NOTE

Characteristics of rare earth element abundances in shallow marine continental platform carbonates of Late Neoproterozoic successions from India

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We have studied the REE distribution in shallow marine continental platform carbonates belonging to two late Neoproterozoic basins of India. Their REE abundance patterns normalized by chondrite display well defined W-type tetrad effect. Based on chondrite-normalized Gd/Ho, La/Nd ratios, the REE abundance patterns have been classified into three groups. \((Y/Ho)\) and \((Y/Dy)\) concentration ratios reflect a combined effect of \(Y\) fractionation relative to neighboring trivalent REEs during carbonate precipitation from seawater and influence of continental contributions with chondritic ratios. Negative Ce anomalies recorded in Krol and Bilara carbonates resembles the Ce anomaly reported from shallow marine waters. However, absence of Ce anomaly and distinct positive anomalies in some of our carbonate samples reflect post-depositional redox condition related to Ce mobilization and preferential enrichment during early diagenesis. Variations in the REE abundance patterns may be attributed to contamination with terrigenous particulates having shale like REE abundances and post-depositional early diagenetic processes.

INTRODUCTION

Owing to their unique 4f electron configurations, rare earth elements (REEs) in the trivalent oxidation states behave as a coherent group in most geological processes. Due to its similarity in ionic size and valency with holmium, yttrium has also been grouped together with REEs. The variations in relative abundances and fractionation behavior of REEs during low temperature aquatic reactions have made it a unique group to contrast and constrain various modern marine environments (De Baar et al., 1988; German and Elderfield, 1990; German et al., 1991) and paleo-geochemical ones (Wright et al., 1987; Holser, 1997). It is also quite well established that REEs display characteristic W-type tetrad effect in the marine realm owing to differences in intrinsic quantum chemical properties (Racah parameters) of the REE complexes in the solution (Masuda and Ikeuchi, 1979; Masuda et al., 1987; Kawabe et al., 1998; Ohta and Kawabe, 2000). The tetrad effects are observed as concave curves consisting of La-Ce-Pr-Nd, Pm-Sm-Eu-Gd, Gd-Tb-Dy-Ho and Er-Tm-Yb-Lu in chondrite-normalized REE abundance patterns. Tetrad effect has been documented from marine chemical sediments like limestone/dolomite (Kawabe et al., 1991; Kawabe et al., 1998; Tanaka et al., 2002) and chert (Minami et al., 1998). On the other hand Minami and Masuda (1997) and Minami et al. (1998) suggested quadratic equations for each tetrad curve which enable quantification of the degree of lanthanide tetrad effect. REEs in marine carbonate rocks have been...
studied by various workers to understand paleo-oceanic redox processes (Bellanca et al., 1997; Liu and Schmitt, 1996), reconstruction of paleo-oceanic REE abundances by calculating $K_d$ (Webb and Kamber, 2000) and effects of diagenetic process (Qing and Mountjoy, 1994) on REE abundances.

In the present work we have determined the REE abundances in carbonate (limestone and dolomite) rocks from two late Neoproterozoic shallow marine platform carbonate sequences from India. The Krol Group (Krol Basin, Lesser Himalaya) represents open marine condition whereas the Bilara Group (Nagaur-Ganganagar Basin, Western India) is characterized by evaporitic sabkha (evaporitic shallow marine) type condition. The fundamental objectives of this paper are: (a) to portray the marked variations in REE abundance patterns in shallow marine continental platform carbonates, (b) to classify the REE abundance patterns into groups based on chondrite-normalized elemental ratios and curvatures of the abundance patterns, and (c) to discuss the possible physico-chemical factors which could have affected the nature of REE abundances.

**Geology and Stratigraphy**

**Krol Basin**

The sedimentary rocks of the Blaini, Krol and Tal Groups (in ascending order) comprise the Late Neoproterozoic-Early Cambrian sequence of the Krol Belt (Fig. 1B) in the Lesser Himalaya. The base of the Tal Group defines the base of Early Cambrian, whereas the Krol Group represents the Late Neoproterozoic succession. This thick pile of sedimentary cover, crops out in several discrete

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**Fig. 1.** (A) Generalized litholog of Blaini, Krol and Tal Groups. Pc/C denotes Proterozoic/Cambrian boundary.
(B) Location and disposition of Mussoorie syncline with respect to Solan, Panchmunda, Nigalidhar, Garhwal and Nainital synclines in the Lesser Himalaya and geological map of western part of Mussoorie Syncline. Star mark denotes sampling location.
REE abundances in late Neoproterozoic continental platform carbonates, India

Synclines extending over a distance of more than 300 km in the northwest-southeast direction (Fig. 1A). The Blaini and Tal Groups represent diamictite and shale/sandstone facies, respectively. The Krol Group is divided into three formations. The Lower Krol Formation (marlstone and sandstone), Middle Krol Formation (purple/green shale and minor carbonate) and the Upper Krol Formation comprising primarily of massive limestone and dolomite with minor shale and chert layers at the lower and middle parts and relatively argillaceous carbonates at the upper part. Sedimentary structures like microbial laminites, stromatolites, fenestral vugs, oolites, ripple laminites, mudchip conglomerates reflect a carbonate tidal flat complex (Mazumdar, 1996; Singh and Rai, 1978). The Krol carbonates deposited in an open marine non-evaporatic setting.

Nagaur Ganganagar Basin

The Nagaur-Ganganagar basin (Fig. 2B) in Western India is an elongated, asymmetrical sedimentary basin trending NNE-SSW. It covers an area more than 100,000 km². The Marwar Supergroup (Pareek, 1981) which constitutes the Late Neoproterozoic-Early Cambrian (?) succession in Western India rests on the Precambrian crystallines. The Marwar Supergroup (Fig. 2A) consists of (i) Jodhpur Group, (ii) Bilara Group and (iii) Nagaur Group in ascending order. The Jodhpur and Bilara Groups represent the clastic (sandstone and shale) facies whereas the Bilara Group is comprised of limestone and dolomite with occasional clay beds and conformably overlies the Jodhpur Group. The base of the Cambrian in this succession is not well defined due to lack of index fauna. Presence of abundant stromatolites, microbial laminites, ripple laminites, mudchip conglomerates indicate shallow marine depositional environment. Hanseran Evaporite Group (HEG) represents the time equivalent facies variant of Bilara Group and is underlain and overlain by Jodhpur and Nagaur Groups, respectively (Dasgupta et al., 1988;
Kumar, 1999). Facies association with evaporite deposits suggest existence of a restricted basinal condition, where the Bilara carbonates represent the fringe of the basin.

**NATURAL OF SAMPLE AND ANALYTICAL METHOD**

The Krol carbonates (numbered as A) analyzed in this study belong to lower and middle parts of Upper Krol Formation and have been sampled along the Mussourie-Buraskhand section of Mussourie syncline. The samples include microbial carbonates, microsparites, and oolites. Petrographic observations show presence of early diagenetic recrystallization features like isopachous layers, and blocky crystals and micro dolomite rhombs associated with post depositional mineralogical stabilization involving transformation of high Mg-calcite and aragonite to low Mg-calcite or early diagenetic dolomite. Samples showing evidence of pervasive burial alteration have been excluded from the present study.

The Bilara carbonates have been sampled along the Bilara Hill (numbered TG) around Bilara Township and along Dhanapa mine section (numbered K) around the Dhanapa village. Petrography reveals well preserved microbial and micropelletal textures with clear blocky cement surrounding relatively fine grained turbid grains indicating early meteoric water diagenesis. Presence of anhydrite has been noted in some samples. Authigenic chert is common and often pervasively replaces the carbonate mineralogy.

Prior to grinding, samples were cut to get rid of any weathered margin or rim. Care was taken to avoid mesoscopically visible calcite veinlets as far as possible. Crushed samples were ground in agate planetary ball mill. Approximately 20 gm of sample powder was dissolved in 1N HCl at 25°C under constant stirring and was filtered through Advantac Toyo 5C filter paper. The contents of acid insoluble residue fraction (IR) in the samples range from 0.5 to 3.5%. Mineralogically the IR fraction is composed of quartz, clays (illite, chlorite and mixed-layered illite-smectite), pyrite (in Krol carbonates only), and organic matter.

Group separation of REEs and Y from the leachate was achieved by co-precipitation with Fe(OH)$_3$ at pH = ~6.5. REE and Y were separated from Fe by cation-exchange purification using Bio-Rad AG 50W X8 (200–400 mesh) resins. Measurement of concentrations of REE, Y, Fe and Ca in final sample solution was carried out by ICP emission spectrometer, SPS 1500R (Seiko Instruments) with an ultrasonic nebulizer attachment (Kawabe et al., 1995). Spectral interferences among the measured elements are corrected by using predetermined linear correction factors for spectral interferences. Analytical uncertainties are ~5% or less. Detailed analytical method for extractions of REE and Y from carbonate matrix is given in Kawabe et al. (1991, 1994).

**RESULTS**

REE and Y concentrations, Ce anomalies and elemental ratios are presented in Table 1. Total REE concentrations in Krol carbonates vary from ~1000 to 7300 ppb. However, baring three samples all fall below 4000 ppb, whereas the Bilara carbonate shows a variation from ~530 to 5300 ppb with most of the samples below 3000 ppb. REE concentrations in our samples are comparable to those reported by Webb and Kamber (2000) and Kamber and Webb (2001) for microbial carbonates. In order to understand the REE partitioning and fractionation during carbonate precipitation from seawater, we have referred to the average REE compositions of the modern shallow water (average of first 30 m of profile SA-7) of the Coral Sea (Zhang and Nozaki, 1996) and the Holocene reefal microbialites carbonate (Webb and Kamber, 2000) formed within Great Barrier Reef complex in the Coral Sea. Carbonates studied in the present work are predominantly of microbial origin. However, compared to the Krol and Bilara carbonates the Holocene microbialites of Webb and Kamber (2000) represent more offshore shallow marine equivalents and are devoid of contamination with terrigenous materials.

The chondrite-normalized abundance patterns of Krol and Bilara carbonates are presented in
Table 1. Rare earth element concentrations, Ce anomaly and elemental ratios in Krol and Bilara Carbonates. A = Krol Carbonate, TG and K = Bilara Carbonate.

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Concentrations in PPB.

Ce<sub>(anom)</sub> = log(Ce/Ce*)<sub>chn</sub>, where Ce = chondrite-normalized ratio and Ce* = interpolated chondrite-normalized ratio.

(La/Nd)<sub>chn</sub> = chondrite-normalized ratio.
Figs. 3A to G. Figure 3H is a composite of chondrite-normalized REE abundance plots for shallow waters of Coral Sea, Holocene reefal micobiialite carbonate and PAAS (McLennan, 1989) for comparison with Krol and Bilara carbonates. The REE data of C1 chondrite values are adopted from the mean values of Anders and Grevesse (1989). The chondrite-normalized REE abundance patterns show well defined W-type tetrad features. It is apparent that the relative tilts (with respect to X-axis) of individual tetrad curvatures show marked variations. The tilts have been expressed in terms of chondrite-normalized ratios of two end-point elements of the first, second and third tetrad curvatures as (La/Nd)\textsubscript{chn}, (Gd/Ho)\textsubscript{chn} and (Er/Lu)\textsubscript{chn}, respectively. We have tentatively classified the Krol and Bilara carbonates into three groups which are graphically represented on the (La/Nd)\textsubscript{chn} vs. (Gd/Ho)\textsubscript{chn} plot (Fig. 4A). Ratios for Coral Sea (SW), Holocene reefal microbialite carbonate (HMB) and PAAS are plotted as reference points. Group-I is characterized by maximum variation in (La/Nd)\textsubscript{chn} whereas (Gd/Ho)\textsubscript{chn} ratio is either equal to or greater than that of PAAS (1.3). Group-III shows minimum variation in (La/Nd)\textsubscript{chn} and with (Gd/Ho)\textsubscript{chn} < 1 and close to that of SW and HMB, whereas Group-II shows intermediate (La/Nd)\textsubscript{chn} and its (Gd/Ho)\textsubscript{chn} ratio is less than that of PAAS and close to 1 (1.0 to 1.2). Group-I comprises of maximum number of samples and also shows a large variation in apparent concavity of the tetrad curvatures.

Fig. 3. Chondrite-normalized REE abundance patterns of Krol and Bilara carbonates, shallow water in the Coral Sea, average Holocene reefal micobiialite carbonate and the average shale (PAAS).
We have used the Y/Ho and Y/Dy ratios as indicators of Y fractionation and the relative continental influence on the REE abundances of carbonate sediments. Both Ho and Dy belong to the third tetrad and behave coherently, whereas Y fractionates from them in marine reaction systems. The average (Y/Ho) and (Y/Dy) ratios of shallow water (average of top 30 m) of Coral Sea are respectively ~78 and 21, whereas that of average shale is 27 and 6.1 respectively. It is evident from Fig. 5 that the (Y/Ho) and (Y/Dy) ratios of Krol and Bilara carbonates fall in between the average shale of PAAS (McLennan, 1989) and shallow waters of Coral Sea. The average ratios for the Holocene reefal microbialites (56 and 15) are also plotted for reference.

Ce anomaly values are presented in Table 1. Ce anomaly has been expressed as logarithm of Ce/Ce* ratio, where Ce is the chondrite-normalized Ce concentration in the samples. Ce* has been calculated by intrapolation of Ce value on the second order polynomial curve fitted through La, Pr and Nd on the chondrite-normalized REE abundance plots. It is apparent that Krol carbonates in the present study either have positive Ce anomaly or no anomaly, while Bilara carbonates show presence of negative Ce anomaly or no Ce anomaly. Ce anomaly values for the average shallow water of Coral Sea and the Holocene Microbialites are respectively –0.18 and –0.12 which are similar to the values reported in our study.
DISCUSSION

Tetrad character and Nature of REE abundances

The chondrite-normalized REE abundances in Krol and Bilara carbonates exhibit variable concave tetrad character (Fig. 3). Group-II and III display distinct W-type tetrad features. In contrast, the first and second tetrads are subtle in Group-I. Some samples of Group-I lack tetrad curvatures and resemble average shale. Seawater shows W-type tetrad effect in its chondrite-normalized REE pattern, which is displayed by marine carbonates as well (Kawabe et al., 1998). REECO$_3^{+}$ (aq) and REE(CO$_3$)$_2^{-}$ (aq) are principal seawater REE species (Liu and Byrne, 1998; Ohta and Kawabe, 2000). Tetrad effect in seawater originates from REE partitioning during ligand-exchange reaction of REE$^{3+}$ between particulate REE and REE(III)-carbonate complexes in seawater, where the particulate REE is assumed to be primarily represented by REE(OH)$_3$. The ligand-exchange reaction can be represented in a simple form by Eq. (1), together with the reaction (Eq. (2)) between REE(III) complexes in seawater (Kawabe et al., 1998),

\[ \text{M(OH)}_3^{(c)} + 2\text{CO}_3^{2-}(aq) + 3\text{H}^+(aq) = \text{M(CO}_3^{2-}(aq) + 3\text{H}_2\text{O}(l) \quad (1) \]

\[ \text{MCO}_3^{+}(aq) + \text{CO}_3^{2-}(aq) = \text{M(CO}_3^{2-}(aq) \quad (2) \]

where M(OH)$_3$ represents each REE$^{3+}$ incorporated into the Fe-Mn oxyhydroxides. When a pair of REE(III) species involved in ligand-exchange reactions have systematically different Racah ($E^1$ and $E^3$) parameters for 4f electron repulsion in REE$^{3+}$, the logarithms of concentration ratios between the pair of species show a REE fractionation trend characterized by tetrad effect (Jørgensen, 1979; Kawabe, 1992; Minami et al., 1998; Kawabe and Masuda, 2001). In fact Racah $E^1$ and $E^3$ parameters for REE sesquioxide (REEO$_{1.5}$) and REE(OH)$_3$ are significantly smaller than those for REECO$_3^{+}(aq)$ and slightly smaller than those of REE(CO$_3$)$_2^{-}(aq)$ in seawater solution (Ohta and Kawabe, 2000). Dissolved REEs are incorporated into marine carbonate lattice sites during co-precipitation. Hence the W-type tetrad signature is transferred to carbonate crystals precipitated from the seawater solution together with small REE fractionation between calcite and/or aragonite and dissolved REE species.

Yttrium fractionation

The similarity of Y with Ho in ionic size and

![Fig. 4. (A) (Gd/Ho)$_{chn}$ vs. (La/Nd)$_{chn}$ and (B) (Er/Lu)$_{chn}$ vs. (La/Nd)$_{chn}$ plots for Krol and Bilara carbonates. PAAS = Post Archean Average Shale, SW = shallow seawater, HMB = Holocene Micobialite.](image)

and resemble average shale. Seawater shows W-type tetrad effect in its chondrite-normalized REE pattern, which is displayed by marine carbonates as well (Kawabe et al., 1998). REECO$_3^{+}$ (aq) and REE(CO$_3$)$_2^{-}$ (aq) are principal seawater REE species (Liu and Byrne, 1998; Ohta and Kawabe, 2000). Tetrad effect in seawater originates from REE partitioning during ligand-exchange reaction of REE$^{3+}$ between particulate REE and REE(III)-carbonate complexes in seawater, where the particulate REE is assumed to be primarily represented by REE(OH)$_3$. The ligand-exchange reaction can be represented in a simple form by Eq. (1), together with the reaction (Eq. (2)) between REE(III) complexes in seawater (Kawabe et al., 1998),

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Yttrium fractionation

The similarity of Y with Ho in ionic size and
REE abundances in late Neoproterozoic continental platform carbonates, India

valency (trivalent), Y has been recognized as a pseudolanthanide. In fact in silicate rocks and clastic sedimentary rocks (e.g., shale) Y behaves in coherence with Ho and shows no evidence of fractionation. This is evident by strictly chondritic (Y/Ho) ratio of ~27 in magmatic rocks and pelites. Ho and Dy fall on the same tetrad curvature and behave extremely coherently. However, Y fractionates from heavy REEs like Ho and Dy in marine reaction systems. Kawabe et al. (1991) recognized that marine carbonates display non-chondritic Y/Ho ratios (i.e., Y/Ho > 27). Later studies on REE and Y abundances in marine realm by Bau et al. (1995) and Nozaki et al. (1997) showed superchondritic Y/Ho ratios in sea water. In Fig. 5, Y/Ho and Y/Dy concentration ratios for Krol and Bilara carbonates shows positive covariance and fall along the line joining PAAS, Holocene microbialite and the surface water of Coral Sea. Both Y/Ho and Y/Dy range from chondritic to superchondritic ratios suggesting variable continental contributions. It is important to note that although Holocene microbialite carbonates are apparently devoid of continental contribution show much lower Y/Ho and Y/Dy ratios than the coexisting seawater composition. We attribute this to fractionation of Y relative to Ho and Dy during carbonate precipitation. Decoupling of Y from Ho and Dy arises out of different ground-level electronic configurations. The REE^{3+} ions are characterized by successive addition of fourteen 4f electrons to the Xe core of La^{3+} configuration. By contrast Y^{3+} has neither 4f electrons nor the Xe core. This in turn would result in marked difference in the thermodynamic parameters viz., stability constants of the carbonate complexation and partition coefficient for Y and other REEs. In other words Y/Ho and Y/Dy ratios in Krol and Bilara carbonates are net results of Y fractionation during carbonate precipitation and contamination with terrigenous materials.

Cerium anomaly

Owing to its unique redox chemistry Ce gets fractionated from other trivalent REEs in the marine realm. Soluble Ce^{3+} under oxidizing condition changes to insoluble and thermodynamically stable Ce^{4+}. Preferential scavenging of Ce^{4+} through organic and inorganic (Mn-oxyhydroxides) particulates results in negative Ce anomaly in seawater. Compared to deeper waters, the shallow waters, especially in the upper photic zone display much less pronounced negative Ce anomaly. The shallow water of Coral Sea has Ce anomaly ~–0.18 whereas its deeper waters exhibit pronounced negative anomalies (~–1.0). Ce oxidation has been attributed to surface catalysis on Mn-oxyhydroxide in oxic condition (Bau, 1999) or to the direct oxidation of Ce^{3+} (aq) by δ-MnO_2 (Ohta and Kawabe, 2001). However, Moffett (1990, 1994) advocated microbially mediated oxidation of Ce as more effective than abiogenic processes of Ce removal. Both Ce and Mn show pronounced sea surface concentration maxima and diminished negative Ce anomaly. Under oxidizing condition such maxima are brought about by photoreductive dissolution of Ce and Mn, as well as photo-inhibition of microbial oxidation of Mn^{2+} and Ce^{3+}. Ce anomalies recorded in our shallow marine Krol and Bilara carbonates (Table 1) are in consonance with that of shallow seawater. Shal-

Fig. 5. (Y/Ho) vs. (Y/Dy) plot for Krol and Bilara carbonates. PAAS = Post Archean Average Shale, SW = shallow seawater, HMB = Holocene Micobialite.
low marine Holocene microbialite has Ce anomaly of around –0.12. Interpretation of Ce anomaly in carbonate sediments is hindered by post-depositional mobilization of Ce during early diagenesis owing to its redox sensitive nature (German and Elderfield, 1990; Holser, 1997). Absence of Ce anomaly or positive Ce anomaly in some samples may be attributed to enrichment of Ce relative to other REE $^{3+}$ through mobilization of Ce as Ce $^{3+}$ under reducing condition during early diagenesis and re-precipitation at the oxidized front. Presence of early diagenetic pyrite and/or high organic matter in the studied samples supports the existence of reducing pore water conditions. However, much work is needed to understand such diagenetic mobilization and enrichment processes in older rocks or sediments.

Variations in REE abundance patterns

The variations in the REE abundance patterns in Bilara and Krol carbonates are attributed to two factors: contamination with continental materials and post depositional diagenetic processes. Although continental material with PAAS-like composition is suggested by Y/Ho and Y/Dy concentration ratios, however, a simple end member (average shale and seawater) mixing model can not account for the variations in the REE abundance patterns and the scatter in the chondrite-normalized elemental ratios (Figs. 4A and B) relative to average shale, seawater and Holocene microbialite carbonates. Relatively high continental contribution as aeolian and/or fluvial particulates with shale-like REE abundances tends to mask the tetrad curvatures and causes LREE enrichment (Fig. 3H). Large variations in the apparent concavity of tetrad curvatures in our samples may be attributed to such processes but are not sufficient to explain the large scatter of the data points in Figs. 4A and B relative to the reference points. REE data for Middle Devonian dolomites from Western Canada (Qing and Mountjoy, 1994) also show large variations in chondrite-normalized La/Nd, Gd/Ho and Er/Lu ratios. It is apparent that the post-depositional early diagenetic processes played a significant role in remobilization as well as fractionation of REEs between sediment and water. The fractionation of HREEs during early diagenetic re-crystallization is primarily controlled by HREE-carbonate complexation in the solution flushing the sediment/pore water system, whereas the LREEs are controlled by reactions involving the continentally derived particulates within the sediment.

Transformation of high magnesium calcite and aragonite grains to low Mg-calcite and dolomite during early meteoric water diagenesis is perhaps the most important process leading to stabilization of carbonate mineralogy (Morse and Mackenzie, 1990). Studies on pore water chemistry of recent carbonate sediments in Bahamas and Bermuda display significant shift in carbonate alkalinity, pH and $P_{CO_2}$ in the waters flushing the sediment, compared to the ambient seawater during early meteoric diagenesis (Plummer et al., 1976; Budd, 1988; Morse and Mackenzie, 1990). Degradation of organic matter in the carbonate as well as percolating soil water from vadose zone reduces the pore water pH owing to enhanced $P_{CO_2}$, which in turn results in dissolution of unstable carbonate phases like aragonite and high Mg-calcite causing rise in alkalinity (HCO$_3^-$) and subsequent precipitation of stable low Mg-calcite. Carbonate alkalinity values in such pore waters have been reported to range from 2.6 to 6.3 meqv/kg (compilation in Morse and Mackenzie, 1990) compared to ambient marine water value of 2.1 meqv/kg. $P_{CO_2(aq)}$ values ~10 times the atmospheric value have been reported from the carbonate pore waters.

Petrographic characters and mineralogy of Krol and Bilara carbonates suggest lines of evidence for meteoric water alteration in most samples. This is further supported by the oxygen isotopic compositions of such carbonates (Mazumdar, 1996; Mazumdar and Bhattacharya, 2001; Mazumdar et al., 2002). It is evident that recrystallization of low Mg-calcite took place under high alkalinity or HCO$_3^-$ concentration in the water flushing the carbonate sediment. Johannesson et al. (1994) reported that lake waters with high carbonate alkalinitities (greater than...
normal seawater value) tend to show HREE enrichment relative to LREEs. Speciation calculation of dissolved REE species by Liu and Byrne (1998) and Ohta and Kawabe (2000) show dominance of REE(CO$_3$)$_2$\(^{(aq)}\) relative to REE(CO$_3$)$^+$\(^{(aq)}\) with increasing alkalinity of the solution. HREE(CO$_3$)$_2$\(^{(aq)}\) are preferentially stabilized in the solution with higher alkalinity. This means partition coefficients or $K_d$ ($[\text{REE}]_{\text{CaCO}_3}/[\text{REE}]_{\text{solution}}$) for HREEs would decrease with increasing alkalinity of the solution relative to $K_d$ for LREEs. Such a process would certainly result in significant remobilization of HREEs during dissolution/reprecipitation process, which is evident from the scatter in Figs. 4A and B. The extent of such remobilization is controlled by water/rock ratio and permeability which in turn is affected by rate and nature of cementation. However, quantification of these parameters is beyond the scope of this paper.

Compared to HREEs, behavior of the LREEs and scatter in (La/Nd)\(_{\text{chm}}\) in our carbonates can not be explained by carbonate complexation reaction. However, reactions involving LREE-enriched particulates in the sediment-water system may impart LREEs into the carbonates during recrystallization. In addition, presence of authigenic clay minerals (mixed-layered illite-smectite) in several samples, especially in Group-I and II, indicates dissolution/reprecipitation of silicate phases. Such reactions mobilize silicate hosted REEs and may affect the LREE abundances during recrystallization of carbonate sediment. Schieber (1988) observed relative enrichment of LREEs in carbonates normalized by associated shales and suggested preferential incorporation of LREEs during diagenesis. However, the detailed fractionation process and the cause for higher (La/Nd)\(_{\text{chm}}\) than average shale need further study.

CONCLUSIONS

(1) Based on chondrite-normalized Gd/Ho, La/Nd ratios, we have been able to classify the Krol and Bilara carbonates into three groups.

(2) (Y/Ho) and (Y/Dy) concentration ratios have been shown to reflect a combined effect of Y fractionation relative to neighboring trivalent REEs during carbonate precipitation from seawater and influence of continental contributions with chondritic ratios. The contrasting behavior of Y has been related to its different electronic configuration which determines it complexation behavior and partition coefficient.

(3) Ce anomaly values reported in this work are in agreement with the Ce anomalies in typical shallow marine conditions. However, absence of Ce anomaly and distinct positive anomalies in some cases reflect post-depositional Ce mobilization during early diagenesis.

(4) Variations in LREE and HREE abundance patterns as well as the scatter in chondritenormalized elemental ratios have been explained as a result of variable contaminations with continental material and early diagenetic process in the carbonate sediments. HREE remobilization and fractionation during dissolution/re-precipitation process involving early mineralogical stabilization has been attributed to high stability of HREE(CO$_3$)$_2$\(^{-}\) complexes in the solution flushing the carbonate sediment during meteoric water diagenesis. Variations in LREE have been linked to contribution of LREE enriched particulates during carbonate recrystallization and also to mobilization of silicate hosted REEs during formation of authigenic clay mineral phases.

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