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Rare earth elements (REE) in deep basin sediments of the Baltic Sea

Helmar Kunzendorf, Henry Vallius

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Abstract Rare earth element (REE) contents in short cores from the Bornholm Basin, the Gotland Basin and the North Central Basin and also systematic data along a piston core from the Gotland Basin are given. Both ICP-MS and instrumental neutron activation analysis were applied. The REE patterns of sediments in the short cores are flat (shale-like) at differing core depths with a slight enrichment of the light REE (LREE; elements La through Gd). There is a decrease of La towards the surface in the sediments of the short cores suggesting that REE may be leached after deposition and then be transported in solution. The REE in Baltic Sea sediments are found to be mostly contained in the terrigenous phase of the sediments. The REE contents in the Bornholm Basin and North Central Basin sediments are generally higher. The REE patterns observed are flat with a slight enrichment of the LREE. Decreased REE in the uppermost samples of the short cores for all three basins suggest that the REE in the Baltic sediments may be opposed to processes that decrease or enrich elemental contents in sediments. Significant variations of the REE with depth in a long sediment core from the Gotland Basin were found. REE contents were especially high (La > 60 mg/kg) during Baltic Ice Lake and middle Yoldia Sea stages. Prominent REE ratios flag probably environmental changes during the sedimentation history of the long core deposition.

Keywords *Baltic Sea, sediments, rare earth elements, depth distribution.*

Helmar Kunzendorf [hk@geogr.ku.dk], Institute of Geography, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark; Henry Vallius [henry.vallius@gsf.fi], Geological Survey of Finland, P.O. Box 96, FIN-02151 Espoo, Finland. Manuscript submitted 3 June 2004; accepted 14 October 2004.

INTRODUCTION

The rare earth elements (REE) are a unique suite of elements that may be studied as a group to outline some geochemical behaviour of rocks and sediments (e.g., Henderson 1984). In short, these elements are regarded relatively immobile during their transport from the primary to the secondary environment (e.g., Öhlander et al. 1996) although examples exist where this has found not to be true. For instance, significant change of REE chemistry has been observed especially during weathering (e.g., Price et al. 1991).

As regards sediments the REE have been used to evaluate the depositional environment of chert and shale sequences (Murray et al. 1990). These authors used the fact that the so-called Ce anomaly, written as Ce/Ce* (Henderson 1984), in marine sediments shows an increasing trend from mid-ocean ridges (Ce/Ce^* about 0.3) towards the continental margins (Ce/Ce^* about 0.9). A study of sediments from the northwestern Pacific Ocean conducted by Bailey (1993) showed that the sediments there were truly detrital and that the detritus was mainly volcanoclastic debris. However, in more limited sedimentary basins the ratios have a limited variation rendering geochemical interpretations.

As regards the marine sediments it is also important to keep control of the provenance of the sedimentary material and therefore, the terrestrial transport of REE to the sea via rivers or through drainage has to be considered. As regards the riverine input of REE into the Baltic Sea detailed studies have been conducted in the past (e.g., Ingri et al. 2000). Recently, Emelyanov et al. (2002) have reported on REE distributions in the different types of bottom sediments of the Baltic. Of interest here is also the recent work by Glasby et al. (2004) studying metal transport into Polish coastal areas.

Relatively few REE data do however exist for the deep basins of the Baltic Sea, especially systematic elemental contents along long sediment cores. In the present paper we report on the REE in short cores from the Bornholm Basin, the Gotland Basin and the North Central Basin, and give also systematic data along a piston core from the Gotland Basin. The data are used to discuss the origin of the REE and these elements' behaviour during changes that occurred over the past ten thousand years.

SETTINGS AND METHODS

Sediments from the Bornholm Basin (BB), The Gotland Basin (GB) and the North Central Basin (NCB) were studied in the present investigation. The deep basins differ markedly in size occupying 1000, 2740 and 170 km^2, respectively, while their maximum water depths are 90, 245 and 230 m, respectively. The sediments of the basins comprise in general post-glacial material. They have sometimes a thin oxidised brownish top but are otherwise grey in colour.

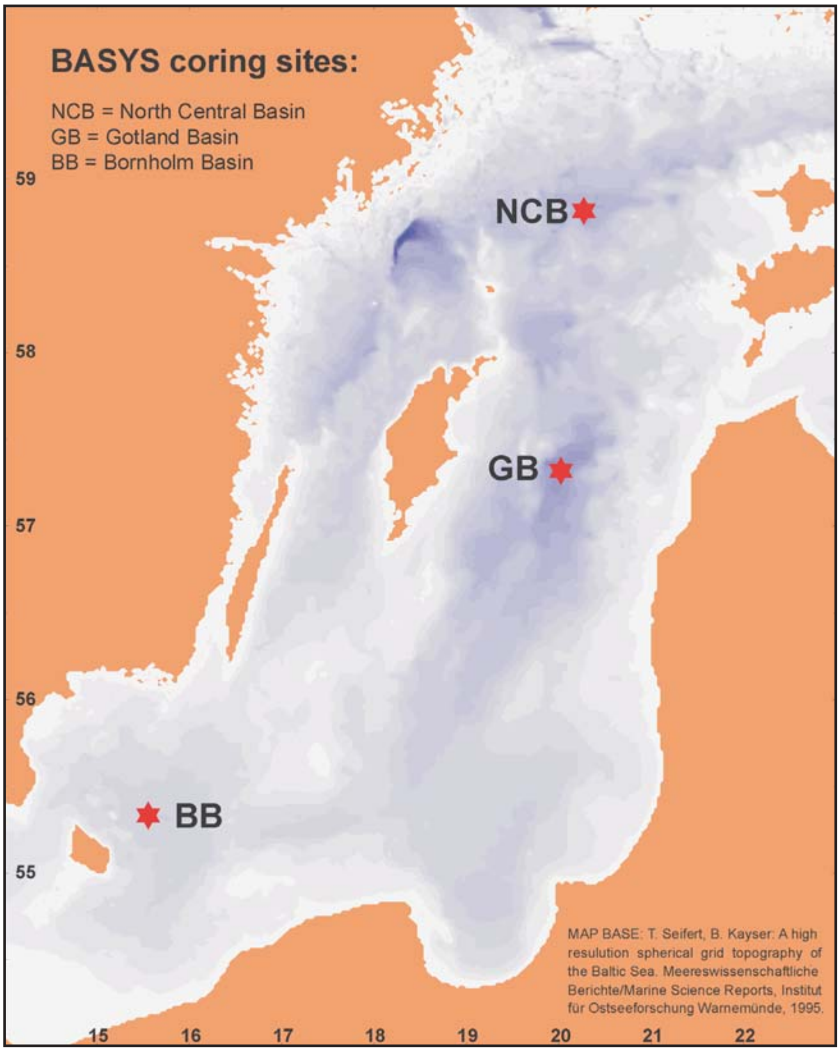

Fig. 1. Position of the three investigated deep basins in the Baltic Sea. After B.Winterhalter, BASYS-7 final report, CD_ROM, 1999.

The basins were sampled during a 3-year European Union Marine Science and Technology project (BASYS) in the late 1990s with cruises by *R/V Aranda* and *R/V Petr Kottsov* (e.g., Winterhalter 2001). The three sampling sites are shown in Fig. 1 and characteristic data on the cores investigated are given in Table 1. Niemistö twin corers were used to take the short (up to 40 cm) cores. They were usually sliced into 1 cm slices onboard ship and frozen for later onshore studies. Long sediment cores were also taken in the central parts of the three deep basins by means of gravity and piston corers. However only one long core from the Gotland Basin (core 211660-2) is included in the discussions on rare earth elements.

In the onshore laboratories, samples were freeze-dried. Chemical analysis was carried out using several independent analytical techniques.

Major elements Al, Ca, Fe, K, Mg, Mn, P and Ti were determined by ICP-AES (Thermo Jarrel Ash Polyscan 61E) after hydrofluoric acid and perchloric acid treatment at the Geological Survey of Finland (Vallius and Kunzendorf 2001), while direct determination without sample digestion was performed for major elements Na, K, Ca, and Fe by instrumental neutron activation (INAA) at the Risø National Laboratory (e.g., Kunzendorf and Sørensen 1989; Kunzendorf et al. 1986).

Twenty-three trace elements and 14 rare earth elements were determined by ICP-AES at the Geological Survey of Finland, while 21 trace and 8 rare earth elements were also determined by INAA.

Age dating of especially long Gotland Basin cores was established by using paleomagnetic measurements calibrated against a master curve from annually laminated lake sediments of Lake Pohjajärvi, Finland, and by ^{14}C AMS dating results (Andrén et al. 2000; Kotilainen et al. 2000).

RESULTS AND DISCUSSION

Short cores

Selected North American Shale composite (NASC; Piper 1974) normalised REE data for 2 short cores from the Bornholm Basin (BBTA98 and B12) are plotted in Fig. 2. The data for core BBTA98 (lower part of Fig. 2) were obtained by INAA and those from B12 by ICP-

Table 1. Sampling station characteristics.

Station	Latitude		Longitude		Water depth (m)	Core no./vessel
Bornholm Basin:						
B12	55°	24.99' N	15°	19.810' E	89	Aranda1999
BBTA98	55°	22.739' N	15°	23.947' E	93	Aranda 1998
Gotland Basin:						
GB	57°	17.0073' N	20°	7.1247' E	241	211660-3, Kottsov
GBT-A	57°	17.00' N	20°	13.42' E	238	Aranda1997
GBT-B	57°	17.01' N	20°	5.72' E	244	Aranda1997
GBT-C	57°	17.0' N	20°	0.14' E	240	Aranda1997
North Central Basin:						
NCBT-A	58°	49.68' N	20°	15.71' E	171	211673-3, Kottsov
NCBT-B	58°	49.1496' N	20°	15.1847' E	175	211670-6, Kottsov
NCBT-C	58°	49.0873' N	20°	13.8466' E	186	211672-2, Kottsov
NCBT-D	59°	48.6092' N	20°	13.0586' E	197	211671-2, Kottsov

AES (upper part). As can be seen, data of two different cores from the same basin obtained by two independent analytical methods show comparable curves. The REE patterns are flat (shale-like) at differing core depths with a slight enrichment of the light REE (LREE; elements La through Gd). Most probably, the relatively low contents in the uppermost sample of core BBTA98 are a reflection of the presence of large amounts of fluffy (suspended) material diluting the sediments and hence the REE contents. Average REE data for the 3 basins and for comparison the North Atlantic Shale composite data are shown in Table 3. Further data on the North Central Basin can be found in Vallius and Leivuori (2001). Obviously, there is little difference to data from other areas.

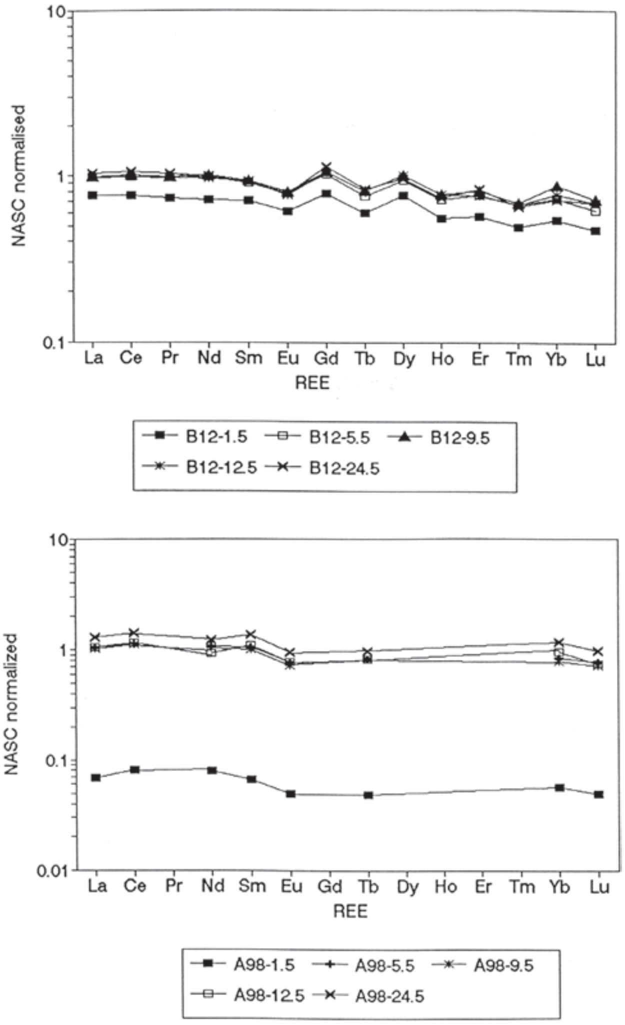

Fig. 2. REE patterns of Bornholm Basin sediments (cores B12, upper figure, and BTA98, lower figure) at various core depths (in cm). Upper part of figure shows data obtained by ICP-MS, lower figure has plotted data obtained by INAA.

Selected chemical data (both major, trace and rare earth elements) from the three deep Baltic basins at two selected depths are given in Table 2. These data show that some element contents are lowest in the uppermost sediment samples (0-1 cm) of the cores and increase with depth, e.g., Al, Fe, K, Ba, Be, Cr, Li, Nb, Rb, Sc, Th, Ti, V and the REE, while others (C, P, As, Cd, Co, Mo, Sb, and Zn) are enriched in the uppermost horizons. As regards the REE, the Gotland Basin sediments show in general lower concentrations than sediments at comparable depths from the other two basins. This is most likely due to the terrestrial/biological input variations observed for the three basins.

A discussion of the REE results of both short and a long core from the Baltic may include the comparison of existing REE data and some work on the behaviour of the REE in the secondary environment in general (Table 3).

Regarding the secondary environment, for instance, a comparison with the REE behaviour in the terrestrial realm represented by studies of the weathering profiles of rare earth elements in till in northern Sweden (Öhlander et al. 1996) showed that there is a strong REE depletion in the uppermost till horizon (E-horizon in the present investigation). It was also shown that the LREE were more depleted than the HREE. This means that REE are actively involved in the weathering processes and they may be fractionated. Morey and Setterholm (1997) showed that the REE are mobilised and fractionated during weathering and that the REE distribution pattern can then be recognised in the sediments. Interestingly, Olmez et al. (1991) had proposed that the REE might be used as a tracer of anthropogenic inputs into the coastal environment because LREE enrichment was observed in offshore sediments close to a wastewater outlet off southern California.

The distribution of La with depth in the three Baltic basins short cores (Fig. 3) clearly shows that there is a decrease of La towards the surface in the cores, the sediment depths of significant decreasing of La being 6 cm in NCBT-B, 5 cm in B12 and about 10 cm in GB. The low REE in these zones could simply be connected with the fluffy material dominating these zones, resulting in a dilution of the REE carrying sediment particles. When the fluffy material is moved by slight bottom currents, the heavier REE bearing particles remain and

Table 2. Element contents at selected depths for the three deep basins (short cores). All data in mg/kg if not stated otherwise.

	B12			GB			NCBT-A		
Depth (cm)	0,5	9,5	24,5	0,5	8,5	24,5	0,5	9,5	24,5
Al (g/kg)	48,7	71,8	72,4	30,6	26,8	68,7	42,4	81,6	81,5
Ca (g/kg)	7,99	7,39	7,85	8,3	17	11,1	8,44	8,03	7,67
Fe (g/kg)	36,4	44,6	54	31,1	47,5	42,4	33,5	50,5	50,5
K (g/kg)	20,1	25	24,5	14,9	11,2	23,1	18,3	29,1	28,7
C (g/kg)	6,2	5,4	3,2	9,7	8,6	3,8	9,9	1,4	2,1
P	1990	1430	1320	1590	1880	1110	2150	1030	915
S	7100	4060	3900	-	-	-	-	-	-
N (g/kg)	0,8	0,7	0,5	1,4	1,2	0,4	1,3	0,3	0,4
As	15,2	13,5	9,03	8,74	9,63	6,39	8,88	9,25	8,28
Ba	338	426	394	316	502	542	426	575	668
Be	1,98	2,65	2,51	1,22	1,12	3,01	1,48	2,76	3,17
Bi	0,37	0,6	0,41	0,3	0,48	0,45	0,29	0,57	0,43
Cd	1,09	1,1	0,3	6,97	10,2	1,01	3,42	0,89	0,21
Co	21,5	19,8	17,3	20,1	36,4	19	19,3	21,3	21,3
Cr	56,4	76,4	69,4	37,6	43,7	84,4	52,3	99,6	105
Cu	38,5	51,2	36,2	99,3	131	45,1	46,6	46,8	40,6
Li	35,9	46,8	44,2	24,1	21,8	59,9	31	62,7	66,2
Mn	13100	2240	1570	276	45500	19500	728	933	815
Mo	16,6	8,25	4,35	104	145	29,9	32,3	4,46	7,15
Nb	6,48	9,01	9,56	4,01	3,67	10,4	6,94	14,6	13,7
Ni	38,7	48	42,2	72,9	107	53,7	69,3	51,5	52,2
Pb	56,7	93,1	57,2	45,6	98,3	52,5	36,7	44,3	31,7
Rb	98,2	134	128	62,1	53,9	156	88,9	186	193
Sb	3,1	3,46	1,42	7,68	11,1	1,95	9,25	1,39	0,68
Sc	9,37	12,8	13,9	6,08	5,26	14,4	8,78	18,1	17,7
Sr	147	120	111	129	167	139	131	129	138
Th	8,79	12,3	12	5,54	4,85	13,8	7,69	17,6	17,5
Ti	1760	2460	2760	1040	974	2730	1820	3870	3700
Tl	0,76	0,9	0,7	1,85	2,95	0,94	0,92	1,11	1,13
U	3,92	4,94	3,78	12,2	14,9	5,19	6,07	6,43	5,63
V	94,3	123	106	85,5	98,6	124	120	131	130
Y	19	27,2	28,3	12,9	13,4	24,7	18,1	32,5	30,7
Zn	167	234	125	448	634	159	374	199	147
La	29	40,6	42,3	18,6	17,9	41,6	29,1	57,4	53,7
Ce	58,7	83,8	87,7	36,5	34,2	84,5	55,7	116	112
Pr	7,04	10	10,4	4,53	4,16	9,9	6,59	13,4	12,9
Nd	27	38,6	37,8	16,4	16,6	36,2	25,2	50,7	46,5
Sm	4,85	7,04	6,82	3,29	3,39	7,29	4,83	9,52	9,41
Eu	0,92	1,29	1,25	0,56	0,69	1,27	0,87	1,56	1,5
Gd	4,63	6,7	7,22	3,14	3,04	6,11	4,53	8,59	8,01
Tb	0,72	1	1,02	0,49	0,45	1,05	0,62	1,23	1,19
Dy	3,78	5,53	5,26	2,26	2,5	5,06	3,3	6,35	6,06
Ho	0,73	1,03	0,99	0,46	0,47	0,92	0,68	1,31	1,18
Er	2,07	3,03	3,09	1,51	1,4	2,99	1,96	3,78	3,38
Tm	0,28	0,43	0,41	0,21	0,19	0,37	0,29	0,51	0,49
Yb	1,97	3,08	2,55	1,29	1,15	2,41	1,57	3,22	2,94
Lu	0,29	0,44	0,42	0,2	0,14	0,39	0,27	0,48	0,44

Table 3. Comparison of average REE contents from this study with literature data. NASC from Piper (1974).

Element	Bothnian Bay	Barents Sea	Bornholm Basin B12	Gotland Basin GB	North C. Basin NCBTA	NASC
La	41.0	34.5	39.2	23.3	40.9	41.0
Ce	87.0	68.4	80.5	47.8	78.1	83.0
Nd	41.2	34.5	34.9	21.1	34.9	38.0
Sm	7.48	6.91	6.79	4.21	6.4	7.5
Eu	1.45	1.45	1.21	0.68		1.61
Gd	6.46	4.78	6.21	3.89	6.49	6.35
Dy	5.95	4.32	5.46	2.95	4.29	5.5
Ho	1.21	0.82	0.97	0.53	0.9	1.34
Er	3.43	2.37	2.67	1.71	2.75	3.75
Yb	3.07	1.97	2.66	1.41	2.34	3.53
Lu	0.49	0.31	0.36	0.23	0.4	0.61

normal sedimentation progresses. This would however not create the graduate downward increase of REE as observed in Fig 3. REE in these surface zones may therefore also be leached after deposition. In this case, they would then possibly be transported in solution or with the particular load coprecipitated or attached to biogenic matter or ferromanganese oxyhydroxides. Interestingly, the decrease of REE is continuous, i.e. depending on the water volume available in the sediments. This means that only loosely compacted sediments are involved in the leaching process while there is little further removal of REE in the more compacted sediments.

Our findings do not compare with the study of Szefer et al. (1999) who found in sediments from the Vistula Lagoon, Poland, only small depletions of HREE. Because both Ce and Eu anomalies were absent the authors concluded that redox processes are not modifying the REE patterns in these coastal sediments.

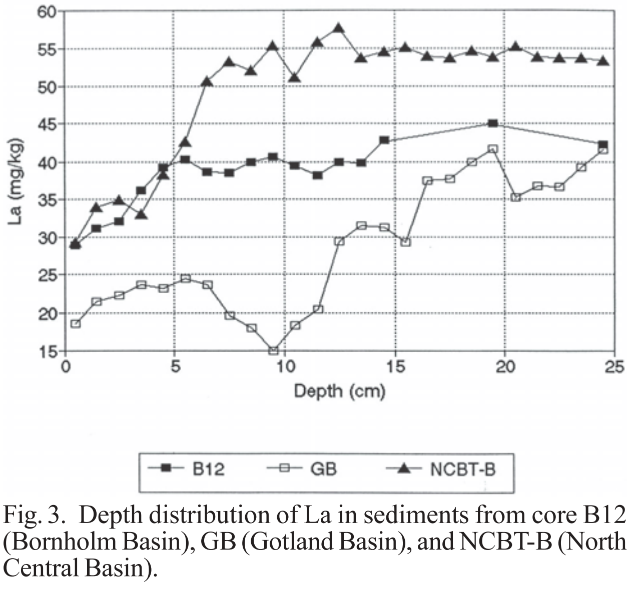

Fig. 3. Depth distribution of La in sediments from core B12 (Bornholm Basin), GB (Gotland Basin), and NCBT-B (North Central Basin).

To understand the REE patterns observed in marine sediments REE carriers to the Sea may be studied. Detailed work is available on this aspect. Ingri et al. (2000) in studying weekly sampled filtered and particulate phases over a period of 18 months in the Kalix River in northern Sweden observed that there is a seasonal variation of the Ce anomaly of the suspended particular phase being caused by enhanced transport from till areas to the river mouth during especially storm events. A slightly LREE enriched pattern was also found for the colloidal fraction while the solution fraction was HREE enriched. By studying the dissolved and suspended matter concentrations of Al, Ba, Fe, Mn, Si, P and Ti in subsurface waters from the Baltic Proper, the Belt Sea- Kattegat area and the Åland Sea it was found that about 20% of the total Al, Fe and Mn, 75% of total Si and 99% of total Ba passed the 0.45 µm filter and that the suspended phase then could be divided into a detrital, a Mn-rich and an organic phase (Ingri et al. 1991).

Similarly, Gustafsson et al. (2000) investigated the particle aggregation processes occurring during the transport from the Kalix River in northern Sweden to the Bothnian Bay. They found a significant aggregation occurred in the low-salinity zone of the Bothnian Bay having impact also on the REE behaviour in the sediments. As regards the REE transport by rivers the study by Tricca et al. (1999) also showed that there is a difference in REE patterns of the dissolved load depending on the physical characters of the rivers. Their study of small rivers (mountain rivers) of the Vosges (France) running to the Rhine river (example of a plain river) suggested that the plain rivers have generally a Ce anomaly and they are also HREE enriched. The same was found for ground waters while the mountainous rivers have a slight enrichment of the middle REE and often also have a Eu anomaly. The REE patterns of the dissolved are quite different to those observed in the suspended load.

Being aware of the problem of correct sampling and analysis of suspended matter, Boström et al. (1981) conducted a thorough investigation of 30 different stations from the entire Baltic Sea. The sampling of the suspended matter was both at the thermocline and near the sea floor. The authors reported the suspended material to be biological matter (75-88%), terrigenous material (12-25%) and some manganese oxyhydroxides. As regards the studied trace elements they found the biogenic phase to be dominated by Ni, V and Ba while the detritus contained much Si, Al, Ti and Fe. In general they predicted that the suspended matter removes much of Mn, Ba, Ni and V from the Baltic Sea. In this respect, the REE patterns observed in the investigated short cores most likely display those of the terrigenous load to the Baltic superimposed by aggregate input of biological origin leading to more or less dilution of the REE contents.

The study by Ingri and Pontér (1987) on ferromanganese nodules from the Gulf of Bothnia and the Barents Sea includes also data on the underlying sediments. For two sediment samples studied the Barents Sea sediment shows a slight depletion of the HREE. Interestingly, these authors documented that the REE in manganese nodules from the Gulf of Bothnia show that Ce may be depleted in nodules close or directly at the redox boundary while nodules growing above the boundary showed a positive Ce anomaly. Their investigation leads to the result that the REE in the nodules are positively correlated with Mn and not with Fe and P as found in other ocean areas (e.g., Elderfield et al. 1981).

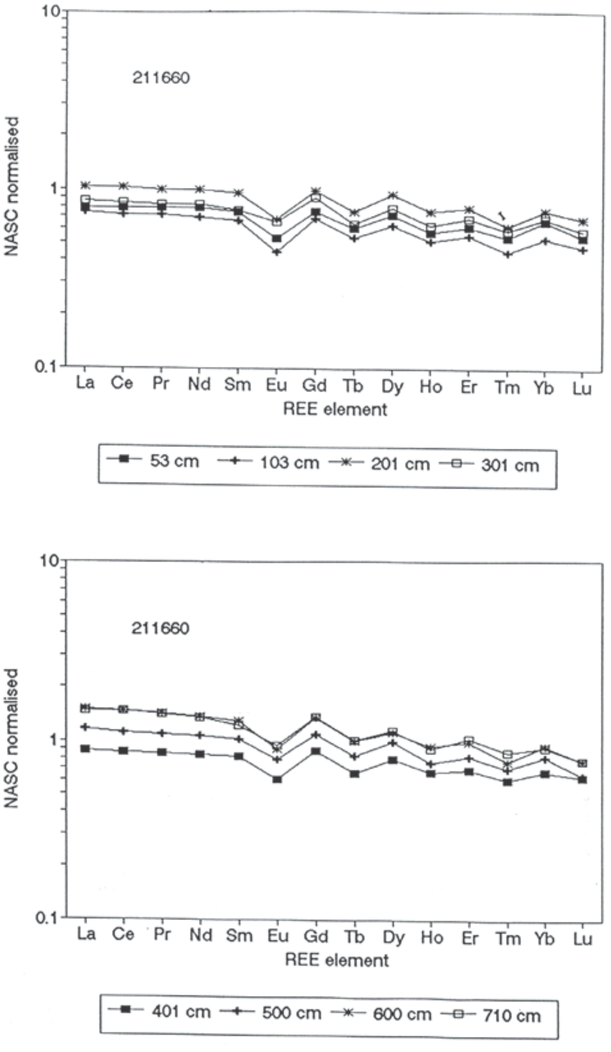

Fig. 4. REE patterns at selected depths along a more than 7 m long core from the Gotland Basin (core 211660).

However, because the data in Fig. 3 suggest a significant REE depletion in the uppermost sediments, it is assumed that the removal is most likely with Fe-Mn particular matter. Mn-Fe oxyhydroxides are created in the uppermost sediments from remobilised Mn-Fe at sediment depths and a coprecipitation of REE in solution occurs at the same time. These Mn-Fe particles are then also involved in the growth of ferromanganese phases at the redox boundaries of Baltic deep basins. A scavenging of REE onto these phases may then occur.

Long Gotland Basin core

Selected REE patterns for samples taken at greater depths for the long Gotland Basin sediment core (211660-2) are plotted in Fig. 4. It appears that the REE patterns do not change significantly with depth suggesting no significant change in provenance during the entire Holocene. However, there is a slight variation in REE contents with sediment depth, in that the highest contents being observed at the bottom of the core (normalised values above 1 at depths > 5 m). All the samples show a slightly negative Eu anomaly, which is the signal Scandinavian terrestrial matter, has left.

Considering all the major element data of the long piston core (not tabulated) it appears that the REE correlate with Al, K, Mg and Ti, i.e. a terrestrial origin (clay) is displayed. However, there is no clear correlation of the rare earths with Fe, which often is observed when ferromanganese phases are present in the sediments. This means that there is little ferromanganese material present and that the low REE contents are a reflection of this.

Selected REE data for the long core (211660-1) are plotted in Figs. 5 and 6. Viewing the bulk La data a significant decrease of contents between 600 and 450 cm is displayed (Fig. 5). However, because there is a good correlation between La and Al the REE data are supposed to depend largely on the clay content in the sediments. The distribution of Al with depth shows an increase of Al from about 6.5% to about 9% between 450 and 600 cm depth, i.e. in the beginning of late Yoldia Sea times (600 cm depth) clay contribution to the sediments started to decrease and continued to do so during Ancylus Lake times (540 to 450 cm). Al contents of the sediments deposited during Litorina Sea and Recent times are characterised by more varying Al

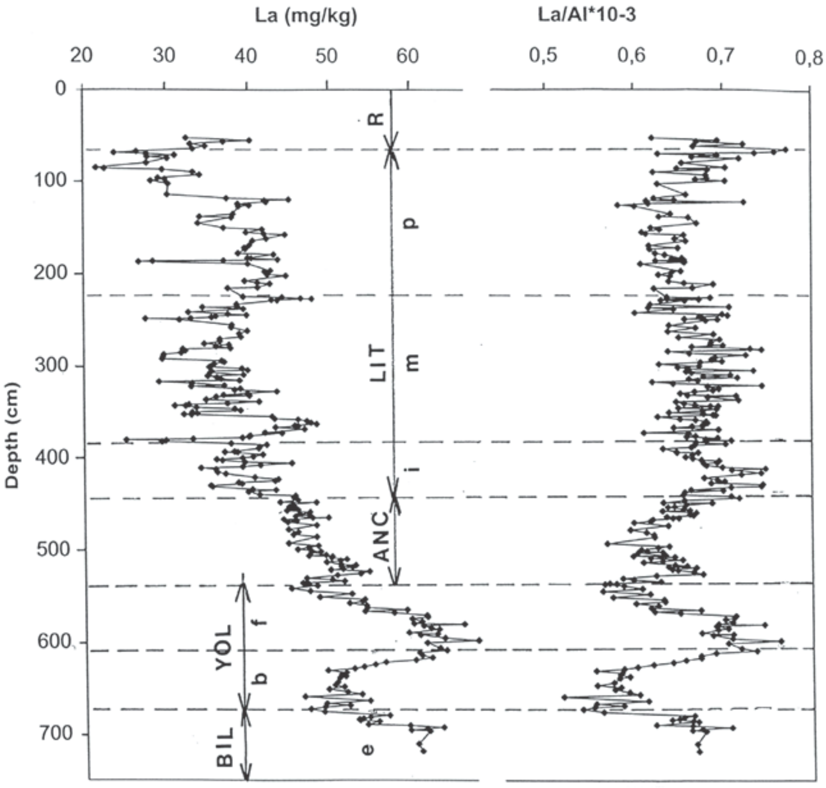

Fig. 5. La and La/Al distributions along the long core from the Gotland Basin. Stippled lines divide the core into geological stages. BIL= Baltic Ice Lake, YOL= Yoldia stage (b=brackish, f=freshwater), ANC= Ancylus Lake stage, LIT= Litorina Sea stage (i= initial, m=middle, p= post), R= Recent.

contents. In figures 5 and 6, stippled lines are chronological borders deduced from the dating given by Andrén et al. (2000). The onset of the Litorina Sea stage (about 450 cm core depth) which can clearly be determined from the Ca data of the core (not plotted, see Kunzendorf et al. 2001) in that Ca increases suddenly at this depth and stays high during the whole Litorina and the present Baltic Sea sediments are therefore also flagged by the onset of lower Al. The cause for Ca increase in Litorina Sea sediments is that seawater contains dissolved Ca being precipitated at varying salinities (e.g. Christiansen et al. 1995). It is seen in Fig. 5 that mainly during the fresh water period of the Yoldia Sea stage the REE contents in the sediments decrease significantly (600 to 550 cm core depth), while they increase during its more brackish period (depths 650 to 600 cm). A significant increase of the REE is also observed from the middle of the Ancylus Lake period to the initial Litorina Sea period, while the

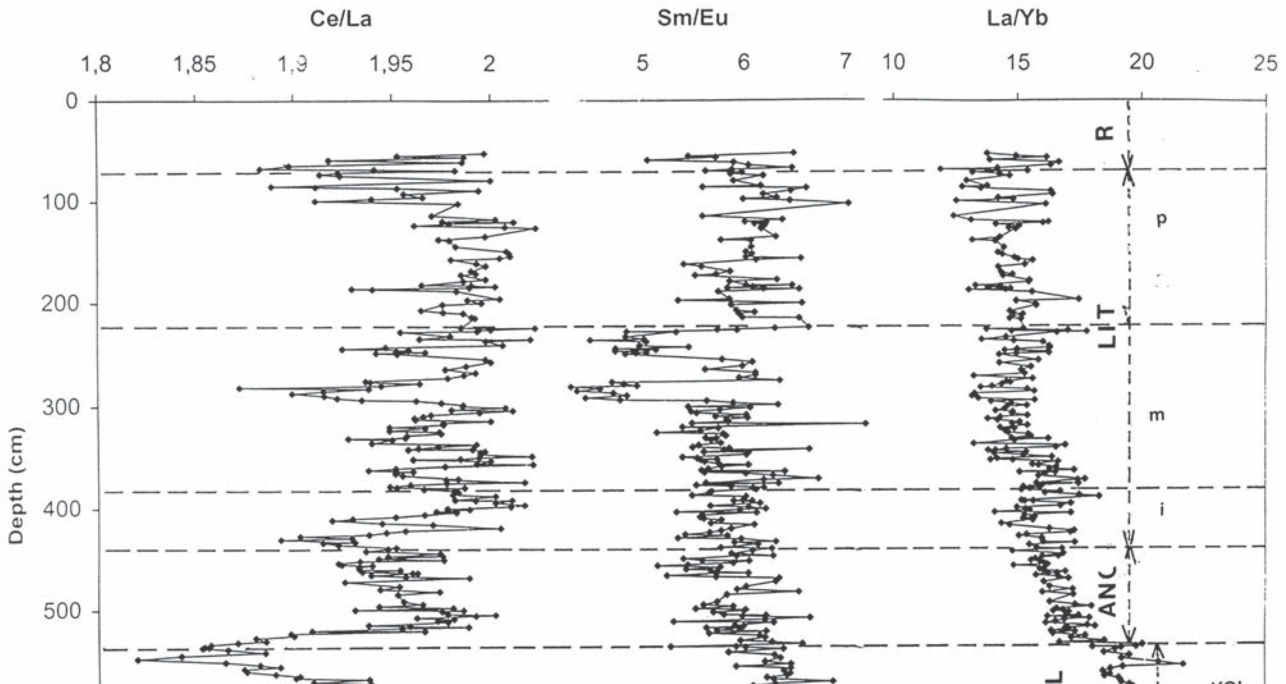

Fig. 6. Ce/La, Sm/Eu and La/Yb distributions along the long sediment core from the Gotland Basin. For abbreviations see Fig. 5.

Table 4. Ecostratigraphic summary of the long core from the Gotland Basin according to Brenner (2001).

Depth (cm)	Ecostratigraphic interval	Characteristic microfossil	Stage
0 -100	IX	Few, good preserved organic walled microfossils; anoxic conditions	Baltic Ice Lake
100-215	VIII		
215-240	VII		
240-315	VI		
315-375	V	Increase marine dinoflagelates	Litorina Sea
375-460	IV	Increasing marine dinoflagelate cysts; continuous increase of salinity	Litorina Sea
460-485	III	High cladoceran remains; high carbon; eutrophication?	Ancylus Lake
485-640	II	Freshwater dinoflagelate *Gonyaulax apiculata* max. on top; nutrient increase	Yoldia Sea to Ancylus Lake
640-	I	Few, good preserved organic walled microfossils; anoxic conditions	Baltic Ice Lake to Yoldia Sea

normalised (to Al) values stay rather constant during most of the Litorina and Recent times.

As regards REE ratios (Fig. 6) there is little variation of Ce/La over the entire Litorina Sea stage and the Ancylus Lake stage but there is a significant gradual decrease of this ratio from the Baltic Ice Lake towards the end of the Yoldia Sea stage. Such a decrease can only be explained by changes in redox conditions. Perhaps with increased oxic conditions preferentially Ce was removed from the sediments towards the end of the Yoldia Sea stage. Similar minima in the Ce/La curve of the long sediment core are also observed at the end of the Ancylus Lake/beginning of the Litorina stages, in the middle of the major and the end of the Litorina Sea stage.

It seems also as if there is a fractionation of the light (La to Eu) compared to the heavy (Gd to Lu) REE because the ratio La/Yb decreases from about 20 at the end of the Yoldia Sea stage to about 15 at the end of the Litorina Sea stage. Likewise is there some irregularity of the Sm/Eu ratio at the end of the major Litorina Sea stage, which may be explained by enhanced transport of terrestrial material from the Scandinavian mainland during respective times.

Microfossil records may be introduced to view the sediment deposition periods and the depositional conditions existing at those times in the Baltic (Table 4). According to Hofmann (2001) the occurrences of *Bosmina longispina, Bosmina longirostris* and *Daphnia* sp. suggest that the sediments between 445 and 691 cm depth (Baltic Ice Lake, Yoldia Sea and Ancylus Lake stages) of another Gotland Basin core (211660-6) were deposited under freshwater conditions. The shift from cladoceran (freshwater) to foraminifers (marine/brackish) determines the transition Ancylus Lake – Litorina Sea. It is found in this core at a depth of ca. 440 cm corresponding to 7200 years BP. There is a significant occurrence of foraminifers from 445 cm upwards until about 64 cm core depth and this is ascribed a saline sediment deposition environment. The Yoldia Sea stage is thought to have slightly brackish water dominance (e.g. Brenner, 2001) because of the presence of only few specimen of *Operculodinium cetrocarpum* in the long Gotland Basin core at depth. These authors also report that it is difficult to observe a difference in amount of organic-walled microfossils at the transition Yoldia Sea/Ancylus Lake stage. Interestingly, however, is the continuously decreasing Ce/La ratio during the Yoldia Sea stage with a minimum at the transition to the Ancylus Lake stage. A redox change from anoxic to more oxic during the entire Yoldia Sea stage could be invoked here resulting in a decreasing precipitation of CeO_2. At the transition to the Ancylus Lake stage and over a short period of time, oxic conditions may have lead again to a Ce/La ratio in the sediments exceeding a value of 1.95 over a relative short time span. Because the number of organic-walled microfossils observed during this stage is very low it was suggested by Brenner (2001), that this could be due to high sedimentation and/or anoxic conditions during sedimentation. At the transition of the Ancylus Lake stage with the Litorina Sea stage the Ce/La ratio is again decreased, to about 1.87, but it then increases again upwards. According to Brenner (2001) the increase of the ratio goes along with an increase of dinoflagellate cysts and because *O. centrocarpum* process lengths are increased, an increasing salinity during these times is indicated.

A further decrease in the Ce/La ratio is observed between 300 and 280 cm depth, corresponding to the middle part of ecostratigraphy zone VI (Brenner 2001).

Comparing the Ce/La ratio observed with the ecostratigraphy presented by Brenner (2001) it appears that clear changes appear in ecozones 2, 4 and 6. If we assume that low Ce/La ratios in sediments are the result of anoxicity in the depositional system, the drop of the ratio in ecozone 2 from about 1.98 to about 1.83 may be an expression of increasing freshwater supply. In this respect the lowest Ce/La ratios in the central part of ecozone 2 flag the change of Yoldia Sea sediments to Ancylus Lake sediments. Wit increasing freshwater supply the Ce/La ratio increases then and stays relatively constant at about 1.97 during Ancylus Lake times. With a continuous increase of salinity during the initial Litorina Sea stage Ce/La ratios increase further but stay relatively constant at about 1.99.

In general, sediment lamination is taken as an expression of anoxic conditions with only bacteria being able to survive. Contrary to this non-laminated sediments are then thought to be deposited under more oxic conditions. At present, about one third of the Baltic seafloor area is covered by laminated sediments (Jonsson et al. 1990). Zeaxanthin is a typical cyanobacterial pigment and may be used as a tracer in sediment studies. Cyanobacteria are characterised by a nitrogen isotope ratio of 0 per mil while other phytoplankton has a ratio of 4-5 per mil.

CONCLUSIONS

The REE in Baltic Sea sediments are mostly contained in the terrigenous phase of the sediments and this explains why there are higher REE contents in the Bornholm Basin and North Central Basin sediments, which are closer to the main land.

The REE patterns observed are flat with a slight enrichment of the LREE. These patterns do change very little with depth in the long core from the Gotland Basin.

Decreased REE in the uppermost samples of the short cores for all three basins suggest that the REE in the Baltic are opposed to processes that decrease or enrich elemental contents in sediments.

There are significant variations of the REE with depth in a long sediment core from the Gotland Basin. REE contents were especially high (La > 60 mg/kg) during Baltic Ice Lake and middle Yoldia Sea stages, with a continuous upwards decrease of REE. However, most of the REE contents may be explained by clay contents because of the good correlation between REE and Al.

Prominent REE ratios flag probably environmental changes during the sedimentation history of the long core. Most pronounced is a decrease of the Ce/La ratio from 2 to 1.8 between 700 and 540 cm depth which can only be explained by redox processes where an increased availability of oxygen will remove Ce from the REE series in the form of CeO_2.

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