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Rare earth element studies of surficial sediments from the southwestern Carlsberg Ridge, Indian Ocean

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Abstract. The rare earth element (REE) contents of sixteen surficial calcareous sediments from the southwestern Carlsberg Ridge, Indian Ocean, have been determined. The total REE vary from 35 ppm to 126 ppm and are inversely related to the calcium carbonate content. REEs show a strong positive correlation with Al + Fe + K + Mg + Na ($r^2 = 0{\cdot}98$) and Mn + Fe + Cu + Ni ($r^2 = 0{\cdot}86$) suggesting that the REE is associated with a combined phase of clays (mainly illite) and Mn-Fe oxyhydroxides. The aeolian input into these sediments is suggested from the weak positive Eu/Eu* anomaly. Shale-normalized (NASC) pattern along with $La_{(n)}/Yb_{(n)}$ ratio suggest enrichment of heavy REE (HREE) relative to the light REE (LREE) with a negative Ce/Ce* anomaly implying retention of a bottom water REE pattern.

Keywords. REE; clays; Mn-Fe oxyhydroxides.

1. Introduction

The rare earth elements (La to Lu, At. No. 57 to 71) are members of group IIIA and have similar chemical and physical properties. Amongst the REEs, Cerium and Europium behave differently: Ce^{3+} under oxidizing conditions becomes insoluble Ce^{4+}, while under reducing conditions Eu^{3+} becomes Eu^{2+}. REE in the marine sediments is used to assess the geochemical processes and the elemental sources.

The Carlsberg Ridge (CR) is a part of the Indian Ocean province and separates the Arabian and Somali basins. Sediments from CR are calcareous in nature and contain clay minerals (< 2 micron size) like illite, smectite, chlorite and kaolinite in a decreasing order and the major and trace element data of these sediments have been reported by Valsangkar *et al* (1992). The mechanism of the uptake of REE into calcareous ooze was attributed to their incorporation in the $CaCO_3$ lattice or adsorption of Fe-Mn oxyhydroxide coatings (Palmer 1985; Shaw and Wasserberg 1985; Wang *et al* 1986). REE distribution patterns and their association with a limited number of calcareous sediments from the Indian Ocean (Central Indian Basin and Wharton Basin) were discussed recently (Nath *et al* 1992; Pattan *et al* 1994, 1995). There are no data available on REE distribution of these CR sediments. Therefore, in the present study, we address the REE distribution, mechanism of incorporation, controlling phases and fractionation patterns.

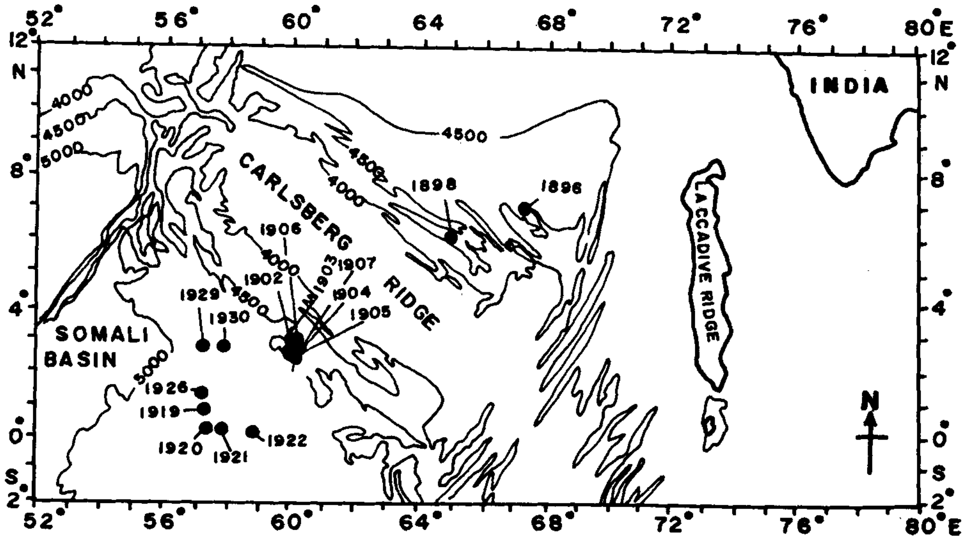

Figure 1. Map showing sample location.

2. Material and methods

Surficial sediments from the southwestern Carlsberg Ridge (figure 1) were collected using a Petterson grab during the 86th and 87th cruise of R V Gaveshani in 1981. The water depth of the samples ranged from 4400 to 5100 m. Aliquotes of dried sediment were digested by HF and $HClO_4$ and cation exchange separation of REEs was carried out using the method of Jarvis and Jarvis (1985). Major, trace and rare earth elements were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) at the Institute of Oceanographic Sciences, Deacon Laboratory. The carbonate contents were estimated from the CO_2, evolved after treating with orthophosphoric acid, measuring with a Coulometrics coulometer. International sediment standards (BCSS-1 and MESS-1) were used to assess the accuracy of the analysis: the accuracy agrees within the precision of the analysis (+/− Al – 4%, Ti – 4·6%, Fe – 2·1%, Mn – 0·8%, Mg – 1·2%, Na – 7·6%, K – 9·8%, P – 6·6%, Cu – 2·1%, Ni – 2·6%, Pb – 4·1%, Zn – 8·1%, La – 3·6%, Ce – 0·6%, Nd – 2·3%, Sm – 2·6%, Eu – 1·6%, Gd – 2·3%, Dy – 0·2%, Er – 6·8%, Ho – 7·2%, Yb – 1·5% and Lu – 0·1%). Factor analysis was carried out using the method described by Fernandez and Mahadevan (1982).

3. Results and discussion

The total REE content of Carlsberg Ridge calcareous sediments range from 35 ppm to 137 ppm (table 1) which is equivalent to 0·17 to 0·63 times that of concentration values in shale (North American Shale Composite). Elderfield *et al* (1981) established that ultrasonically cleaned forams contain around 5 ppm of REE, whereas, Pattan *et al* (1995) showed that a bulk calcareous ooze from Ninetyeast Ridge contained ~ 9 ppm. The high REE abundances in the sediments studied here are most likely a consequence of the presence of clay minerals or Mn-Fe oxyhydroxides. The strong positive relation between Al + Fe + K + Mg + Na and Mn + Fe + Cu + Ni ($r^2 = 0{\cdot}97$) suggests that the non-calcareous component of the sediments is a combined phase of clays and Mn-Fe oxyhydroxides (figure 2).

The $CaCO_3$ content of the sediments varies from 36·5% to 84·2% (table 1) with the highest $CaCO_3$ (84·2%) content corresponding to the lowest total REE content (35·6 ppm) suggesting that the REE abundance varies inversely with the carbonate content (figure 3), and in agreement with the findings of Wang *et al* (1986) and Pattan *et al* (1995). Factor analyses show three factors with total variance of 82% (figure 4). Factor 1 has a total variance of 43% with positive loadings of Ca and Sr and this factor can be designated as biogenic. Further Al, Fe, Mn, Mg, Na, K, Ti, P, As, Ba, Cu, Ni, Cr, and REEs are negatively loaded suggesting a complex phase. The positive loadings of Ca and Sr indicate that foraminifer tests are the main dilutant for the rest of the elements. Factor 2 constitutes nearly 30% of variance with weak positive loadings of Ca, Sr and Eu. It has negative loadings of aluminosilicate and Fe-Mn oxyhydroxide group suggesting that it is a combined phase of clay and Fe-Mn oxyhydroxide. Factor 3 has least variance (8·5%) and has weak positive loadings of Ca, Sr and negative loadings of P, As and Ba. In all the three factors Ca and Sr are positively loaded suggesting that they are the main dilutant for the rest of the elements.

REE displays a strong positive correlation ($r^2 = 0{\cdot}98$) with Al + Fe + K + Mg + Na reflecting their co-precipitation/co-deposition into clay minerals (figure 3). Piper (1974) demonstrated that about 50% of the REEs in marine sediments are leachable with HCl indicating that they are typically adsorbed onto clays. Valsangkar *et al* (1992) determined the presence of clay minerals such as illite (27–67%), smectite (13–41·5%), chlorite (9·7–25·6%) and kaolinite (3·3 – 11·5%) in the order of abundance in these sediments. Sirocko *et al* (1991) also noted the presence of a considerable amount of illite of aeolian origin in the study area. The samples studied here are from the western side of Carlsberg

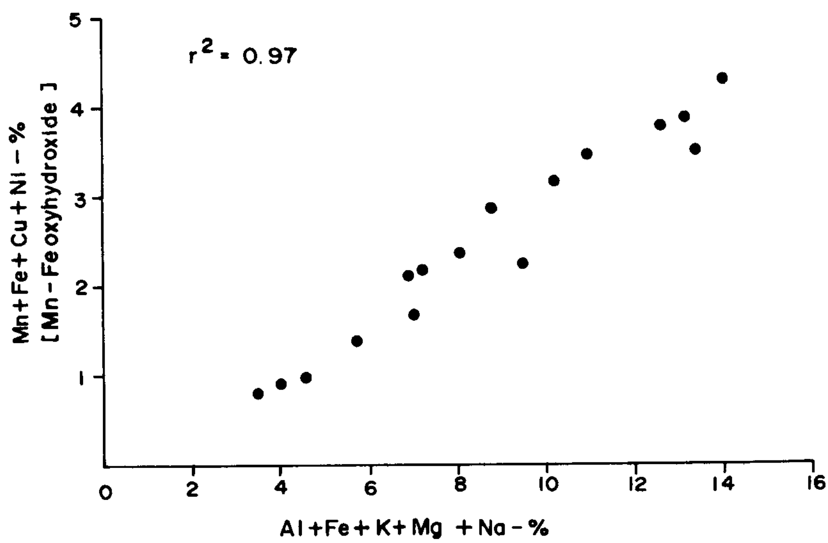

Figure 2. Relation between Al + Fe + K + Mg + Na and Mn + Fe + Cu + Ni of sediments.

Table 1. Chemical composition of major, trace and REE concentration in calcareous sediment from SW Carlsberg Ridge, Indian Ocean.

Sample no.	Al	Fe	Mn (%)	Mg	$CaCO_3$	Na	K	Ti	P	As	Ba	Co	Cr (ppm)	Cu	Pb	Ni	Sr
1896	2·56	1·72	0·37	1·07	70·13	1·00	0·55	0·16	0·09	12	1030	17	35	126	58	128	1371
1898	5·05	3·15	0·61	1·81	40·49	1·42	1·19	0·30	0·09	7	1450	28	49	181	12	229	1070
1902	3·09	2·11	0·23	1·30	65·09	0·74	0·66	0·20	0·09	8	1278	17	43	94	7	96	1538
1903	4·17	1·57	0·63	1·61	84·20	1·23	0·91	0·26	0·09	11	1266	24	54	152	10	223	1294
1904	5·65	3·64	0·65	2·08	36·50	1·39	1·28	0·34	0·11	10	1700	33	77	199	20	251	934
1905	5·27	3·26	0·2	2·17	43·00	1·27	1·41	0·31	0·10	11	1249	27	80	107	14	135	927
1906	5·18	3·37	0·48	1·89	41·47	1·54	1·12	0·32	0·11	19	1865	29	64	182	16	200	1037
1907	3·73	2·44	0·25	1·53	55·56	1·69	0·82	0·22	0·10	14	1486	19	48	112	18	116	1343
1918	2·83	2·02	0·13	1·13	64·02	0·58	0·51	0·17	0·10	14	1663	15	32	99	24	59	1358
1919	2·20	1·28	0·09	0·91	69·39	0·87	0·45	0·11	0·10	9	1859	12	23	78	3	50	1454
1920	2·85	1·57	0·10	0·99	59·46	0·99	0·60	0·14	0·10	8	1997	24	54	152	7	57	1200
1921	1·47	0·93	0·07	0·91	75·11	0·93	0·32	0·08	0·09	9	1691	9	18	56	5	37	1666
1922	1·38	0·88	0·07	0·79	79·39	0·66	0·30	0·07	0·09	1	1648	8	17	57	23	214	527
1926	3·19	2·65	0·2	1·22	61·55	1·04	0·68	0·19	0·09	3	1253	21	39	97	12	94	135
1929	1·23	0·76	0·05	0·55	51·41	0·75	0·25	0·07	0·07	1	911	6	14	39	3	21	1070
1930	4·56	2·86	0·59	1·70	48·58	0·98	0·98	0·09	0·09	9	1380	26	59	146	11	198	1185

Table 1. (*Continued*).

Sample no.	La	Ce	Nd	Sm	Eu %	Gd	Dy	Ho	Er	Yb	Lu	$La_{(n)}/Yb_{(n)}$	Ce/Ce*	Eu/Eu*
1896	14·9	24·1	14·1	3·3	0·7	2·9	2·7	0·6	1·6	1·5	0·2	0·80	0·79	1·06
1898	24·0	45·2	21·1	4·6	1·1	4·0	4·0	0·8	2·3	2·3	0·4	0·89	0·94	1·09
1902	17·8	28·5	16·5	3·8	0·9	3·4	3·3	0·7	1·9	1·8	0·2	0·82	0·79	1·10
1903	8·9	9·6	8·4	2·0	0·5	1·7	1·8	0·4	1·1	1·1	0·2	0·70	0·51	1·14
1904	27·3	60·3	25·5	5·7	1·4	5·1	4·9	1·0	2·8	2·6	0·4	0·98	1·07	1·09
1905	24·1	45·0	22·0	5·0	1·2	4·4	4·3	0·9	2·5	2·4	0·4	0·88	0·91	1·11
1906	25·9	46·9	24·2	5·4	1·3	4·8	4·7	0·9	2·7	2·6	0·4	0·86	0·93	1·11
1907	19·9	34·6	18·3	4·1	1·0	3·7	3·6	0·7	2·0	2·0	0·3	0·84	0·87	1·15
1918	17·9	25·3	16·4	3·8	0·9	3·5	3·5	0·7	1·9	1·9	0·3	0·81	0·71	1·15
1919	15·0	19·3	14·1	3·3	0·8	3·0	3·0	0·6	1·8	1·7	0·3	0·76	0·61	1·16
1920	18·3	25·7	16·7	3·9	1·0	3·6	3·6	0·7	2·1	2·0	0·3	0·80	0·75	1·15
1921	11·3	12·5	11·0	2·6	0·6	2·4	2·4	0·5	1·4	1·4	0·2	0·69	0·54	1·14
1922	11·1	12·4	10·2	2·4	0·6	2·3	2·3	0·5	1·4	1·3	0·2	0·70	0·54	1·18
1926	16·2	27·1	15·1	3·6	0·9	3·1	3·1	0·6	1·8	1·7	0·3	0·82	0·56	1·10
1929	19·3	34·6	17·7	4·0	0·9	3·5	3·4	0·7	1·9	1·9	0·3	0·90	0·87	1·11
1930	22·0	38·2	19·7	4·4	1·1	3·1	3·8	0·7	2·1	2·1	0·3	0·88	0·87	1·11

$Ce/Ce^* = 5Ce_{(n)}/(4La_{(n)} + Nd_{(n)})$.

$Eu/Eu^* = \log(2Eu_{(n)}/Sm_{(n)} + Gd_{(n)})$, where n is shale value.

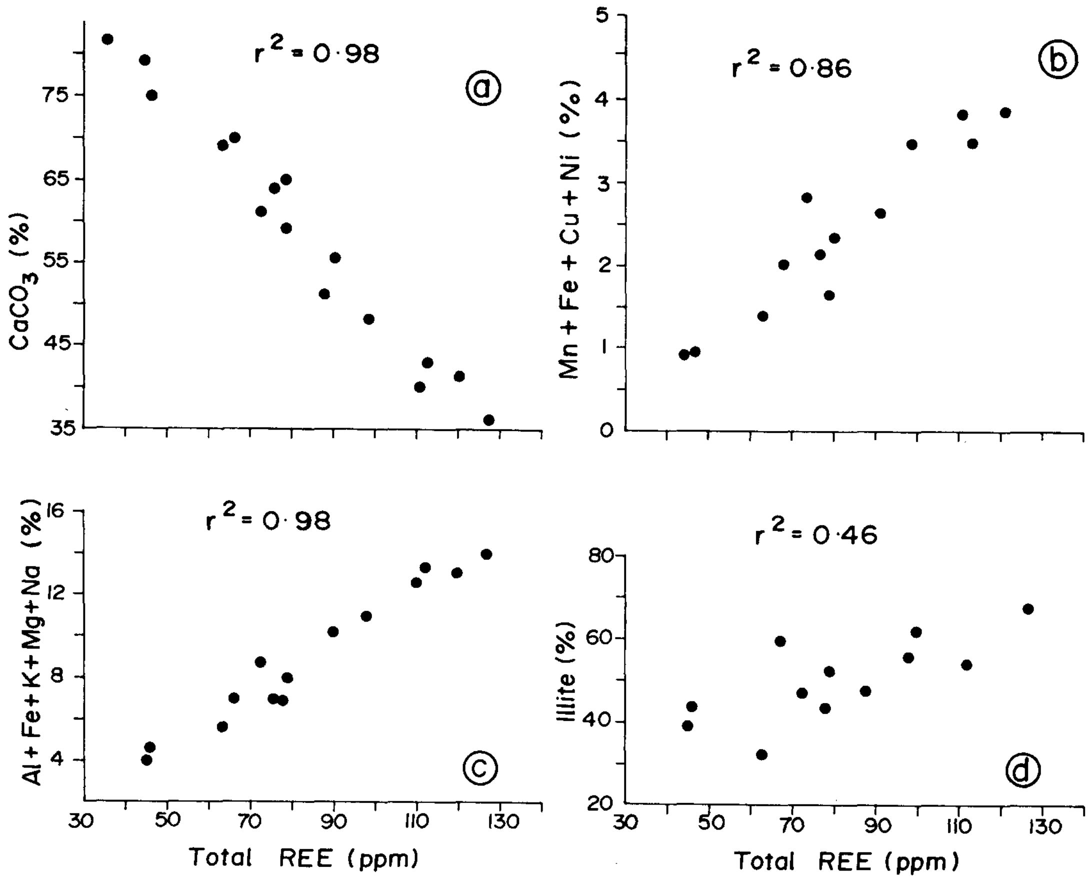

Figure 3. REE relation with $CaCO_3$(%), Al + Fe + K + Mg + Na(%), and Mn + Fe + Cu + Ni(%) and Illite(%) in the Carlsberg Ridge sediments. (Illite values are from Valsangkar *et al* 1992).

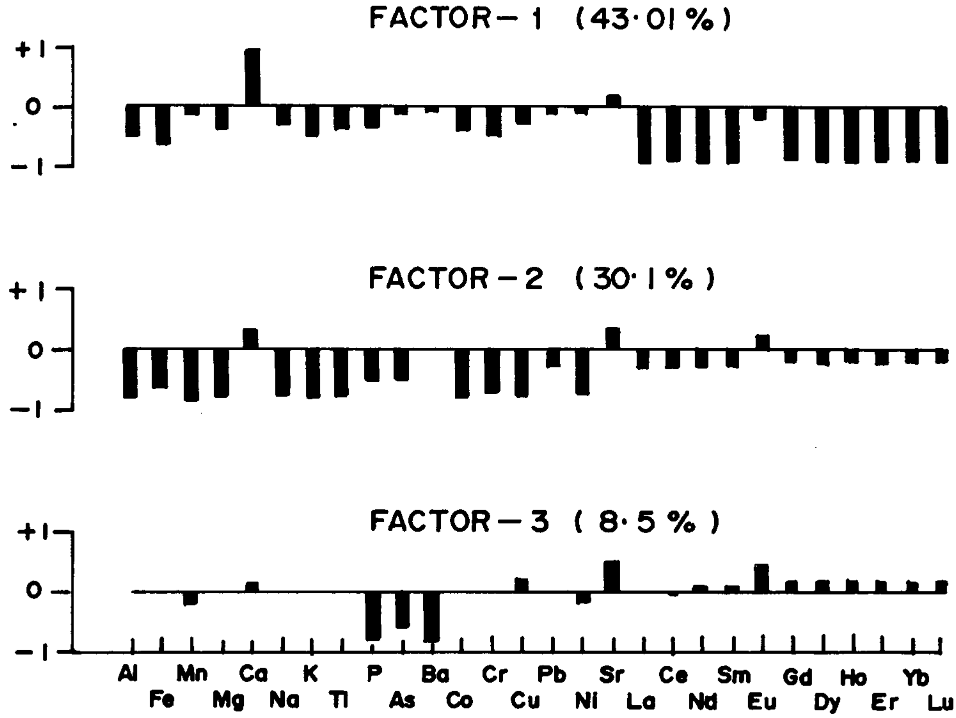

Figure 4. R-mode loadings for major, trace and REE.

Ridge. The Carlsberg Ridge may act as a topographic barrier for the transport of sediments from the Indus River by bottom waters. Illite shows a moderate positive association ($r^2 = 0{\cdot}46$) with REEs suggesting that the REE is adsorbed/co-precipitated by illite (figure 3). Illite has a comparatively high cation exchange capacity (CEC) from 10 to 40 mequiv/100g; as a result, it might have adsorbed REEs (Weaver and Pollard 1973). REE also shows a good positive correlation with Mn + Fe + Cu + Ni ($r^2 = 0{\cdot}86$) suggesting that REE is incorporated in a Mn-Fe oxyhydroxide phase (figures 3 and 4). Therefore REEs are associated with a combined phase of clays and Mn-Fe oxyhydroxides.

Ce/Ce* values more than one and less than one indicate positive and negative anomalies respectively (Toyoda *et al* 1990). Ce/Ce* anomaly of these calcareous sediments is generally negative ranging from 0·51 to 0·94 except one sample (1904) which has a weak positive anomaly (1·07) and is associated with high Mn, Fe, Cu, Ni, Al, Ti, Mg and K values compared to other samples. It has been observed that the greater the negative Ce/Ce* values, the higher the carbonate content and vice versa (table 1, figure 5). This is in agreement with previous observations (Wang *et al* 1986; Liu *et al* 1988; Toyoda *et al* 1990; Pattan *et al* 1995). The negative Ce anomaly of these sediments indicates that sea water is in an oxidizing environment, because Ce will be depleted in sea water by oxidative scavenging resulting in retention of Ce depleted pattern in these carbonate sediments (Wang *et al* 1986). The shale-normalized (NASC) REE pattern displays a weak positive Eu/Eu* anomaly (1·03 to 1·18, figure 5). The Eu/Eu* anomaly is an indication of aeolian and hydrothermal input (Elderfield 1988), strong reducing conditions (McLennan 1989) or the presence of detrital feldspar

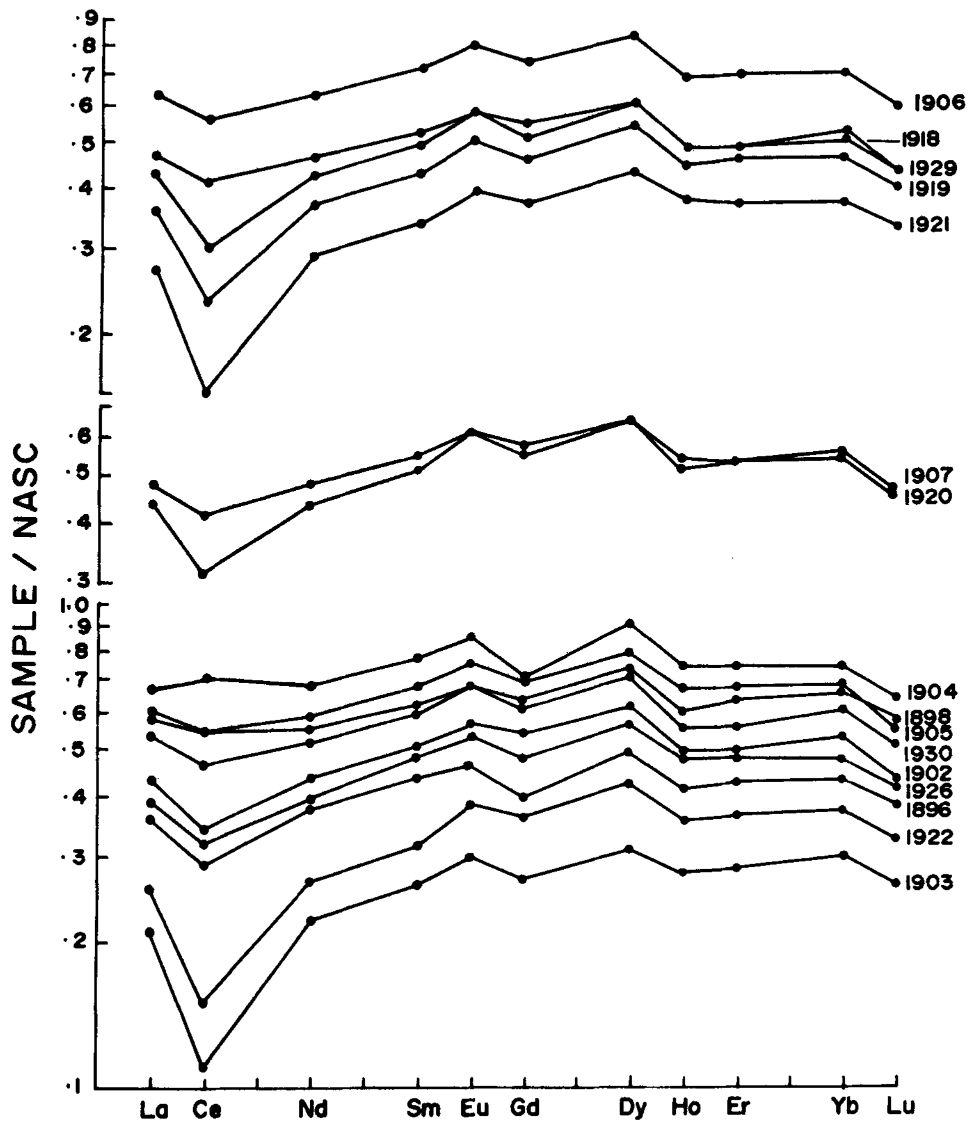

Figure 5. Shale-normalized REE pattern of Carlsberg Ridge sediments.

(Murray *et al* 1991). The positive Eu/Eu* observed here may be attributed to aeolian input because Eu shows positive loadings with calcium and strontium in factor 2 and 3 (figure 4). This suggests that the aeolian dust may sink along with foraminiferal tests. The aeolian input is also substantiated by the occurrence of palygorskite in the sediments (Sirocko *et al* 1991; Valsangkar *et al* 1992). Further in factor 1, all the REEs except Eu are negatively loaded and Eu is positively loaded with Ca and Sr suggesting that Eu has an additional source, probably aeolian.

Shale-normalized patterns (figure 5) together with $La_{(n)}/Yb_{(n)}$ ratio (table 1) indicate enrichment of the heavy REE (HREE) relative to light REE (LREE). In general, bottom deep water shows enrichment of HREE over LREE with a negative Ce/Ce* anomaly.

The LREE depletion in sea water is due to its lesser degree of complexation with sea water ligands compared to HREE. As a result LREE is effectively scavenged leaving behind HREE enrichment (Elderfield and Greaves 1982; De Baar *et al* 1985; Elderfield 1988). Therefore the enrichment of HREE relative to LREE in these sediments reflects the retention of the bottom water REE pattern.

4. Conclusion

- The REE contents and Ce/Ce* anomaly of calcareous sediments from the south-western Carlsberg Ridge are inversely related to the calcium carbonate.
- REEs are associated with a combined phase of clay and Mn-Fe oxyhydroxides, perhaps because of co-deposition.
- The fractionation pattern of these sediments suggests retention of deep-sea water REE pattern.

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