

Signatures of rare-earth elements in banded corals of Kalpeni atoll—Lakshadweep archipelago in response to monsoonal variations

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Concentrations of rare-earth elements (REE) have been determined in seasonal bands of *Porites* species collected from the Lakshadweep lagoon. Total REE (Σ REE) are very low (< 3 ppm) in these corals. Seasonal variations in REE appear to have occurred with Σ REE and the light rare-earths (LREE) enriched in the high density (representing monsoon season) bands. In contrast, the heavy rare-earths (HREE) are enriched in the low density bands. LREE enrichment in the high density bands is attributed to their higher availability during the rainy season due to the increased weathering of the continental sources. Elemental ratios and SEM photographs reveal the increased incorporation of terrigenous material into the growth bands during the monsoon season.

The growth bands of scleractinian corals were found to record the variations in environmental conditions in which they grow¹⁻⁷. Trace metal concentrations in skeletal aragonite of corals have been suggested to reflect the concentrations in surface seawater (ref. 8 and references therein). Since the corals consist of dark and light bands of different densities and an adjacent pair of low and high density bands represent one year's growth⁹, studies on trace metal variations in the growth bands shall yield valuable information on the changing chemistry of surface ocean waters. Studies on corals around India and in the Indian Ocean assume further significance since they tend to record the intensity of the monsoons. Monsoons govern the sea-surface temperature and thus the annual density banding of the corals¹⁰.

REE in sedimentary phases are increasingly being used as indicators of several geological and oceanographic processes, the paleo-redox conditions, depositional environment, and also to assess the crustal sources (ref. 11 and references therein). While myriad data are available on REE in marine sediments especially carbonates and non-carbonates¹², very few data are reported in corals¹³⁻¹⁶ and data from the Indian Ocean region are especially scarce. In addition, earlier studies were carried out on bulk coral samples. No attempt has been made so far, to study the variation in REE in seasonal bands. The present study aims to understand the incorporation

of REE in corals in monsoon and non-monsoon seasons. Deciphering the location of REE in various phases of corals has also been attempted to explore the possibility of utilising this data for paleoclimatic inferences. Diagenetic processes may alter the REE composition of sedimentary phases^{17,18} but may not be affecting the corals since these are of very recent origin. This paper reports the rare-earth elements (REE) variation in a coral *Porites* sp. collected from the Kalpeni Island, Lakshadweep region.

Materials and Methods

Samples of hard coral *Porites* sp. were collected from the lagoons of the Kalpeni atoll (lat. 10°05'N, long. 73°39'E) at a depth of 1.5 m. Slices of coral were taken along the growth axis using a dental drill, and X-radiography was carried out using the industrial X-ray films. Sixteen subsamples were separated representing the seasonal bands (high density and low density). The age of the growth bands was determined by assuming the sample collection time as the first year (1985 in this case)¹⁹.

The analyses were carried out using inductively coupled plasma mass spectrometer (ICP-MS). Powdered sample (0.1 g), of each seasonal band, was treated with 10 ml of acid mixture (7 ml, 48% HF and 3 ml conc. HNO₃) in a teflon beaker and digested through repeated heating on a sand bath. Subsequently Indium (1 ppm) solution was added as a

tracer²⁰. Spectroscopic grade aqueous metal solutions and high purity double distilled water, made from a quartz unit, were used in the preparation of multi element standards. The rock standards of basalt (GSJ, Japan) and gabbro (CCRMP, Canada) were analysed alongwith the samples to check the reliability of analysis. The accuracy of the analysis varied between 3-10%.

The REE abundances have been normalized to that of average shale, as is commonly done in various studies of marine systems. This allows to remove the effect of the odd-even abundance distribution of the elements and to allow assessment of deviation from upper crustal abundances with the system in question. Shale may or may not precisely represent the defacto terrigenous component contained in the corals, but is useful as a common reference material that enables a direct comparison to other sedimentary materials²¹.

Results and Discussion

Concentration of REE's (La, Ce, Sm, Eu, Gd, Dy, Er, Yb and Lu) in sixteen samples (eight monsoon and eight non-monsoon) during the period 1978-1985, are presented in Table 1. Total REE concentrations (Σ REE) in all the growth bands are very low, with most of them containing Σ REE < 3 ppm. The monsoon bands show more fluctuation in REE concentrations than the non-monsoon bands. This probably reflects the variability of REE in surface waters during the monsoons.

The REE distribution reveals significant

differences between the monsoon and non-monsoon seasons for six of the eight years data considered here. Light REE (LREE) fractionation represented by

$$La_n/Lu_n = [(La_{sample}/La_{shale})/(Lu_{sample}/Lu_{shale})]$$

shows LREE depletions (range 0.1 to 0.91, Table 2). These La_n/Lu_n values are lower than those proposed for terrigenous particulates entering into the oceans (~1.3 - Sholkovitz²²; ~1.0 Condie²³) indicating a reduced terrigenous influence. However, on a seasonal basis, La_n/Lu_n values were higher in six years of monsoonal bands and lower in corresponding non-monsoonal bands (Table 2). The ratios approach 1 (max. 0.91) in some of the high density monsoonal bands indicating an increased influence of terrigenous input during the monsoon. LREE enrichment in monsoonal bands is also shown in Fig. 1. Monsoon to non-monsoon concentration ratios for Σ REE, La and Lu (representing total, light and heavy REE) show that La and Σ REE in six of the eight bands are above 1. Lu on the other hand is mostly below 1. LREEs are more susceptible to removal than HREE during weathering^{24,25}. In the monsoon season, due to higher rainfall, increased weathering and consequently greater run-off, there is a chance of higher LREE removal and supply to ocean. Hence, they are available for the incorporation into coral matrices or adsorption onto surfaces. In contrast, heavy REE (HREE) form more stable complexes in seawater with carbonate and carboxylate ions²⁶ and remain in solution.

Instead of using elemental concentration, the use

Table 1—REE concentration (ppm) in various seasonal bands of *Porites* sp. of Kalpeni lagoon sample

Year		La	Ce	Sm	Eu	Gd	Dy	Er	Yb	Lu	Σ REE
1985	HD	1.45	0.13	0.22	0.04	0.20	0.04	0.06	0.03	0.03	2.2
1985	LD	0.87	0.15	0.20	0.03	0.13	0.05	0.06	0.04	0.02	1.62
1984	HD	1.39	0.20	0.24	0.02	0.20	0.03	0.04	0.03	0.02	2.17
1984	LD	0.78	0.10	0.20	0.02	0.18	0.03	0.04	0.08	0.03	1.46
1983	HD	0.89	0.14	0.20	0.03	0.10	0.04	0.04	0.11	0.05	1.60
1983	LD	1.51	0.17	0.15	0.02	0.07	0.07	0.03	0.07	0.04	2.13
1982	HD	1.84	0.33	0.21	0.03	0.19	0.03	0.03	0.13	0.05	2.84
1982	LD	0.69	0.17	0.18	0.03	0.30	0.05	0.02	0.09	0.02	1.55
1981	HD	0.55	0.19	0.21	0.01	0.15	0.07	0.01	0.10	0.03	1.32
1981	LD	0.50	0.12	0.10	0.02	0.09	0.03	0.02	0.13	0.06	1.07
1980	HD	0.56	0.16	0.15	0.01	0.11	0.03	0.06	0.07	0.01	1.16
1980	LD	0.52	0.14	0.17	0.02	0.30	0.04	0.03	0.09	0.03	1.34
1979	HD	0.99	0.22	0.30	0.05	0.19	0.02	0.02	0.01	0.04	1.84
1979	LD	0.44	0.13	0.17	0.04	0.17	0.03	0.02	0.01	0.04	1.05
1978	HD	1.29	0.22	0.08	0.02	0.13	0.01	0.01	0.03	0.04	1.83
1978	LD	0.89	0.15	0.16	0.04	0.21	0.03	0.03	0.04	0.05	1.60

HD = High density (monsoonal band)

LD = Low density (non-monsoonal band)

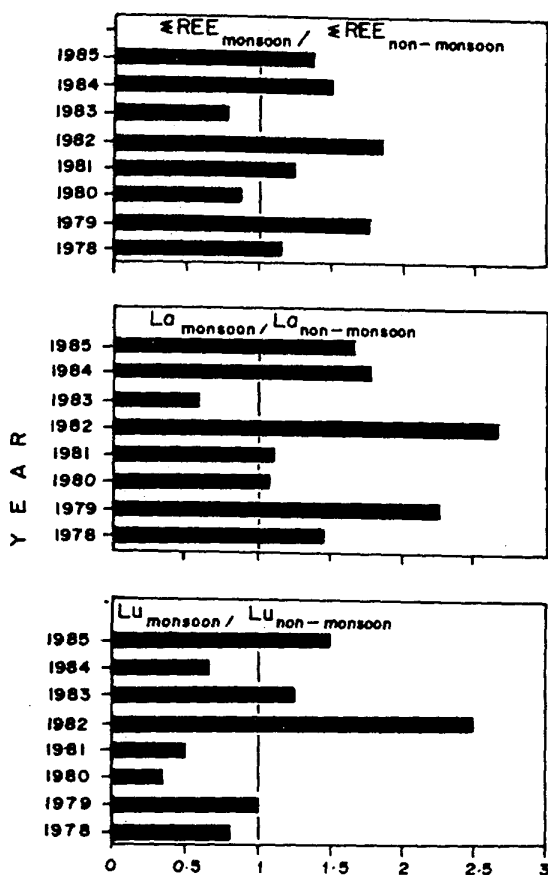


Fig. 1—Annual variations in concentration ratios in monsoonal to non-monsoonal bands for (a) Σ REE, (b) La and (c) Lu

of elemental ratios may be preferred to compare the relative contributions of seawater, detrital and other sources to the observed REE abundances. Therefore, the ratios of different elements for each seasonal band of coral are listed in Table 2.

A comparison with cobalt will give information regarding the phases hosting the REE²⁷. The Co/La ratios observed here (0.87-4.09) are less than that in seawater (10) and higher than that in shale (0.38)²⁷. This indicates that REE in these corals have both seawater and detrital sources. The Cr/La ratios (2.31-6.17) are much lower than the corresponding seawater value (67) and higher than the shale (1.8)²⁷ that further support the presence of REE derived from both authigenic and terrestrial sources.

Support for the incorporation of terrigenous material into the polyps of corals also comes from the observation of trapped clay particles in the high density bands under the scanning electron microscope¹⁹.

Table 2—Relative variations of the REE's and selected major and minor elements in the seasonal bands

Year		La/Lu	Co/La	Cr/La	Ca (%)	Fe (ppm)
1985	HD	0.81	1.33	2.31	37.55	47
1985	LD	0.61	2.17	3.30	38.66	40
1984	HD	0.91	1.71	3.73	38.65	19
1984	LD	0.41	2.38	4.14	36.54	56
1983	HD	0.24	2.48	6.17	36.85	44
1983	LD	0.62	1.15	2.60	39.49	60
1982	HD	0.49	0.87	2.36	38.66	58
1982	LD	0.61	1.48	0.09	39.84	56
1981	HD	0.20	3.58	—	36.54	70
1981	LD	0.10	3.52	—	38.10	55
1980	HD	0.63	2.73	—	35.10	66
1980	LD	0.20	2.75	—	37.43	58
1979	HD	0.31	2.36	—	30.12	60
1979	LD	0.15	4.09	—	30.49	56
1978	HD	0.46	1.66	—	34.24	63
1978	LD	0.24	1.98	—	34.14	60

HD = High density (monsoonal band)

LD = Low density (non-monsoonal band)

Sprin²⁸ reported that more than half of REE in marine clays are in the adsorbed form. These data suggest that the adsorption of REE's onto clays and carbonates in the ocean might be an important mechanism of their removal from seawater. While describing the scavenging processes, Craig²⁹ and Turekian³⁰ reported that many trace elements in seawater could be adsorbed onto the surface of fine suspended particles. Fe-oxides have a strong capacity for adsorption of REE³¹. Similar to REEs, higher iron concentrations (Table 2) are also observed in the monsoonal bands (except in 1983). Strong covariance between REE and Fe concentrations has also been noticed³² during the estuarine mixing, implying that their removal mechanisms are strongly coupled. The kinetics of REE removal was also found to be rapid and comparable to Fe^{33,34}. Palmer³⁵ has also noticed that a major portion of REE in Foraminifera is adsorbed on the Fe-oxide coatings of their tests. A third and insignificant phase hosting REE in corals could be the lattice of aragonite, as found in calcite lattice of Foraminifera³⁵. Sm and other REE have a capacity to replace Ca in the calcium carbonate matrices^{25,36}.

Calcium, a major element in corals, ranged between 30.1% and 39.8% (Table 2). The concentrations of the higher end are close to the Ca values in pure CaCO₃. Ca is depleted in the monsoonal bands (except in 1978 and 1984) in contrast to the distribution of REE and Fe. Similar negative relationship between REE and Ca were also reported

in carbonate sediments¹⁷⁻³⁷. It has also been observed that the growth rate of coral is quite low in monsoon season in comparison to that in non-monsoonal season⁷. Coral growth rates for the period 1978-1985, calculated using the method proposed by Buddemeier *et al.*³⁸ and Highsmith³⁹, ranged between 7.50 and 12.35 mm/y for the non-monsoonal bands compared to that between 4 and 6.5 mm/y for the monsoonal bands. This in turn relates the REE concentration increase in REE in monsoonal seasons to an increased exposure time in seawater (and therefore adsorption capacity) and that to a diminished accumulation rate during the non-monsoonal seasons. Similar inverse relationship between the sedimentation rate/nodule growth rate and REE uptake were found in manganese nodules³¹⁻⁴⁰.

Rare-earth element distributions in seasonal bands of reef building corals reveal differences in REE incorporation between monsoonal and non-monsoonal periods. The LREE are enriched in the high density (monsoon) bands and depleted in the low density (non-monsoon) bands indicating the influence of SW monsoon. Three processes possibly govern the REE distribution in these corals: 1) adsorption onto Fe-oxide coating, 2) detrital input and 3) incorporation into aragonite lattice.

Present results suggest a monsoonal control on REE distribution in the growth bands of corals. Additional REE studies of this type, together with detailed studies employing oxidative and reductive cleaning techniques and determination of REE in various phases, would help to clarify the use of REE variations in seasonal bands of corals as a tool for determining the intensity of monsoonal variations on time scales short compared to those in sedimentary records. Efforts in this direction are in progress.

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