, 1988; Piepgras and Jacobsen, 1992; Bertram and Elderfield, 1993; Greaves et al., 1999), v) authigenic removal of REE from the water column and early diagenesis (Sholkovitz, 1988). Seawater contributes lesser amount of REE to the chemical sediments but the samples with non-seawater like pattern exhibits higher REE concentration (Nothdurft et al., 2004) due to the contamination of non-carbonate materials such as silicates, Fe-Mn oxides, phosphates or sulfides during the chemical leaching (Zhao et al., 2009). Deciphering the processes responsible for REE fractionation is most
important because the REE are considered as useful tracers of various geological and oceanographic processes (Piper, 1974a; Murray and Leinen, 1993). Calcite and dolomite also typically have fairly low REE abundances, similarly resulting in a dilution effect. If carbonate minerals precipitated in equilibrium with seawater, then they typically possess negative Ce anomalies, which may also be reflected in the REE patterns of limestone (Palmer, 1985).

Significant variations in ΣREE content are noticed in the different types of limestones (Table 2). The average REE concentrations of Shahabad limestones (GL: 35.82 ppm, 25.55 ppm, BL: 35.02 ppm.) are more or less comparable with typical marine value (~ 28 ppm, Bellanca et al., 1997), However, they are higher than the shallow marine continental platform carbonates of Late Neoproterozoic successions of Lesser Himalaya and lower than the shallow marine carbonates of southern India (Maastrichtian limestones, Kudankulam carbonates, Arabian Sea and Indian Ocean carbonate sediments, and Neorproterozoic shales; Table 3). Differences in ΣREE content among the individual samples are mainly due to variations in the amount of terrigenous sediment included in these limestones. REEs (La to Lu) show strong positive inter-elemental relationships (> 0.78), indicating their coherent nature, which reveals that they are highly linked with seawater during the REE fractionation. In addition to that, Ce content is also associated with detrital sediments.

PAAS-normalized REE+Y patterns of the Shahabad limestones exhibits seawater-like REE+Y patterns with LREE depletion and relative HREE enrichment (some samples show flat HREE pattern) with negative Ce anomalies and positive Eu anomalies. The observed (Nd/Yb)SN ratio (avg. = 0.64 ± 0.08) of limestones of the Shahabad Formation is more or less similar to the
of modern shallow seawater \[(Nd/Yb)_{SN} \text{ ratio} \sim 0.205 \text{ to } 0.497 \text{ for } 50\text{m water depth}; \text{ Zhang and Nozaki, 1996; De Baar et al., 1985 respectively}\], which suggest that these limestones retained their original seawater characteristics. The \[(La/Yb)_{SN} \text{ ratios}\] range from 0.52 to 0.89 with an average of 0.73. The \[(La/Yb)_{SN} \text{ ratio}\] for Shahabad limestone samples are lesser than the value proposed by Condie (1991) \[(La/Yb)_{SN} = 1\] and Sholkovitz (1990) \[(La/Yb)_{SN} = 1.3\] for terrigenous particulate matter, which indicates that the REE signals were influenced by the LREE depleted carbonate component.

The \[(Dy/Yb)_{SN} \text{ ratio}\] in the Shahabad limestones vary from \sim 0.96 \text{ to } 1.51 \text{ (average } 1.20 \pm 0.13\), which is similar to the modern seawater \(~ 0.8 \text{ - } 1.1\). However, \[(Dy/Yb)_{SN} \text{ ratios}\] in some samples are greater than 1.20. The high \[(Dy/Yb)_{SN} \text{ ratios}\] in Shahabad limestones show an enrichment in HREE rather than LREE, similar to modern seawater. \[(Dy/Yb)_{SN} \text{ ratio}\] is recorded typically between 1.1 and 2.0 for Early Cambrian phosphorites of South China (Shields and Stille, 2002), and can be as low as 0.8 (Hein et al., 1999; Siegmund, 1995), which is identical from modern seawater. A Permian open marine limestone show signs of \[(Dy/Yb)_{SN} \text{ ratios}\] of 1.0 Kawabe et al. (1991) and REE patterns, which are matching to modern, near-surface, open Pacific seawater (Zhang and Nozaki, 1996). Late Devonian microbial carbonates, Western Australia also appear to have retained REE patterns similar to modern seawater and marine microbialite with a mean \[(Dy/Yb)_{SN} \text{ ratio}\] of 0.9 (Nothdurft, 2001). Modern examples yielding identical REE patterns to modern seawater with \[(Dy/Yb)_{SN} \text{ ratio}\] of 0.8 (Webb and Kamber, 2000). \[(Dy/Yb)_{SN} \text{ ratios}\] of the Shahabad limestones \sim 1.1 \text{ to } 2.0\) are comparable to Cambrian phosphorites of South China. HREE depletion and other non-seawater REE patterns in ancient sediments are likely to be derived from post-depositional REE exchange with non-detrital
components and non-quantitative uptake of REE from host sediments (e.g. Shields and Webb, 2004).

The effects of LREE/HREE fractionation in modern and ancient marine systems can be represented by the Er/Nd ratio (German and Elderfield, 1989). Er/Nd ratio in normal seawater is about 0.27 (De Baar et al., 1988). The high Er/Nd ratio of limestones effectively reveals the seawater signature retained by the marine carbonate. Addition of detrital material or diagenesis can reduce the Er/Nd value to less than 0.1 due to preferential concentration of Nd relative to Er (De Baar et al., 1988; German and Elderfield, 1989; Bellanca et al., 1997). The Er/Nd ratio of the Shahabad limestones are ranging from 0.12 to 0.19 in GL, 0.13 to 0.20 in YL; and 0.12 to 0.19 in BL (Table 4), which supports its pristine character for most of the samples. Few limestone samples show the values closer to 0.10, which indicates the influence of detrital materials.

Most of the Shahabad limestones have consistent seawater-like REE+Y patterns. Though, carbonates precipitated from seawater may be experienced variable degrees of contamination that would have suppressed the seawater signature. Variety of contaminants, such as i) shale contamination, which is one of the major input source for marine REE (Elderfield et al., 1990; Nothdurft et al., 2004); 2). Fe and Mn oxides may incorporate REE disproportionately and unpredictably (Bau et al., 1996); and 3). Phosphates (have high affinity for REEs in diagenetic fluids (Byrne and Sholkovitz, 1996).

The influence of terrigenous materials in limestone may be assessed by the relative abundance of Al, Zr, Y, Hf and Th values. Al, Fe, Ti, Sc, Th, Cr, Rb and Ce show significant
positive correlations between one another (Table not shown here). It suggests that Ce is partially associated with detrital input along with the original seawater fractionation. Positive correlation of $\Sigma$REE with $\text{Al}_2\text{O}_3$ (statistically significant at a significance level of 0.001; linear correlation coefficient $r = 0.912$) (Fig. 5b) and negative correlation of $\Sigma$REE with $\text{CaO}$ (statistically significant at a significance level of 0.001; linear correlation coefficient $r = -0.642$) (Fig. 5c) implies the presence of terrigenous fractions, which may be the possible source for REE in these limestones. The terrigenous source of REE is further confirmed by the strong positive correlation of $\Sigma$REE with $\text{Fe}_2\text{O}_3$, Ni, Th, Cr, Sc, and Y (Fig. 5d-i). Among the REEs, LREE show higher positive correlation with elements like $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$ and $\text{MgO}$, than to middle REE (MREE) and heavy REE (HREE). The major elements particularly $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$, and MnO show a distinct correlation among them, and $\text{SiO}_2$ is partly associated with these elements and showing statistically good positive relationship, which confirms the presence of detrital input into the basin. But Ca and P show negative relationship when compared to the other detrital components, which indicates that these elements are originally precipitated in the shallow marine condition.

The $\text{La/Sc}$, $\text{Th/Sc}$, $\text{Th/Cr}$ and $\text{Cr/Th}$ ratios are widely used to understand the provenance composition of the source region, which has shown by variation in these ratios based on the contribution from felsic and mafic rocks (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995; Armstrong-Altrin et al., 2004; Armstrong-Altrin, 2009). $\text{La/Sc}$, $\text{Th/Sc}$, $\text{Th/Cr}$ and $\text{Cr/Th}$ ratios of Shahabad limestones (Table 4), are compared with shales of the same basin, felsic and mafic rocks (fine fraction) as well as to the average upper continental crust (UCC) and
PAAS values (Table 5), which suggest that these ratios are within the range of felsic rocks and comparable to the shales of Bhima Basin.

5.2. Y/Ho ratio

Recently, Yttrium is inserted between Ho and Dy in the REE pattern according to its identical charge and similar radius (REE+Y pattern; Bau, 1996). Yttrium is not removed from seawater like its geochemical twin Ho, due to differing surface complex stabilities, thus leading to a significantly superchondritic marine Y/Ho ratio (e.g., Bau, 1996). Seawater generally displays high Y/Ho ratios (~44-74), whereas terrigenous materials and volcanic ash have constant chondritic Y/Ho ratios of ~28. Modern seawater has considerably higher Y/Ho ratios than the river water and estuaries (Nozaki et al., 2000; Lawrence et al., 2006). Y/Ho ratios show a significant variation among the open-ocean seawater and the ocean margin seawater between 108 and 94, respectively (Nozaki et al., 1997; Johannesson et al., 2006). Though the ionic radii of Ho$^{3+}$ and Y$^{3+}$ are identical, both are expected similar geochemical behavior in natural waters but Y/Ho ratios are not constant in the oceans and vary with depth (Nozaki et al., 1997), which indicates the fractionation of these elements from biogeochemical processes (Johannesson et al., 2006). Y/Ho ratio in open seawater is typically between 60 and 90, but is strongly reliant on salinity (Lawrence et al., 2006). The marine carbonates show higher Y/Ho ratios than the freshwater carbonates (Webb and Kamber, 2000; Shields and Webb, 2004).

In the present study, the limestones of Shahabad Formation show large variations in Y/Ho ratios (GL: ~25.0 to 70.0; YL: ~16.7 to 40.0; BL: ~26.7 to 110.0; with an overall
average of 38.1 ± 21.4, n = 18). The highest value is recorded in BL. BL display REE+Y signatures similar to modern open ocean seawater and have the highest Y/Ho ratios and moderate LREE depletion ((Nd/Yb)\textsubscript{SN} = 0.53), whereas many samples display very low Y/Ho values (Y/Ho < 35; n = 13; Table 4). The observed large variations in the Y/Ho ratios indicate that the Shahabad limestones are contaminated by the influence of terrigenous materials.

5.3. Europium anomaly

Eu is the only REE shows a changing valency in the near surface environment (Brookins, 1989), where Eu\textsuperscript{3+} reduced to Eu\textsuperscript{2+} under extremely reducing conditions. Redox potential of Eu/Eu\textsuperscript{*} in aqueous solutions depends mainly on temperature and to a lesser extent on pressure, pH, and REE speciation (Bau, 1991); which explains the positive Eu anomalies typically found in acidic, reducing hydrothermal fluids. Under the elevated temperature Eu\textsuperscript{3+}/Eu\textsuperscript{2+} redox potential decreases (Sverjensky, 1984). Abundance of Eu anomalies plays significantly important roles to understanding the physical and chemical conditions of many geological systems (Walker et al., 1983; Dymek and Klein, 1988; Derry and Jacobsen, 1990). Eu is normally enriched in Archaean seawater derived carbonates, and this enrichment is not due to redox state of the water (Bolhar and Kranendonk, 2007).

The Shahabad limestones display a large variations in Eu anomaly (Eu/Eu\textsuperscript{*}), which range from 0.95 to 1.7 in the GL, 1.09 to 3.69 in the YL, and 1.22 to 1.58 in the BL (normalized by PAAS values; Table 4). The shale normalized positive Eu anomalies are found either in waters affected by eolian input (Elderfield, 1988) via river, hydrothermal solutions, and the sediments
resulting from high T-basalt alteration along mid-ocean ridges, back arc spreading centre (Michard et al., 1983; German et al., 1993; Siby et al., 2008), and diagenesis (Murray et al., 1991b) or variations in plagioclase content (Nath et al., 1992; Madhavaraju and Lee, 2009). Positive Eu anomalies are uncommon in seawater, which generally results by input from hydrothermal discharges along mid-ocean ridges (Klinkhammer et al., 1983, 1994). Positive Eu anomalies have been extensively well documented for hydrothermal vent fluids and sediment particulates in active ridge system (Michard et al., 1983; Michard, 1989; German et al., 1990, 1999; Douville et al., 1999). Using the pore water REE data of Buzzards Bay sediments, Elderfield and Sholkovitz (1987) and MacRae et al. (1992) have shown that sediments can attain the positive Eu anomaly within a time span of 10,000 - 12,000 yr of diagenetic history. Derry and Jacobsen (1990) and Danielson et al. (1992) also proved that the marine positive Eu anomaly is caused by an increased oceanic input of hydrothermally originated fluids at mid oceanic ridges.

A slight increase in the primary or detrital feldspar component could lead to positive Eu anomalies in bulk sediments (Murray et al., 1991a; Madhavaraju et al., 2010). The elemental ratios like K/Al and Na/Al are useful to understand the presence of detrital feldspar in the bulk sediments (Madhavaraju and Lee, 2009). In the present study, K/Al and Na/Al ratios do not show any correlation with Eu/Eu* (r = -0.23, r = -0.23, n = 18), which suggest that the observed positive Eu anomaly in these limestones may not be due to the inclusion of feldspars in them. The correlation between Mn and Sr are useful to understand the diagenetic alterations in the limestones (Brand and Veizer, 1980). In this study, Mn and Sr have no correlation between them, which suggests that these limestones have not undergone significant diagenetic alterations. The
sediimentary barite (Eu$^{2+}$ substitutes for Ba$^{2+}$), some iron formations and sulfides (via interaction of hydrothermal sulfides with felsic volcanic rocks) are generally exhibiting positive europium anomalies (Cullers and Graf, 1984). In the present study, significant positive correlation is observed between Eu/Eu$^*$ and Ba content, which clearly indicate the evidence of hydrothermal activity in the studied carbonate rocks. However, no correlation is seen between CaO and Eu/Eu$^*$ ($r = 0.09$) suggests the negligible role of biological productivity on the Ba enrichment in the Shahabad limestones. The positive Eu/Eu$^*$ ratios of Shahabad limestone may be the product of either admixture of hydrothermal fluids or co-precipitation of hydrothermal Fe-sulphides. The limestones of Shahabad formation exhibits small pyrite crystals and are characterized by syn-sedimentary exhalative base metal sulphide mineralization. Earlier studies indicate that the hydrothermal vein type uranium mineralization is seen in the limestones of Shahabad Formation and also on the deformed basement granitoids (Achar et al., 1997; Banerjee, 1999; Senthil kumar and Srinivasan., 2002; Pandit et al., 2002; Dhana Raju, 2002; Nagarajan et al., 2007b). So far, no eolian materials were reported in the limestones of Shahabad Formation of Bhima Basin. Hence, we consider that the observed positive Eu anomalies are mainly produced by the hydrothermal activity in the Bhima Basin.

5.4. Cerium anomaly and paleo-redox conditions

The use of cerium anomaly was first proposed by Elderfield and Greaves (1982) as a consequence of the change in the ionic state of Ce as a function of oxidation state. Ce anomaly is mainly observed in the seawater (Elderfield and Greaves, 1982). Processes invoked to explain the development of Ce anomalies include (1) biologically mediated oxidation of Ce (III) to Ce
(IV) in coastal and open ocean (Sholkovitz et al., 1994), (2) Ce (III) to Ce (IV) redox shift across anoxic/oxic interfaces in the water columns of marine basins (German and Elderfield, 1989; Sholkovitz et al., 1992) and (3) the development of largest Ce anomalies in rivers with the highest pH (Goldstein and Jacobsen, 1988). The presence or absence of Ce anomalies in ancient marine authigenic sediments has the potential for establishing paleo-redox variations in ancient oceans (Wright et al., 1984; Liu et al., 1988; Komiya et al., 2008).

The organisms extracting phosphate from oxic seawater usually show a negative Ce anomaly (Wright et al., 1987) and may result from the presence of calcareous and siliceous organisms, phillipsites and smectite (Goldberg et al., 1963; Piper, 1974a, b; Desprairies and Bonnot-Courtois, 1980; Tlig and Steinberg, 1982), whereas Fe oxide-rich oxic sediments, such as red clay, have a positive Ce anomaly (Piper, 1974b; Thomson et al., 1984). Conversely, in suboxic seawater, Ce containing sediments are mobilized and Ce is released into the water column, which resulted in a less negative to positive Ce anomaly in seawater (De Baar, 1991). The negative Ce anomaly reflects the incorporation of REE directly from seawater or pore water under oxic condition. This also implies the mixing of two-component systems with terrigenous clay (detrital) in the marine sediments. However, accurate measurements of Ce anomalies in marine limestones provide important aspects of the geological record i.e., terrigenous input and redox condition at the time and place of deposition (MacLeod and Irving, 1996; Madhavaraju and Ramasamy, 1999; Armstrong-Altrin et al., 2003; Madhavaraju and Lee, 2009; Madhavaraju et al., 2010).

The Shahabad limestones show small variations in Ce/Ce$^+$ ratios (GL: 0.35 to 0.63; YL: 0.50 to 0.64; BL: 0.58 to 0.66; Table 4). The Shahabad limestones show distinct negative Ce
anomaly (average Ce/Ce* ratio for GL = 0.54 ± 0.1, YL = 0.57 ± 0.05, BL = 0.62 ± 0.12). The seawater is characterized by Ce/Ce* ratio ranges from < 0.1 to 0.4 (Elderfield and Greaves, 1982; Piepgras and Jacobsen, 1992) while the average shales yield Ce/Ce* ratios of about 1.0 (Murray et al., 1991a; Cullers and Berendsen, 1998; Cullers and Stone, 1991). The carbonate minerals precipitated in equilibrium with seawater show distinct negative Ce anomalies and this may also be reflected in the bulk REE pattern (Piper, 1974a; Palmer, 1985). Negative Ce anomaly is reported mostly within the ocean basins because seawater is typically depleted in Ce due to the preferential removal of Ce⁴⁺ from the water column (Elderfield and Greaves, 1982). Because of the minor Ce anomaly, the extent of the La anomalies can be quantified and expressed as an apparent negative anomaly (Zhao et al., 2009). Ce and La anomalies are best studied in a bivariate plot (Bau and Dulski, 1996; Zhao et al., 2009) that discriminates them for the related two anomalies (Fig. 4). The Shahabad limestones are plotted in this discrimination diagram (Pr/Pr* vs Ce/Ce*), which suggest that these samples have original negative Ce anomalies. Since there is no chemical reason for the creation of Nd or Pr anomalies, existence of a true Ce anomaly should lead Pr/Pr* ≥ 1. Samples show Pr/Pr* = 1 would suggest that the anomalous La enrichment must be sole cause of any Ce anomaly. The extent of Ce depletion reflects oxygenation state of the water (Komiya et al., 2008; Zhao et al., 2009). In the present study, the limestones of Shahabad Formation show negative Ce anomalies, suggesting that these limestones were deposited under oxygenated environment. In addition, there is no remarkable variation in Ce anomalies in these limestones, suggest that there were not much fluctuation in bottom water oxygen level. Both Ce anomalies and Ce concentrations can probably explain by variations in terrigenous sediments in the limestone samples but not due to diagenesis.
The Shahabad limestones show small variations in Mn concentration (GL = ~ 133 to 396 ppm; YL = ~ 170 to 304 ppm; BL = ~ 268 to 488 ppm). The fluctuation in Mn values in these limestones may be due to the variations in the paleoredox conditions. Variation in the solubility of Fe and Mn may lead to significant fractionation of these metals across the redox boundaries with the most Fe being fixed in sulphide under low Eh conditions, while Mn tends to incorporate under more oxygenated conditions above the redox boundary (Krauskopf, 1979; Bellanca et al., 1996). Based on this observation, Machhour et al. (1994) and Bellanca et al. (1996) have proposed the relationship \( \text{Mn}^* = \log \left( \frac{\text{Mn}_{\text{sample}}/\text{Mn}_{\text{shale}}}{\text{Fe}_{\text{sample}}/\text{Fe}_{\text{shale}}} \right) \) to find out the redox conditions of the depositional environment and Mn* values have been used by various authors (Machhour et al., 1994; Bellanca et al., 1996; Cullers, 2002; Nagarajan et al., 2007a; Madhavaraju and Lee, 2009) to find out the redox potential of the depositional environment. The mean shale values used for Mn and Fe are 600 ppm and 46,150 ppm, respectively (Wedepohl, 1978). All the three limestone types show significant positive Mn* values (GL = ~ 0.16 to 0.48; YL = ~ 0.11 to 0.75; BL = ~ 0.28 to 0.45; Table 4), which suggests that these Shahabad limestones have been deposited under oxic conditions.

6. CONCLUSION

The REE contents in the limestones of Shahabad Formation are very low compared to recent marine sediments. The depletion of LREE and enrichment of HREE and (La/Yb)\text{SN} ratio in the Shahabad limestones suggests retention of the seawater REE pattern. The negative Ce anomaly and significant positive Mn* ratio reflects the incorporation of REE directly from seawater or from pore water under oxic condition. This also implies the mixing of two-
component systems with terrigenous clay (detrital) in the marine sediments. Variations in Y/Ho ratio, positive correlation of $\Sigma$REE with $\text{Al}_2\text{O}_3$ and negative correlation of $\Sigma$REE with $\text{CaO}$ implies the presence of terrigenous fractions, which is also the possible source for REE in these limestones. The terrigenous source of REE is further confirmed by the strong positive correlation of $\Sigma$REE with Fe, Ni, Cr, Sc, and Y. The REE+Y pattern of Shahabad limestones mostly shows original characters and some of them are modified by detrital input into the system.

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REFERENCES


Banner, J.L. and Hanson, G.N., 1990, Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. Geochimica et Cosmochimica Acta, 54, 3123-3137.


Bau, M., 1996, Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. Contributions to Mineralogy and Petrology, 123, 323-333.


Bellanca, A., Masetti, D., and Neri, R., 1997, Rare earth elements in limestone/marlstone couplets from the Albian-Cenomanian Cismon section (Venetian region, northern Italy): assessing REE sensitivity to environmental changes. Chemical Geology, 141, 141-152.


Piper, D.Z., 1974a, Rare earth elements in the sedimentary cycle, a summary. Chemical Geology, 14, 285-304.


Tlig, S. and M’Rabet, A., 1985, A comparative study of the Rare Earth element (REE) distributions within the lower Cretaceous dolomites and limestones of Central Tunisia, Sedimentology, 32, 897-907.


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