

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 ΣREE with Al_2O_3 , negative correlation of ΣREE with CaO and differences in Y/Ho ratios. V, Cr, and Sc, are positively correlated with Ti, and strong positive correlation of ΣREE 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, 2000). 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. GEOLGICAL 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, sigmoidal 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 Gulbarga 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 km². 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 Katamadevarhalli 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 $\text{HNO}_3 + \text{HF}$ 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 HNO_3 and 1 ml of HClO_4 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 HClO_4 . Later, the solution was evaporated to dryness, and extracted with 10 ml of 1% HNO_3 . 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 $\pm 2\%$. The precision of Ce, Pr, Eu, Gd Ho, Er are better than $\pm 5\%$. The accuracy of Sm is better than $\pm 10\%$. 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. Σ REE 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 Σ REE 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 exhibit 1) seawater like REE+Y pattern with LREE depletion [average

$(\text{Nd}/\text{Yb})_{\text{SN}}$ (SN = shale normalized) = 0.64 ± 0.08 ; $(\text{Nd}/\text{Yb})_{\text{SN}}$ ratio of modern shallow seawater = ~ 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 ± 0.16 ; $\text{Gd}_{\text{SN}}/\text{Gd}^*$ ratio of modern shallow seawater is ~ 1.30 to 1.05 ; De Baar et al., 1985 and Zhang and Nozaki, 1998); 4. Super chondritic Y/Ho ratio (avg. $\text{Y}/\text{Ho} = 38.13 \pm 21.35$; Y/Ho of seawater is ~ 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 Σ REE 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 Neoproterozoic shales; Table 3). Differences in Σ REE 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 $(\text{Nd}/\text{Yb})_{\text{SN}}$ 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} ratio ~ 0.205 to 0.497 for 50m water depth; Zhang and Nozaki, 1996; De Baar et al., 1985 respectively], which suggest that these limestones retained their original seawater characteristics. The (La/Yb)_{SN} ratios range from 0.52 to 0.89 with an average of 0.73. The (La/Yb)_{SN} 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} ratio in the Shahabad limestones vary from ~ 0.96 to 1.51 (average 1.20 ± 0.13), which is similar to the modern seawater (~ 0.8 - 1.1). However, (Dy/Yb)_{SN} ratios in some samples are greater than 1.20. The high (Dy/Yb)_{SN} ratios in Shahabad limestones show an enrichment in HREE rather than LREE, similar to modern seawater. (Dy/Yb)_{SN} 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} 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} ratio of 0.9 (Nothdurft, 2001). Modern examples yielding identical REE patterns to modern seawater with (Dy/Yb)_{SN} ratio of 0.8 (Webb and Kamber, 2000). (Dy/Yb)_{SN} ratios of the Shahabad limestones (~ 1.1 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 ΣREE with Al_2O_3 (statistically significant at a significance level of 0.001; linear correlation coefficient $r = 0.912$) (Fig. 5b) and negative correlation of ΣREE with 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 ΣREE with Fe_2O_3 , Ni, Th, Cr, Sc, and Y (Fig. 5d-i). Among the REEs, LREE show higher positive correlation with elements like Al_2O_3 , Fe_2O_3 , TiO_2 and MgO, than to middle REE (MREE) and heavy REE (HREE). The major elements particularly Al_2O_3 , Fe_2O_3 , TiO_2 , and MnO show a distinct correlation among them, and 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 La/Sc, Th/Sc, Th/Cr and 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). La/Sc, Th/Sc, Th/Cr and 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 ($(\text{Nd}/\text{Yb})_{\text{SN}} = 0.53$), whereas many samples display very low Y/Ho values ($\text{Y}/\text{Ho} < 35$; $n = 13$; 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^{3+} reduced to Eu^{2+} under extremely reducing conditions. Redox potential of Eu/Eu^* 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 $\text{Eu}^{3+}/\text{Eu}^{2+}$ 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^*), 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

sedimentary 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 Ce^{4+} 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 $Pr/Pr^* \geq 1$. 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 $Mn^* = \log [(Mn_{sample}/Mn_{shale}) / (Fe_{sample}/Fe_{shale})]$ 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 $(La/Yb)_{SN}$ 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 ΣREE with Al_2O_3 and negative correlation of ΣREE with 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 ΣREE 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

- Achar, K.K., Pandit, S.A., Natrajan, V., Kumar, M.K., and Dwivedy, K.K., 1997, Uranium mineralization in the Neoproterozoic Bhima Basin, Karnataka, India. Paper presented in International Atomic Energy Agency-Technical Committee Meeting on “Recent Developments in Uranium Resources and Demand”, June 10-13, Vienna, Austria. pp.1-22.
- Alibo, D.S. and Nozaki, Y., 1999, Rare earth elements in seawater: Particle association, shale-normalization and Ce oxidation. *Geochimica et Cosmochimica Acta*, 63, 363-372.
- Armstrong-Altrin, J.S., 2009, Provenance of sands from Cazones, Acapulco, and Bahía Kino beaches, Mexico. *Revista Mexicana de Ciencias Geológicas*, 26 (3), 764-782.
- Armstrong-Altrin, J.S., Verma, S.P., Madhavaraju, J., Lee, Y.I., and Ramasamy, S., 2003, Geochemistry of Late Miocene Kudankulam Limestones, South India. *International Geology Review*, 45(1), 16-26.
- Armstrong-Altrin, J.S., Lee, Y.I., Verma, S.P., and Ramasamy, S., 2004, Geochemistry of sandstones from the Upper Miocene Kudankulam Formation, southern India: Implications for provenance, weathering, and tectonic setting. *Journal of Sedimentary Research*, 74, 285-297.
- Bakkiaraj, D., Nagendra, R., Nagarajan, R., and Armstrong-Altrin, J.S., 2010, Geochemistry of Siliciclastic rocks of Sillakkudi Formation, Cauvery Basin, Southern India; Implications for Provenance. *Journal of the Geological Society of India*, 76, 453-467.
- Banerjee, D.C., 1999, Uranium exploration in the Proterozoic Basins in India - Present status and future strategy, India. *Developments in uranium resources, production, demand and the environment Proceedings of a technical committee meeting held in Vienna, 15-18 June*, pp.81-94.
- 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.
- Banner, J.L., Hanson, G.N., and Meyers, W.J., 1988, Water-rock interaction history of regionally extensive dolomites of the Burlington–Keokuk Formation (Mississippian): isotopic evidence. In: Shukla, V., Baker, P. (eds.), *Sedimentology and Geochemistry of Dolostones*, SEPM Special Publication, vol. 43. SEPM, Tulsa, pp. 97-114.
- Bau, M., 1991, Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. *Chemical Geology*, 93, 219-230.

- 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.
- Bau, M. and Dulski, P., 1996, Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth and Planetary Science Letters*, 143, 245-255.
- Bau, M., Koschinsky, A, Dulski, P., and Hein, J. R., 1996, Comparison of the partitioning behaviours of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater. *Geochimica et Cosmochimica Acta*, 60, 1709-1725.
- Bellanca, A., Masetti, D., and Neri, R., 1997, Rare earth elements in limestone/marlstone couplets from the Albian-Cenomanian Cison section (Venetian region, northern Italy): assessing REE sensitivity to environmental changes. *Chemical Geology*, 141, 141-152.
- Bellanca, A., Claps, M., Erba, E., Masetti, D., Neri, R., Premoli Silva, I., and Venecia, F., 1996, Orbitally induced limestone/marlstone rhythms in the Albian–Cenomanian Cison section (Venetian region, northern Italy): sedimentology, calcareous and siliceous plankton distribution, elemental and isotope geochemistry. *Palaeogeography Paleoclimatology Paleoecology*, 126, 227-260.
- Bertram C.J. and Elderfield H., 1993, The geochemical balance of the rare earth elements and neodymium isotopes in the oceans. *Geochimica et Cosmochimica Acta*, 57, 1957-1986.
- Bolhar, R. and Kranendonk, M.J.V., 2007, A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates. *Precambrian Research*, 155, 229-250.
- Brand, U. and Veizer, J., 1980, Chemical diagenesis of a multi component carbonate system: 1. Trace elements. *Journal of Sedimentary Petrology*, 50, 1219-1236.
- Brookins, D.G., 1989, Aqueous geochemistry of rare earth elements. In: Lipin, B.R., McKay, G.A.Ž. (eds.), *Geochemistry and Mineralogy of Rare Earth Elements*. *Reviews in Mineralogy and Geochemistry*, 21, 201-225
- Byrne, R.H. and Sholkovitz, E.R., 1996, Marine chemistry and geochemistry of the lanthanides. In: Gschneidner, K.A., Jr. and Eyring, L., (eds.), *Handbook on the Physics and Chemistry of Rare Earths*. Elsevier Science, Amsterdam, 23, 497–592.
- Chaudhuri, S. and Cullers, R.L., 1979, The distribution of rare earth elements in deeply buried Gulf coast sediments. *Chemical Geology*, 24, 327-338.
- Condie, K.C., 1991, Another look at rare earth elements in shales. *Geochimica et Cosmochimica Acta*, 55, 2527-2531.

Cox, R., Low, D.R., and Cullers, R.L., 1995, The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States: *Geochimica et Cosmochimica Acta*, 59(14), 2919-2940.

Cullers, R.L., 1994, The controls on the major and trace element variation of shales, siltstones and sandstones of Pennsylvanian – Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, USA. *Geochimica et Cosmochimica Acta*, 58(22), 4955-4972.

Cullers, R.L., 1995, The controls on the major and trace element evolution of shales, siltstones and sandstones of Ordovician to Tertiary age in the Wet Mountain region, Colorado, U.S.A. *Chemical Geology*, 123(1-4), 107-131.

Cullers, R.L., 2000, The geochemistry of shales, siltstones and sandstones of Pennsylvanian-Permian age, Colorado, U.S.A.: implications for provenance and metamorphic studies. *Lithos*, 51, 305-327.

Cullers, R.L., 2002, Implications of elemental concentrations for provenance, redox conditions, and metamorphic studies of shales and limestones near Pueblo, CO, USA. *Chemical Geology*, 191(4), 305-327.

Cullers, R.L. and Graf, J., 1984, Rare earth element in igneous rocks of the continental crust: intermediate and silicic rocks, ore petrogenesis. In: Henderson, P. (ed.), *Rare earth geochemistry*. Elsevier, 275-316.

Cullers, R.L. and Stone, J., 1991, Chemical and mineralogical composition of the Pennsylvanian Mountain, Colorado, U.S.A. (an uplifted continental block) to sedimentary rocks from other tectonics environments. *Lithos*, 27, 115-131.

Cullers, R.L. and Berendsen, P., 1998, The provenance and chemical variation of sandstones associated with the Mid-continent rift system, USA. *European Journal of Mineralogy*, 10, 987-1002.

Cullers, R.L. and Podkovyrov, V.N., 2000, Geochemistry of the Mesoproterozoic Lakhanda shales in southeastern Yakutia, Russia: implications for mineralogical and provenance control, and recycling. *Precambrian Research*, 104(1-2), 77-93.

Cullers, R.L., Basu, A., and Suttner, L., 1988, Geochemical signature of provenance in sand-size material in soils and stream sediments near the Tobacco Root batholith, Montana, USA. *Chemical Geology*, 70(4), 335-348.

Danielson, A., Moller, P., and Dulski, P., 1992, The europium anomalies in banded iron formations and the thermal history of the oceanic-crust. *Chemical Geology*, 97(1-2), 89-100.

De Baar, H.J.W., 1991, On cerium anomalies in the Sargasso Sea. *Geochimica et Cosmochimica Acta*, 55, 2981-2983.

De Baar, H.J.W., Bacon, M.P., and Brewer, P.G., 1985, Rare earth elements in the Pacific and Atlantic oceans. *Geochimica et Cosmochimica Acta*, 49, 1943-1959.

De Baar, H.J.W., German, C.R., Elderfield, H., and Van Gaans, P., 1988, Rare earth element distributions in anoxic waters of the Cariaco Trench. *Geochimica et Cosmochimica Acta*, 52, 1203-1219.

Derry, L.A. and Jacobsen, S.B., 1990, The chemical evolution of Precambrian seawater: Evidence from REEs in banded iron formations. *Geochimica et Cosmochimica Acta*, 54, 2965-2977.

Desprairies, A. and Bonnot-Courtois, C., 1980, Relation entre la composition des smectites d'alteration sous-marine et leur cortège de terres rares. *Earth and Planetary Science Letters*, 48, 124-130.

Dhana Raju, R., Kumar, M.K., Babu, E.V.S.S.K., and Pandit, S.S., 2002, Uranium mineralisation in the Neoproterozoic Bhima Basin at Gogi and near Ukinal: An ore petrological study. *Journal of the Geological Society of India*, 59, 299-321.

Douville, E., Bienvenu, P., Charlou, J. L., Donval, J. P., Fouquet, Y., Appriou, P., and Gamo, T., 1999, Yttrium and rare earth elements in fluids from various deep-sea hydrothermal systems. *Geochimica et Cosmochimica Acta*, 63, 627-643.

Dymek, R. and Klein, C., 1988, Chemistry, petrology and origin of banded iron-formation lithologies from the 3800 Ma Isua Supracrustal Belt, West Greenland. *Precambrian Research*, 39, 247-302.

Elderfield, H., 1988, The oceanic chemistry of the rare-earth elements. *Philos. Transactions Royal Society of London*, 325, 105-126.

Elderfield, H. and Greaves, M.J., 1982, The rare earth elements in seawater. *Nature*, 296, 214-219.

Elderfield, H. and Pagett, R., 1986, Rare earth elements in ichthyoliths: variations with redox conditions and depositional environments. *Science and Total Environment*, 49, 175-197.

Elderfield, H. and Sholkovitz, E.R., 1987, Rare earth elements in the pore waters of reducing nearshore sediments. *Earth and Planetary Science Letters*, 82, 280-288.

Elderfield, H., Upstill-Goddard, R., and Sholkovitz, E.R., 1990, The rare-earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta*, 54, 971-991.

Foote R.B., 1876, Geological features of the south Mahratta country and adjacent districts. *Memoir Geological Survey of India*, 12 (2), 70-138.

- Frimmel, H.E., 2009, Trace element distribution in Neoproterozoic carbonates as palaeoenvironmental indicator. *Chemical Geology*, 258, 338-353.
- Fu, X., Wang, J., Zeng, Y., Tan, F., and He, J., 2011, Geochemistry and origin of rare earth elements (REEs) in the Shengli River oil shale, northern Tibet, China. *Chemie der Erde*, (in press).
- German, C.R. and Elderfield, H., 1989, Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin. *Geochimica et Cosmochimica Acta*, 53, 2561-2571.
- German, C.R. and Elderfield, H., 1990, Application of the Ce anomaly as a paleoredox indicator: the ground rules. *Paleoceanography*, 5, 823-833.
- German, C.R., Klinkhammer, G.P., Edmond, J.M., Mitra, A., and Elderfield, H., 1990, Hydrothermal scavenging of rare earth elements the ocean. *Nature*, 345, 516-518.
- German, C.R., Higgs, N.C., Thomson, J., Mills, R., Elderfield, H., Blusztajn, J., Fler, A.P., and Bacon, A.P., 1993, A geochemical study of metalliferous sediment from the TAG hydrothermal mound, 26°08' N, Mid-Atlantic Ridge. *Journal of Geophysical Research*, 98, 9683-9692.
- German, C.R., Hergt, J., Palmer, M.R., and Edmond, J.M., 1999, Geochemistry of a hydrothermal sediment core from the OBS vent-field, 21°N East Pacific Rise. *Chemical Geology*, 155, 65-75.
- Goldberg, E.D., Koide, M., and Schmitt, R.A., 1963, Rare earth distributions in the marine environment. *Journal of Geophysical Research*, 68, 4209-4217.
- Goldstein, S.J. and Jacobsen, S.B., 1988, Rare earth elements in river waters. *Earth and Planetary Science Letters*, 89, 35-47.
- Greaves M.J., Elderfield H., and Sholkovitz E. R., 1999, Aeolian sources of rare earth elements to the Western Pacific Ocean. *Marine Chemistry*, 68, 31-38.
- Haskin, M.A. and Haskin, L.A., 1966, Rare earths in European shales, a redetermination. *Science*, 154, 507-509.
- Hein, J.R., Fan, D., Ye, J., Liu, T., and Yeh, H.-W., 1999, Composition and origin of Early Cambrian Tiantaishan phosphorite-Mn carbonate ores, Shaanxi Province, China. *Ore Geology Reviews*, 15, 95-134.
- Holser, W.T., 1997, Evaluation of the application of rare-earth elements to paleoceanography. *Palaeogeography Palaeoclimatology Palaeoecology*, 132, 309-323.
- Janardhana Rao, L.H., Srinivasarao, C., and Ramakrishnan, T. L., 1975, Reclassification of the rocks of Bhima basin, Gulburga district, Mysore state. *Miscellaneous Publications, Geological Survey of India*, 23 (1), 177-184.

Jayananda, M., Martin, H., Peucat, J.J., and Mahabaleswar, B., 1995, Late Archaean crust-mantle interactions: geochemistry of LRR-enriched mantle derived magmas. Example of the Clospet batholith, southern India. *Contribution to Mineralogy and Petrology*, 119(2-3), 314-329.

Jayaprakash, A.V., 1986, Stylolites and their relationship with the composition of Shahabad Limestone, Bhima Group. *Records of Geological Survey of India*, 115 (5), 5-8.

Johannesson, K.H., Hawkins Jr. D.L., and Cortés, A., 2006, Do Archaean chemical sediments record ancient seawater rare earth element patterns? *Geochimica et Cosmochimica Acta*, 70, 871-890.

Kale, V.S., 1990, Problems of the Purana Basins. In: Tandon, S.K. and Gupta, K.R. (eds.), *Challenging areas in Earth Sciences for the Nineties*. Memoir Geological Society of India, No. 18, p.77-93.

Kale, V.S. and Phansalkar, V.G., 1991, Purana Basins of Peninsular India: A Review, *Basin Research*, 3, 1-36.

Kale, V.S. and Peshwa, V.V., 1995, *The Bhima Basin: Field Guide*. Geological Society of India, 142p.

Kale, V.S., Mudholkar, A.V., Phansalkar, V.G., and Peshwa, V.V., 1990, Stratigraphy of the Bhima Group. *Journal of the Paleontological Society of India*, 35, 91-103.

Kamber, B.S. and Webb, G.E., 2001, The geochemistry of late Archaean microbial carbonate: implications for ocean chemistry and continental erosion history. *Geochimica et Cosmochimica Acta*, 65, 2509-2525.

Kato, Y., Nakao, K., and Isozaki, Y., 2002, Geochemistry of Late Permian Triassic pelagic cherts from southwest Japan: implications for an oceanic redox change. *Chemical Geology*, 182, 15-34.

Kawabe, I., Kitahara, Y., and Naito, K., 1991, Non-chondritic Yttrium/Holmium ratio and lanthanide tetrad effect observed in pre-Cenozoic limestones. *Geochemical Journal*, 25, 31-44.

Kemp, R.A. and Trueman, C.N., 2003, Rare earth elements in Solnhofen biogenic apatite: geochemical clues to the palaeoenvironment. *Sedimentary Geology*, 155, 109-127.

King, W., 1872, *The Cuddapah and Kurnool formations in Madras Presidency*. Memoir Geological Survey of India, 8(1), 1-346.

Klinkhammer, G., Elderfield, H., and Hudson, A., 1983, Rare earth elements in seawater near hydrothermal vents. *Nature*, 305, 185-188.

Klinkhammer, G.P., Elderfield, H., Edmond, J.M., and Mitra, A., 1994, Geochemical implications of rare earth element patterns in hydrothermal fluids from mid-ocean ridges. *Geochimica et Cosmochimica Acta*, 58, 5105-5113.

Komiya, T., Hirata, T., Kitajima, K., Yamamoto, S., Shibuya, T., Sawaki, Y., Ishikawa, T., Shu, D., Li, Y., and Han, J., 2008, Evolution of the composition of seawater through geologic time, and its influence on the evolution of life. *Gondwana Research*, 14, 159-174.

Krauskopf, K.B., 1979, *Introduction to Geochemistry*: Tokyo, McGraw-Hill Kogakusha, 617 p.

Lawrence, M.G., Greig, A., Collerson, K.D., and Kamber, B.S., 2006, Rare earth element and Yttrium variability in South East Queensland waterways. *Aquatic Geochemistry*, 12, 39-72.

Liu, Y.G., Miah, M.R.U., and Schmitt, R.A., 1988, Cerium, a chemical tracer for paleo-oceanic redox conditions. *Geochimica et Cosmochimica Acta*, 52, 1361-1371.

Machhour, L., Philip, J., and Oudin, J-L., 1994, Formation of laminite deposits in anaerobic-dysaerobic marine environments. *Marine Geology*, 117, 287-302.

MacLeod, K.G. and Irving, A.J., 1996, Correlation of cerium anomalies with indicators of paleoenvironment. *Journal of Sedimentary Research*, 66 (5), 948-955.

MacRae, N.D., Nesbitt, H.W., and Kronberg, B.I., 1992, Development of a positive Eu anomaly during diagenesis. *Earth and Planetary Science Letters*, 109, 585-591.

Madhavaraju, J., González-León, C.M., Lee, Y.I., Armstrong-Altrin, J.S., Reyes-Campero, L.M., 2010, Geochemistry of the Mural Formation (Aptian-Albian) of the Bisbee Group, Northern Sonora, Mexico. *Cretaceous Research*, 31, 400-414.

Madhavaraju, J. and Lee, Y.I., 2009, Geochemistry of the Dalmiapuram Formation of the Uttatur Group (Early Cretaceous), Cauvery basin, southeastern India: Implications on provenance and paleo-redox conditions. *Revista Mexicana de Ciencias Geológicas*, 26 (2), 380-394.

Madhavaraju, J. and Ramasamy, S., 1999, Rare earth elements in limestones of Kallankurichchi Formation of Ariyalur Group, Tiruchirapalli Cretaceous, Tamil Nadu. *Journal of the Geological Society of India*, 54, 291-301.

Mahadevan, C., 1947, The Bhima Series and other rocks of Gulbarga District. *Journal of Hyderabad Geological Survey*, 5, 1-60.

Malur, M.N. and Nagendra, R., 1994, Lithostratigraphy of the Bhima Basin (Central Part), Karnataka, Southern India. *Journal of the Paleontology Society of India*, 39, 55-60.

Mathur, S.M., 1977, Some aspects of the stratigraphy and limestone resources of the Bhima Group. *Indian Mineralogist*, 18, 59-64.

- Mazumdar, A., Tanaka, K., Takahashi T., and Kawabe, I., 2003, Characteristics of rare earth element abundances in shallow marine continental platform carbonates of Late Neoproterozoic successions from India. *Geochemical Journal*, 37, 277-289.
- McLennan, S.M., 1989, Rare earth elements in sedimentary rocks; influence of provenance and sedimentary processes. In: Lipin, B.R. and McKay, G.A. (eds.), *Geochemistry and Mineralogy of Rare Earth Elements*. *Reviews in Mineralogy*, 21, p. 169-200.
- Michard, A., 1989, Rare earth element systematics in hydrothermal fluids. *Geochimica et Cosmochimica Acta*, 53, 745-750.
- Michard, A., Albarede, F., Michard, G., Minister, J.F., and Charlou, J.L., 1983, Rare earth elements and uranium in high temperature solutions from East-Pacific Rise hydrothermal vent field (13°N). *Nature*, 303, 795-797.
- Misra, R.N., Jayaprakash, A.V., Hans, S.K., and Sundaram, V., 1987, Bhima Group of Upper Proterozoic - A Stratigraphic puzzle. *Memoir Geological Society of India*, 6, 227-237.
- Morad, S., Al-Aasm, I.S., Sirat, M., and Sattar, M.M., 2010, Vein calcite in Cretaceous carbonate reservoirs of Abu Dhabi: Record of origin of fluids and diagenetic conditions. *Journal of Geochemical Exploration*, 106, 156-170.
- Muecke, G.K., Pride, C., and Sarkar, P., 1979, Rare earth element geochemistry of regional metamorphic rocks. *Physics and Chemistry of the Earth*, 11, 449-464.
- Murphy, K. and Dymond, J., 1984, Rare earth element fluxes and geochemical budget in the eastern equatorial Pacific. *Nature*, 307, 444-447.
- Murray, R.W. and Leinen, M., 1993, Chemical transport to the seafloor of the equatorial Pacific Ocean across a Latitudinal transect at 135°W. Tracking sedimentary major, trace and rare earth element fluxes at the Equator and the Intertropical Convergence Zone. *Geochimica et Cosmochimica Acta*, 57, 4141-4163.
- Murray, R.W., Buchholtz Brink, M.R., Brink, M.R., Jones, D.L., Gerlach, D.C., and Russ III, G.P., 1990, Rare earth elements as indicators of different marine depositional environments in chert and shale. *Geology*, 18, 268-271.
- Murray, R.W., Buchholtz, M.R., and Brumsack, H.J., 1991a, Rare earth elements in Japan Sea sediments and diagenetic behavior of Ce/Ce*, results from ODP leg 127. *Geochimica et Cosmochimica Acta*, 55, 2453-2466.
- Murray, R.W., Buchholtz Brink, M.R., Brink, M.R., Gerlach, D.C., Russ III, G.P., and Jones, D.L., 1991b, Rare earth, major and trace elements in chert from the Franciscan complex and Monterey group, California: assessing REE sources to fine grained marine sediments. *Geochimica et Cosmochimica Acta*, 55, 1875-1895.

- Murray, R.W., Buchholtz Ten Brink, M.R., Gerlach, D.C., Russ, G.P.III., and Jones, D.L., 1992, Interoceanic variation in the rare earth, major and trace element depositional chemistry of chert: perspectives gained from the DSDP and ODP record. *Geochimica et Cosmochimica Acta*, 56, 1897-1913.
- Nagarajan, R., Armstrong-Altrin, J.S., Nagendra, R., Madhavaraju, J., and Moutte, J., 2007a, Petrography and geochemistry of terrigenous sedimentary rocks in the Neoproterozoic Rabanpalli Formation, Bhima Basin, southern India: Implications for paleoweathering condition, provenance, and source rock composition. *Journal of the Geological Society of India*, 70(2), 297-312.
- Nagarajan, R., Madhavaraju, J., Nagendra, R., Armstrong-Altrin, J.S., and Moutte, J., 2007b, Geochemistry of Neoproterozoic shales of Rabanpalli Formation, Bhima Basin, Northern Karnataka, Southern India: Implications for provenance and paleoredox conditions. *Revista Mexicana Ciencias Geológicas*, 24(2), 150-160.
- Nagarajan, R. Sial, A. N., Armstrong-Altrin, J.S. Madhavaraju, J., and Nagendra R., 2008, Carbon and oxygen isotope geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima Basin, Karnataka, Southern India. *Revistas Mexicana de Ciencias Geologicas*, 25, 225-235.
- Nagendra, R. and Nagarajan, R., 2003, Geochemical studies of Shahabad Limestone (Younger Proterozoic), Bhima Basin, Karnataka. *Indian Mineralogist*, 36, 13-23.
- Nath, B.N., Roelandts, I., Sudhakar, M., and Plueger, W.L., 1992, Rare Earth Element patterns of the Central Indian Basin sediments related to their lithology. *Geophysical Research Letters*, 19, 1197-1200.
- Nath, B.N., Bau, M., Ramalingeswara Rao, B., and Rao, Ch.M., 1997, Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone: *Geochimica et Cosmochimica Acta*, 61(12), 2375-2388.
- Newbold, T.J., 1842, Notes, principally geological, from Bijapore to Bellary, via Kannighirri. *Journal of Asiatic Society of Bengal*. XI, 941-955.
- Nothdurft, L.D., 2001, Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: a proxy for ancient seawater chemistry. Honours thesis, Queensland Univ. Tech. Brisbane, 103p.
- Nothdurft, L.D., Webb, G.E., and Kamber, B.S., 2004, Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: confirmation of a seawater proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263-283.
- Nozaki, Y. and Alibo, D.S., 2003, Importance of vertical geochemical processes in controlling the oceanic profiles of dissolved rare earth elements in the northeastern Indian Ocean. *Earth and Planetary Science Letters*, 205, 155-172.

- Nozaki, Y., Zhang, J., and Amakawa, H., 1997, The fractionation between Y and Ho in the marine environment. *Earth and Planetary Science Letters*, 148, 329-340.
- Nozaki, Y., Lerche, D., Alibo, D.S., and Snidvongs, A., 2000, The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. *Geochimica et Cosmochimica Acta*, 64, 3983-3994.
- Palmer, M.R., 1985, Rare earth elements in foraminifera tests. *Earth and Planetary Science Letters*, 73, 285-298.
- Pandit, S.A. Natarajan, V., and Dhana Raju, R., 2002, Exploration for Uranium in the Bhima Basin in Parts of Karnataka, India. *Exploration and Research for Atomic Minerals*, 14, 59-78.
- Piegras, D.J. and Jacobsen, S.B., 1992, The behaviour of rare earth elements in seawater: Precise determination of ferromanganese crusts. *Geochimica et Cosmochimica Acta*, 56, 1851-1862.
- Piper, D.Z., 1974a, Rare earth elements in the sedimentary cycle, a summary. *Chemical Geology*, 14, 285-304.
- Piper, D.Z., 1974b, Rare earth elements in ferromanganese nodules and other marine phases. *Geochimica et Cosmochimica Acta*, 38, 1007-1022.
- Scherer, M. and Seitz, H., 1980. Rare-earth element distribution in Holocene and Pleistocene corals and their distribution during diagenesis. *Chemical Geology*, 28, 279-289.
- Schieber, J., 1988, Redistribution of rare earth elements during diagenesis of carbonate rocks from Mid-Proterozoic Newland Formation, Montana, USA. *Chemical Geology*, 69(1-2), 111-126.
- Senthil kumar, P. and Srinivasan, R., 2002, Fertility of Late Archean basement granite in the vicinity of U-mineralised Neoproterozoic Bhima basin, Peninsular India. *Current Science*, 82(5), 571-576.
- Shields, G. and Stille, P., 2002, Diagenetic constraints on the use of cerium anomalies as palaeoseawater redox proxies: an isotopic and REE study of Cambrian phosphorites. *Chemical Geology*, 175, 29-48.
- Shields, G.A. and Webb, G.E., 2004, Has the REE composition of seawater changed over geologic time. *Chemical Geology*, 204, 103-107.
- Sholkovitz, E.R., 1988, Rare earth elements in the sediments of the North Atlantic Ocean, Amazon delta, and East China Sea: reinterpretation of terrigenous input patterns to the oceans. *American Journal of Science*, 288, 236-281.

Sholkovitz, E.R., 1990, Rare earth elements in marine sediments and geochemical standards. *Chemical Geology*, 88, 333-347.

Sholkovitz, E.R., Piegras, D.J., and Jacobsen, S.B., 1989, The pore water chemistry of rare elements Buzzard Bay sediments. *Geochimica et Cosmochimica Acta*, 53, 2847-2856.

Sholkovitz, E.R., Shaw, T.J., and Schneider, D.L., 1992, The geochemistry of rare earth elements in the seasonally anoxic water column and pore waters of Chesapeake Bay. *Geochimica et Cosmochimica Acta*, 56, 3389-3402.

Sholkovitz, E.R., Landing, W.M., and Lewis, B.L., 1994, Ocean particle chemistry: the fractionation of the rare earth elements between suspended particles and seawater. *Geochimica et Cosmochimica Acta*, 58, 1567-1580.

Siby, K., Nath, B.N., Ramaswamy, V. Naman, D. Gnaneshwar Rao, T. Kamesh Raju, K.A., Selvaraj, K., and Chen, C.T.A., 2008, Possible detrital, diagenetic and hydrothermal sources for Holocene sediments of the Andaman backarc basin, *Marine Geology*, 247, (3-4), 178-193.

Siegmund, H., 1995, Fazies und Genese unterkambrischer Phosphorite und mariner Sedimente der Yangtze Plattform, Su'dchina. *Berliner geowissenschaftliche Ahandlungen, Reihe A* 173, 114.

Sverjensky, D.A., 1984, Europium redox equilibria in aqueous solution. *Earth and Planetary Science Letters*, 67, 70-78.

Taylor, S.R. and McLennan, S.M., 1985, *The Continental Crust: its Composition and Evolution*. Blackwell Scientific Publications. Oxford, 312p.

Thomson, J., Carpenter, M. S. N., Colley, S., and Willson, T. R. S., 1984, Metal accumulation rates in northwest Atlantic pelagic sediments. *Geochimica et Cosmochimica Acta*, 48, 1935-1948.

Tlig, S. and Steinberg, M., 1982, Distribution of rare earth elements (REE) in size fractions of recent sediments of the Indian Ocean. *Chemical Geology*, 37, 317-333.

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.

Toyoda, K., Nakamura, Y., and Masuda, A., 1990, Rare earth elements of Pacific pelagic sediments. *Geochimica et Cosmochimica Acta*, 54, 1093-1103.

Turekian, K.K. and Wedepohl, K.H., 1961, Distribution of elements in some major units of earth's crust. *Geological Society of America Bulletin*, 72(2), 175-192.

Veizer, J., 1983, Chemical diagenesis of carbonates: theory and application of trace element technique. In: Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J., and Land, L.S. (eds.), *Stable Isotopes in Sedimentary Geology*. Society of Economic Palaeontologists and Mineralogists. p. 3-100.

Walker, J.C.G., Klein, C., Schidlowski, M., Schopf, J.W., Stevenson, D.J. and Walter, M.R., 1983, Environmental evolution of the Archean-Early Proterozoic earth. In: Schopf, W.J. (ed.), *Earth's Earliest Biosphere, Its Origin and Evolution*. Princeton University Press, Princeton, p. 260–290.

Wang, Y.L., Liu, Y.G., and Schmitt, R.A., 1986, Rare earth element geochemistry of south Atlantic deep sediments, Ce anomaly change at ~54 My. *Geochimica et Cosmochimica Acta*, 50, 1337-1355.

Wani, H. and Mondal, M.E.A., 2010, Petrological and geochemical evidence of the Paleoproterozoic and the Meso-Neoproterozoic sedimentary rocks of the Bastar craton, Indian Peninsula: Implications on paleoweathering and Proterozoic crustal evolution. *Journal of Asian Earth Sciences*, 38, 220-232.

Webb, G.E. and Kamber, B.S., 2000, Rare earth elements in Holocene reefal microbialites: a new shallow seawater proxy. *Geochimica et Cosmochimica Acta*, 64, 1557-1565.

Wedepohl, K.H., 1978, Manganese: abundance in common sediments and sedimentary rocks. *Handbook of Geochemistry*. Springer, Berlin, pp. 1-17.

Wright, J., Seymour, R.S., and Shaw, H.I., 1984, REE and Nd isotopes in conodont apatite variations with geological age and depositional environment. *Geological Society of America, Special Paper*, 196, 325-340.

Wright, J., Schrader, H., and Holser, W.T., 1987, Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. *Geochimica et Cosmochimica Acta*, 51, 631-644.

Wronkiewicz, D.J. and Condie, K.C., 1990, Geochemistry and mineralogy of sediments from the Ventersdorp and Transvaal Supergroups, South Africa: Cratonic evolution during the early Proterozoic. *Geochimica et Cosmochimica Acta*, 54(2), 343-354.

Zhang, J. and Nozaki, Y., 1996, Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. *Geochimica et Cosmochimica Acta*, 60, 4631-4644.

Zhang J. and Nozaki Y., 1998, Behavior of rare earth elements in seawater at the ocean margin: A study along the slopes of the Sagami and Nankai troughs near Japan. *Geochimica et Cosmochimica Acta*, 62, 1307-1317.

Zhao, Y.Y., Zheng, Y.F., and Chen, F., 2009, Trace element and strontium isotope constraints on sedimentary environment of Ediacaran carbonates in southern Anhui, South China. *Chemical Geology* 265, 345-362.

Zhong, S. and Mucci, A., 1995, Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25°C and 1 atm, and high dissolved REE concentrations. *Geochim. Cosmochim. Acta* 59, 443-453.

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