



Distribution of REEs in box-core sediments offshore an industrial area in SE Sicily, Ionian Sea: Evidence of anomalous sedimentary inputs

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ABSTRACT

The distribution of rare earth elements and yttrium (REEs + Y) has been investigated in box-core sediments recovered from four stations in the Sicilian coastal zone seawards of Augusta, one of the most industrialized and contaminated areas in the Mediterranean region. Shale-like REE patterns and low Y/Ho ratios (close to the chondritic ratio) suggest a dominant terrigenous (geogenic) source for REE. Slight enrichment of LREE over the HREE is interpreted as due to preferential adsorptive transfer of LREE from seawater to sediment particles. Samples from offshore cores exhibit slightly positive Gd and negative Ce anomalies. It is here hypothesized that main drivers of anthropogenic Gd flux towards the offshore are dredged contaminated materials that, recovered from the Augusta Bay, have been repeatedly discharged offshore. Consistent with the redox-chemistry of Ce, these anomalous sedimentary inputs induce a decrease of O₂ concentration in the sediment, which in turn triggers Ce regeneration.

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1. Introduction

The stable rare earth elements (REEs), from La to Lu, and Y behave as an unusually coherent group of elements, exhibiting limited mobility and fractionation during most geologic processes (McLennan, 1991; Rolinson, 1993). Despite partitioning related to specific geochemical conditions produces Eu²⁺ and Ce⁴⁺, the REEs are generally trivalent under a wide range of oxygen fugacity, show small differences in chemical and physical properties and exhibit a systematic decrease in ionic radius (Byrne and Kim, 1993; Byrne et al., 1996; Johannesson et al., 1999 among others). Consequently, the REEs have been widely used as geochemical tracers in a variety of processes involving cosmo-chemistry, igneous petrology, tectonic setting (Hanson, 1980; Henderson, 1984; Taylor and McLennan, 1985) and for investigations of water–rock interaction and weathering processes including transport of weathering products to the oceans (e.g., Nesbitt, 1979; Sholkovitz, 1995; Byrne and Liu, 1998; Sholkovitz et al., 1999; Sholkovitz and Szymczak, 2000; Leybourne et al., 2006). Previous studies of REE geochemistry in marine systems have shown that the REE distribution can be a useful tool for clarifying depositional and diagenetic processes (Cullers et al., 1987; McLennan, 1991; Bellanca et al., 1997; Piper et al., 2007).

Recent work has addressed the use of REEs in investigating the environmental impact of human activity and demonstrated that the REE natural distribution in water, soil, and sediment from densely industrialised and populated regions can be altered by anthropogenic influences (Bau and Dulski, 1996a; Fuganti et al., 1996; Nozaki et al., 2000a; Elbaz-Poulichet et al., 2002; Oliveira et al., 2003; Kulaksiz and Bau, 2007; Rabiet et al., 2009). Many of these investigations have explored REE patterns in estuarine zone and lagoonal systems (Szefer et al., 1999; Nozaki et al., 2000b; Borrego et al., 2004), whereas relatively few studies have focused REE records in terms of environmental markers in coastal marine sediments (Yusof et al., 2001). In particular, minor attention has been centred on REE composition of offshore sediments, although the environment quality in deeper water regions is a major concern, especially in a semi-enclosed basin such as the Mediterranean Sea.

The Augusta area (Fig. 1) along the Ionian Sea coast (SE Sicily) has been recognized to be a site of high environmental risk by the World Health Organization (Martuzzi et al., 2002) and Italian Government (GURI, L. 426/1998). Here, the combination of industrial, agricultural and urban effluents, as well as dry and wet deposition, plays a determining role on the evolutionary process of chemical characteristics in the Augusta marine system. Since 1950s, electric power generation and chlor-alkali plants, fertilizer, magnesite, and cement factories, oil refineries, and sewage disposal have been established along the Augusta Bay, that is also the location of Sicily's major port. The effects of the most recent industrial activities are recorded in coastal and offshore sediments

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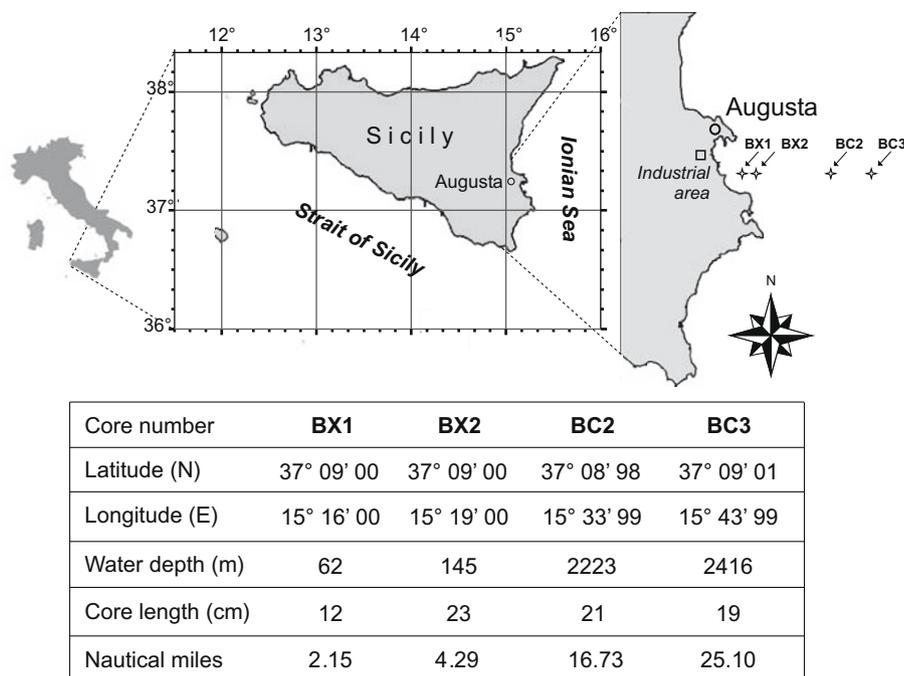


Fig. 1. Location of sampling stations in the Augusta area together with core length, water depth and geographic parameters at each station (modified after Di Leonardo et al., 2008).

for which Di Leonardo et al. (2007, 2008) documented high contaminant levels, especially Hg ($0.02\text{--}1.67\ \mu\text{g g}^{-1}$), and a significant impact on benthic foraminiferal communities.

This paper presents REE and Y concentrations of four sediment cores collected along a transect coast–offshore in front of the Augusta industrial area (Fig. 1). These data are used in conjunction with other geochemical tracers (major and trace elements, Total Organic Carbon) to identify the origin of REE anomalies and to evaluate the potential impact of the REE input on coastal to offshore marine sediments. The importance of previous documentation is that the REE behaviour can be analyzed in a well-defined sedimentary and environmental context.

2. Materials and methods

Four box-cores were collected, using a United States Geological Survey (USGS)-modified Naval Electronics Laboratory (NEL) box-corer sampler, in the Sicilian coastal zone seawards of the industrial area of Augusta (Fig. 1). Sampling was carried out during two oceanographic cruises on board the oceanographic R/V “URANIA”, in the summers of 2003 and 2004, along a west–east transect. Sediments were immediately sub-sampled on board using an acrylic tube, sealed in polyethylene flasks, and stored at $-20\ ^\circ\text{C}$ until analysis. On return to the laboratory, the cores have been sliced at 1 cm intervals with a stainless steel bandsaw, oven dried at $40\ ^\circ\text{C}$, and powdered manually in an agate mortar prior to geochemical analyses.

REE analyses have been performed on 47 selected samples by inductively coupled plasma-mass spectrometry (Perkin Elmer Elan 6000), after digesting 0.5 g of sediment with a mixture of hydrofluoric, nitric, and perchloric acids. Certified reference materials (GXR-1, GXR-2, GXR-4, GXR-6) have been used for quality control. Detection limits are $0.05\ \mu\text{g g}^{-1}$ for Eu and $0.1\ \mu\text{g g}^{-1}$ for other REE and Y.

REEs concentrations are normalized to the average of North American, European and Russian shale composites adopted in previous studies (Piper, 1974; Gromet et al., 1984; De Baar et al., 1985;

Sholkovitz, 1988; Murray et al., 1991). Y concentrations are normalized to North American Shale Composite (NASC). The Ce and Gd anomalies are defined by $\text{Ce}/\text{Ce}^* = 2(\text{Ce}_n)/(\text{La}_n + \text{Pr}_n)$ and $\text{Gd}/\text{Gd}^* = \text{Gd}_n/(0.33 \text{Sm}_n + 0.67 \text{Tb}_n)$, respectively. Ce^* and Gd^* are the expected Ce and Gd values from the linear smooth trend across the lanthanide series and the subscript “n” represents shale-normalized REEs. Negative or positive anomalies are defined as Ce/Ce^* or Gd/Gd^* smaller or greater than 1, respectively.

Bulk mineralogy of the box-cores from the Augusta area is documented by Di Leonardo et al. (2008). The coastal core BX1 contains aluminosilicates and quartz associated to biogenic carbonate, which becomes more abundant in the shallower sediments; in the sites BX2, BC2 and BC3 dominant phases are aluminosilicates and quartz. Cores BX1 and BX2 have been previously dated using ^{210}Pb and ^{137}Cs specific activities (Di Leonardo et al., 2007); the bottom sediments at the two sites are approximately 45 years old. Although ^{210}Pb activities measured for cores BC2 and BC3 do not permit the estimation of a net sediment accumulation rate, their patterns have been interpreted as indicative of a rapid accumulation rate due to variations in sediment source/composition (Di Leonardo et al., 2008).

3. Results

Total REE + Y concentrations of the Augusta sediments range from 107 to $271\ \mu\text{g g}^{-1}$, showing lower values in the coastal station BX1 and higher and more variable values in the offshore cores BC2 and BC3 (Table 1). Shale-normalized REE abundances decrease systematically from La to Lu with slightly positive Gd anomalies (Fig. 2). The REE patterns of Augusta sediments are quite similar to that of the Atlantic Ocean carbonate terrigenous mud (re. Fig. 2). Variations in behaviour across the REE series are indicated by the degree of light rare earth elements (LREE) enrichment with respect to heavy rare earth elements (HREE), here defined as the ratio of $\text{La}_n/\text{Yb}_n = (\text{La}_{\text{sample}}/\text{La}_{\text{shale}})/(\text{Yb}_{\text{sample}}/\text{Yb}_{\text{shale}})$. The La_n/Yb_n ratios exhibit mean values of 1.7 for cores BX1 and BX2, 1.9 for BC2 and 2.0 at site BC3, consistent with the enrichment of LREE over

Table 1
REE + Y concentrations ($\mu\text{g g}^{-1}$) and shale-normalized REE index ratios of the box-cores from the Augusta area.

	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	REE + Y	LREE/HREE	La _n /Yb _n	La _{ex}	Y/Ho
<i>Box-core BX1</i>																					
BX1 0–1	0.5	25.5	40.0	5.8	22.9	3.9	1.0	4.4	0.5	2.6	17.3	0.6	1.5	0.2	1.4	0.2	127.7	8.7	1.6	15.7	57.2
BX1 1–2	1.5	29.6	48.1	6.9	24.6	4.1	1.1	3.9	0.5	2.8	19.0	0.7	1.5	0.2	1.5	0.2	144.7	10.1	1.7	12.2	53.3
BX1 2–3	2.5	22.6	42.1	5.5	20.4	4.1	0.9	4.1	0.5	2.9	15.7	0.6	1.6	0.112	1.2	0.1	122.4	8.6	1.6	13.5	52.6
BX1 3–4	3.5	29.5	62.1	8.0	26.7	5.6	1.4	4.8	0.9	3.6	19.7	0.7	2.2	0.3	1.6	0.3	167.4	9.2	1.6	16.3	54.9
BX1 4–5	4.5	31.4	60.1	7.1	24.5	4.4	1.0	3.9	0.5	3.1	16.9	0.6	1.8	0.3	1.5	0.2	157.3	10.8	1.8	11.4	56.0
BX1 6–7	6.5	31.4	63.4	6.9	26.8	5.2	1.1	5.0	0.7	3.0	15.7	0.7	2.0	0.3	1.7	0.3	164.2	9.8	1.6	16.8	45.0
BX1 7–8	7.5	25.3	49.9	6.1	22.2	4.2	0.9	3.7	0.5	2.9	14.1	0.6	1.5	0.2	1.2	0.1	133.3	10.1	1.8	12.0	47.9
BX1 8–9	8.5	23.3	46.6	5.7	20.7	4.0	0.9	3.6	0.5	2.7	13.7	0.5	1.5	0.2	1.1	0.1	125.1	10.0	1.8	11.2	56.4
BX1 9–10	9.5	31.4	68.4	8.0	27.2	5.9	1.4	4.7	0.9	3.6	17.6	0.7	2.1	0.3	1.7	0.3	174.2	10.0	1.6	16.6	49.8
BX1 10–11	10.5	26.9	53.4	6.6	23.6	4.7	1.0	4.5	0.6	3.2	17.5	0.6	1.6	0.2	1.3	0.2	145.9	9.5	1.8	13.1	57.8
BX1 11–12	11.5	30.4	55.8	6.4	26.6	4.8	1.0	4.7	0.6	2.7	14.8	0.7	1.8	0.2	1.6	0.2	152.3	10.0	1.6	16.5	42.9
<i>Box-core BX2</i>																					
BX2 1–2	1.5	42.4	74.0	9.8	36.1	5.7	1.5	6.4	0.7	3.9	23.8	0.9	2.1	0.5	2.2	0.3	210.3	9.9	1.6	13.1	50.5
BX2 3–4	3.5	37.3	76.5	9.1	32.4	6.2	1.3	6.0	0.7	4.2	21.0	0.8	2.3	0.3	1.8	0.2	200.1	10.0	1.8	13.9	50.8
BX2 4–5	4.5	45.6	83.2	9.7	39.4	6.6	1.5	7.7	1.0	3.9	22.2	1.0	2.6	0.5	2.5	0.3	227.6	9.6	1.6	21.0	42.7
BX2 6–7	6.5	44.8	82.3	11.0	38.2	6.2	1.7	7.4	0.9	4.4	24.0	1.0	2.4	0.5	2.4	0.3	229.4	9.6	1.6	13.0	49.2
BX2 7–8	7.5	37.1	76.2	9.2	32.3	6.3	1.3	6.4	0.7	4.3	21.3	0.8	2.3	0.3	1.9	0.2	201.5	9.6	1.7	10.4	53.3
BX2 9–10	9.5	36.9	76.3	9.0	32.0	6.1	1.3	6.1	0.7	4.3	21.3	0.9	2.2	0.3	1.9	0.2	199.6	9.7	1.7	10.5	45.8
BX2 10–11	10.5	32.7	68.9	8.4	29.6	5.8	1.2	5.8	0.7	4.1	18.9	0.8	2.2	0.3	1.7	0.2	181.4	9.2	1.6	11.3	46.4
BX2 11–12	11.5	29.1	63.0	7.6	27.8	5.3	1.1	5.2	0.7	3.7	16.9	0.7	2.0	0.3	1.5	0.2	165.1	9.3	1.7	10.7	48.0
BX2 13–14	13.5	48.2	87.4	10.6	40.9	6.7	1.6	8.0	1.0	4.3	24.2	1.0	2.5	0.5	2.5	0.4	239.7	9.7	1.6	18.4	46.2
BX2 15–16	15.5	39.5	80.9	9.6	33.9	6.4	1.4	6.9	0.9	4.4	21.9	0.9	2.4	0.3	1.9	0.2	211.3	9.6	1.8	11.0	46.8
BX2 18–19	18.5	23.1	48.4	6.2	21.9	4.4	0.9	3.9	0.5	4.3	15.4	0.7	1.7	0.93	1.5	0.2	132.4	8.7	1.3	3.7	44.3
BX2 21–22	21.5	38.6	81.3	10.9	33.8	6.4	1.7	6.1	0.9	4.6	23.8	0.9	2.5	0.5	2.3	0.3	214.5	9.6	1.4	4.6	50.5
<i>Box-core BC2</i>																					
BC2 1–2	1.5	54.1	121.1	14.9	46.9	9.2	2.0	8.5	1.2	5.4	25.7	1.0	2.9	0.6	2.4	0.4	296.4	11.1	1.9	19.3	48.8
BC2 3–4	3.5	27.1	56.3	7.2	25.7	5.2	1.0	4.8	0.6	3.5	19.0	0.7	1.9	0.3	1.4	0.1	150.9	9.1	1.7	6.7	43.5
BC2 5–6	5.5	54.1	96.9	12.9	45.8	7.2	1.8	8.5	0.9	4.8	28.6	1.1	2.5	0.5	2.6	0.3	268.3	10.4	1.8	19.3	48.7
BC2 6–7	6.5	31.4	64.6	8.0	28.5	5.5	1.1	5.3	0.7	3.8	17.4	0.7	2.0	0.3	1.6	0.2	171.1	9.5	1.7	7.2	49.3
BC2 7–8	7.5	27.5	59.0	7.2	25.6	5.2	1.0	4.7	0.6	3.6	16.9	0.7	1.9	0.3	1.5	0.1	155.8	9.3	1.6	3.8	48.0
BC2 8–9	8.5	50.0	111.0	13.3	41.7	8.5	1.9	7.4	1.2	5.2	27.0	1.0	3.0	0.6	2.4	0.4	274.6	10.7	1.8	15.2	51.0
BC2 10–11	10.5	35.8	74.6	8.9	31.4	6.1	1.2	6.0	0.7	4.0	18.1	0.8	2.0	0.3	1.5	0.2	191.5	10.2	2.0	8.1	44.5
BC2 13–14	13.5	54.2	114.4	12.0	46.5	8.6	1.6	8.8	1.1	4.2	20.8	1.0	2.8	0.5	2.4	0.4	279.3	11.2	1.9	19.4	40.3
BC2 14–15	14.5	36.9	78.1	9.3	32.7	6.4	1.2	6.0	0.7	3.8	17.5	0.7	2.0	0.3	1.5	0.1	197.2	10.9	2.1	10.1	49.6
BC2 16–17	16.5	51.2	91.4	11.0	43.2	7.0	1.5	8.0	0.9	3.9	22.7	0.9	2.4	0.3	2.3	0.3	247.1	10.8	1.9	16.4	48.4
BC2 18–19	18.5	48.8	95.3	10.0	40.1	7.2	1.4	7.7	1.0	3.9	19.9	1.0	2.7	0.5	2.4	0.4	242.1	10.4	1.7	23.3	38.8
BC2 19–20	19.5	47.4	84.9	11.2	40.3	6.3	1.5	7.2	0.7	4.3	26.2	0.9	2.2	0.5	2.2	0.3	236.1	10.5	1.8	12.6	55.0
<i>Box-core BC3</i>																					
BC3 0–1	0.5	39.3	84.3	10.1	35.4	6.9	1.3	7.2	0.9	4.1	18.2	0.8	2.1	0.3	1.4	0.1	212.3	10.5	2.4	14.2	44.8
BC3 3–4	3.5	42.0	87.1	10.2	35.8	6.9	1.4	6.8	0.7	4.0	19.3	0.8	2.0	0.3	1.5	0.1	218.7	11.3	2.4	13.6	47.1
BC3 5–6	5.5	45.1	87.8	11.7	40.0	6.7	1.7	7.4	0.9	4.6	23.4	0.9	2.4	0.5	2.2	0.3	235.5	10.1	1.8	10.6	49.7
BC3 7–8	7.5	7.5	79.3	9.2	32.4	6.3	1.2	6.3	0.7	3.9	19.5	0.8	2.0	0.3	1.6	0.2	202.2	10.5	2.1	10.4	47.5
BC3 8–9	8.5	44.3	80.1	10.5	38.2	6.1	1.4	7.4	0.7	4.1	23.1	0.9	2.2	0.5	2.1	0.2	221.8	10.0	1.8	10.7	49.3
BC3 9–10	9.5	26.6	57.1	7.2	25.9	5.1	1.0	4.7	0.6	3.4	14.2	0.7	1.7	0.3	1.3	0.1	149.8	9.6	1.7	7.4	41.3
BC3 10–11	10.5	52.3	95.5	11.0	44.5	7.3	1.5	8.8	1.0	4.3	22.8	1.0	2.7	0.5	2.5	0.3	255.9	10.1	1.8	17.5	43.8
BC3 12–13	12.5	48.3	97.8	12.6	40.3	7.1	1.8	7.5	1.0	4.9	26.5	0.9	2.6	0.6	2.3	0.3	254.5	10.3	1.8	13.5	55.6
BC3 14–15	14.5	23.0	46.2	6.0	21.4	4.2	0.8	3.6	0.5	2.8	11.9	0.6	1.5	0.2	1.2	0.1	123.9	9.7	1.6	7.9	41.7
BC3 16–17	16.5	30.8	63.2	7.7	26.9	5.4	1.1	5.2	0.6	3.5	16.6	0.7	1.9	0.3	1.4	0.1	165.3	9.9	1.9	9.2	47.2
BC3 17–18	17.5	47.4	101.8	12.5	39.2	7.7	1.7	6.9	1.0	5.0	25.1	0.9	2.7	0.5	2.1	0.3	254.7	10.9	1.9	12.6	53.0
BC3 18–19	18.5	44.6	84.7	11.2	37.1	1.2	1.5	6.9	0.7	4.3	23.9	0.9	2.2	0.5	2.1	0.3	227.1	10.3	1.8	9.8	50.7

HREE (Fig. 2). Moreover, these values are greater than the value of 1.3 reported by Sholkovitz (1990) for terrigenous particulate matter.

The Augusta sediments exhibit on average Ce/Ce* values close to 1 (Fig. 3). However, the Ce/Ce* depth profile for single core is irregular, exhibiting a weakly negative Ce anomaly for some horizons (Ce/Ce* down to 0.81). In particular, the core BX1 shows lower Ce/Ce* values in the surface layers. To exclude that observed Ce anomalies are an artificial reflection of anomalous La abundances (see Bau and Dulski, 1996b; and Olivier and Boyet, 2006 for a discussion), Ce anomalies have been evaluated by the Pr/Pr* ratio [$\text{Pr}_n / (0.5\text{Ce}_n + 0.5\text{Nd}_n)$]. Pr/Pr* values higher than 1 suggest real Ce anomalies for the Augusta sediments.

Gd/Gd* ratios for the four cores vary in the range 1.0–1.7; at the coastal station BX1, the Gd/Gd* depth profile exhibits a clear up-core increasing trend (Fig. 3). Y/Ho atomic ratios range from 39

to 58 (Table 1), with fluctuating values throughout the cores and showing averagely higher values at the coastal station BX1.

4. Discussion

Sediments from the Augusta area show generally decreasing concentrations of REEs in contrast with increasing Ca-carbonate contents. Clay-rich sediments from offshore cores BX2, BC2 and BC3 have major capacity of REE preservation owing to the great availability of clay minerals to incorporate REEs into their crystal-line structure and/or to adsorb REEs onto their surfaces. Contrarily, coastal sediments of the box-core BX1 have a lower potential to immobilize REEs owing to their coarser-sized fabric including abundant carbonate phases. Thus appreciably lower REE concentrations at station BX1, compared to more distal sites, suggest that

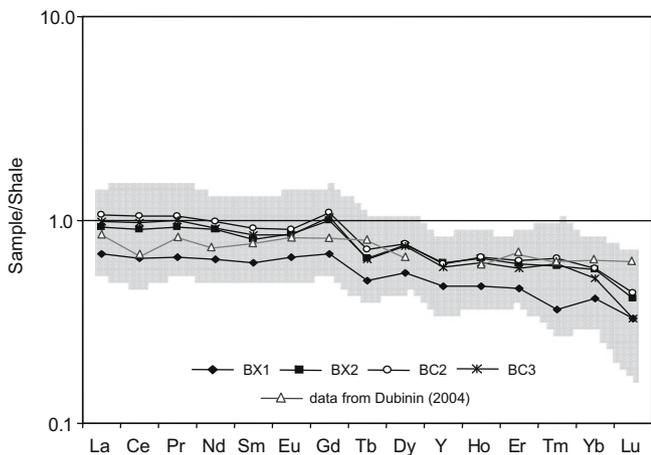


Fig. 2. Average shale-normalized REE + Y distribution patterns for the box-cores from the Augusta area. NASC-normalized carbonate-terrigenous mud pattern from the Atlantic Ocean (Dubinin, 2004; St. 3840; 0–2 cm) is reported for comparison. The grey band marks REE + Y distribution patterns for all analyzed samples.

the carbonate diluting effect is an important factor controlling the bulk REE distribution.

The shale-normalized REE + Y patterns of Augusta sediments do not display particular spikes that could reflect significant contamination by individual REE. The patterns reflect a dominant terrigenous derivation of rare earth elements because sediments derived from land particles carried into the ocean basins have generally a flat shale-normalized pattern. To evaluate the amount of La in ex-

cess of the La inventory supported by detrital inputs, the component La_{ex} has been calculated according to Murray et al. (1992):

$$La_{ex} = La_{sample} - [Al_{sample} * (La_{NASC}/Al_{NASC})]$$

where La_{NASC} and Al_{NASC} values are those reported in Gromet et al. (1984). Low values of La_{ex} (on average 13%; Table 1) suggest that a large proportion of La is derived by detrital material and that a LREE terrigenous source is to be assumed. On the other hand, the estimated excess of La is consistent with La_{n}/Yb_n values for the Augusta sediments slightly higher than the value reported for terrigenous particulate matter (see above). This moderate enrichment in LREEs with respect to HREEs reflects the fractionation of HREE/LREE, occurring through the water column, as LREEs are preferentially adsorbed onto particle surfaces (e.g., Koeppenkastrup and De Carlo, 1992; Sholkovitz et al., 1994), whereas HREEs are preferentially retained in solution, due to the increasing stability of solvated complexes of the heavier members of REE series, depending on their smaller ionic radii (Sholkovitz et al., 1994; Byrne and Sholkovitz, 1996).

4.1. Y/Ho ratio

The Y/Ho ratio is commonly used as proxy of terrestrial contribution to sediments, because Y behaves in accord with Ho and no fractionation between the two elements occurs terrestrially while Y fractionates from Ho in marine reaction systems. Despite their similar seawater speciation and although these elements have similar ionic radii, Y distinctly deviates from Ho due to the competitive reactions during scavenging by marine particulate matter (Zhang et al., 1994; Nozaki et al., 1997; Bau, 1999). Owing to Y being less

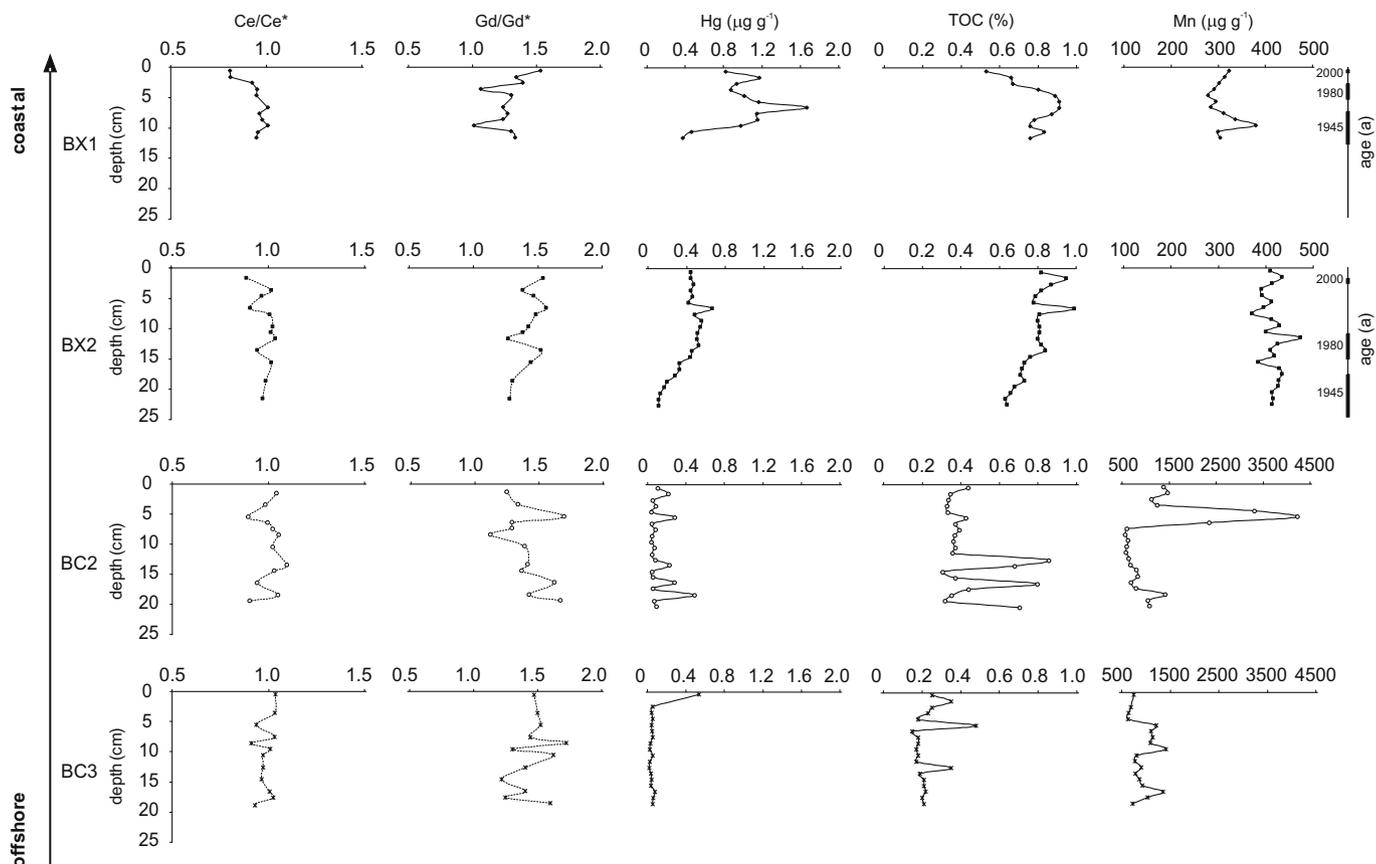


Fig. 3. Ce/Ce*, Gd/Gd* anomalies vs. depth in the studied box-cores; Hg, TOC and Mn concentrations vs. depth reported from Di Leonardo et al. (2008) (note the different scale for Mn values of BC2 and BC3). Based on ^{210}Pb dating, vertical scale on the right shows the year of sediment deposition (data from Di Leonardo et al., 2007).

effectively scavenged from seawater than Ho, marine Y/Ho atomic ratios (i.e. 90–120) are approximately two times higher than the chondrite and shale Y/Ho atomic ratios (~ 55) (Zhang et al., 1994; Bau et al., 1995; Nozaki et al., 1997). The relatively low Y/Ho ratios of the Augusta sediments (on average 48.6), close to the chondritic ratio, indicates large contribution of terrestrial detritus. Similar values of the Y/Ho ratio (on average close to 43) have been measured by Censi et al. (2007) for suspended particulate matter in the Ionian Sea and interpreted in terms of delivery of pyroclastic products from the explosive activity of Mount Etna.

Unexpectedly, Y/Ho ratios do not correlate with Al (not shown) and Zr (Fig. 4) which are commonly thought to represent detritus input by riverine and aeolian sources, respectively (Wehausen and Brumsack, 2000). The lack of correlation between Y/Ho ratios and Al and Zr, coupled with wide fluctuations of the Y/Ho ratios throughout the cores, markedly for the more distal cores BC2 and BC3, could reflect heterogeneous provenance of sedimentary materials. Consistently, at offshore core sites, substantial proportions of land-derived organic material have been documented by Di Leonardo et al. (2008) who suggested that the region has experienced changes in natural sediment source/composition induced by repeated discharge of contaminated dredged materials.

4.2. Ce/Ce*

Cerium may change the oxidation degree in natural processes and consequently fractionate from other rare earth elements. Because in the pE–pH range of seawater Ce behaves differently from La and Pr, the value of Ce anomaly is thought to be indicative of redox state (see Elderfield, 1988; Byrne and Sholkovitz, 1996, for a review). In the marine environment, Ce is present in two oxidation states: Ce³⁺ and Ce⁴⁺. In coastal and shallow-water sediments, Ce⁴⁺ is reduced to Ce³⁺ which is mobile through the porewater (Sholkovitz and Elderfield, 1988) and then subjected to lateral transport toward the open ocean. In contrast, in oxidizing environment Ce occurs as Ce⁴⁺ in the insoluble form CeO₂, that tends to be more rapidly removed by particle scavenging than other REEs (Nozaki et al., 2000b). Consequently, fractionation of Ce relative to other REEs is expected to occur in the presence of strong redox gradients.

In the studied cores, the Ce/Ce* values generally close to 1, which is the value reported for the average shale (Haskin and Haskin, 1966; Murray et al., 1991), match the shale-like REE patterns and low Y/Ho ratios indicating dominant contribution of detrital particles to sediments of the Augusta area.

The upcore increasing negative Ce/Ce* anomaly observed at site BX1 (Fig. 3) could be ascribed to a decrease in detrital contribution, the carbonate phases (essentially biogenic calcite) being dominant

component at the top of the core (CaCO₃ = 63%; Di Leonardo et al., 2007). Marine carbonate is recognized to tend to inherit the seawater Ce anomaly. However, if the Ce depletion is attributed to enhanced deposition of marine carbonate, a more pronounced negative Ce anomaly should be expected for the BX1 core profile. In this coastal core, organic matter may play an important role in scavenging dissolved REEs. Recent experimental studies on the competition between carbonate and organic matter for REE complexation prove that in a wide range of natural conditions dissolved organic REE complexes are more important than carbonates complexes (re. Pourret et al., 2007 and references therein). According to the model of Haley et al. (2004), organic matter, Fe-oxide, Ce-oxide, and Mn-oxide are major carriers of REEs in oxic sedimentary environments. In the water column, following organic particulate degradation, precipitating Fe-oxide efficiently scavenges REEs, then sinking together with Ce-oxide to the sediment where they accumulate in the presence of sufficient oxygen for their stabilization. This model could explain a partial compensation for Ce depletion resulting from abundant carbonate in shallower sediments of the core BX1. At this station, upcore increasing Fe/Al ratios (from 0.46 to 0.69; Di Leonardo (2007)) are consistent with this reasoning. Moreover, based on the decreasing trend in the TOC profile (Fig. 3), it seems reasonable to suppose that good oxygenation conditions occurred at shallower sediment depth in the coastal area of the Augusta area. Interestingly, the core BX2 displays lower values of Ce/Ce* in coincidence with relatively high values observed in TOC and Hg profiles (Fig. 3) at 1.5, 6.5 and 13.5 cm, respectively. For cores BC2 and BC3, even if REE dataset is not complete, concurrence of lower Ce/Ce* values with higher TOC and Hg concentrations has been recorded at 5.5 and 16.5 cm and at 5.5 cm, respectively. Exclusively at 5.5 cm in both BC2 and BC3 cores, these lower Ce/Ce* values are concurrent with very pronounced Mn peaks. Di Leonardo et al. (2008) ascribed these brief Hg and TOC excursions to repeated discharge of material dredged in the Augusta Bay, primarily enriched in Hg deriving presumably from the nearby chlor-alkali plant. By using the Mn patterns across the offshore cores BX2, BC2 and BC3 as a proxy for redox conditions, these authors argue that the emplacement of dredged contaminated materials induced a decrease in O₂ concentration at the sediment–water interface. Based on the reasoning that at the sediment–water interface or in porewater of oxygen-poor sediments Ce in the trivalent state is rapidly regenerated relative to the neighbouring LREEs (Haley et al., 2004), the negative values of Ce anomaly in cores BX2, BC2 and BC3 would mark human-induced modifications of the sediment redox environment at offshore core sites in the Augusta area.

4.3. Evaluation of anthropogenic REE input

In southern–eastern Sicily, the settlement of an industrial area in the Augusta coastal belt since the middle of the 20th century has enormously contributed to degrading of delicate marine and terrestrial ecosystems. Coastal and offshore sediments became strongly contaminated due to indiscriminate discharge of pollutants, especially Hg among other trace metals, used and probably unloaded by a chlor-alkali plant located in the Augusta Bay. This strong industrialisation has certainly altered the natural fluxes of elements in the coastal sedimentary environment over time and surprisingly changed the natural sediment source/composition even at water depth of up to 2200 m and at 16 nautical miles from the coast (Di Leonardo et al., 2007, 2008).

The versatility and specificity of the REEs make them important from the technological, environmental, and economic point of view (Mitchell et al., 2002; Adachi et al., 2004; Wei-Qiang et al., 2005). In fact, environmental applications of REEs have increased markedly over the past three decades (Fuganti et al., 1996; Fedele

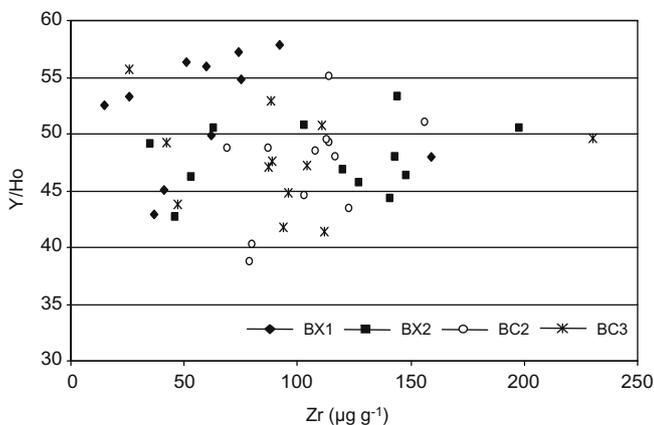


Fig. 4. Diagram showing the relationship between Y/Ho ratio and Zr ($\mu\text{g g}^{-1}$) in the box-cores from the Augusta area.

et al., 2008). Gd oxide is used for many different high-technology applications, such as infrared absorbing automotive glass, petroleum fluid-cracking catalyst, Gd–Y garnets, microwave applications, and colour tube phosphors screens. It can also be used in optical glass manufacturing and in the electronic industry (Pedreira et al., 2004). In densely populated and highly industrialized countries, pronounced positive Gd anomaly suggests an anthropogenic source of the element, which commonly is derived from the use of phosphate fertiliser and/or Gd complexes utilized as contrast medium in magnetic resonance imaging for medical diagnosis (Bau and Dulski, 1996a; Kümmerer and Helmers, 2000; Elbaz-Poulichet et al., 2002; Kulaksiz and Bau, 2007; Rabiet et al., 2009). Another potential anthropogenic REE source can be ascribed to zeolites doped with REEs, which have been used as fluid-cracking catalysts in petroleum industry since the 1960s (Kulkarni et al., 2006). These cracking catalysts, produced from two major REE ore minerals, bastnasite and monazite, record an REE signature distinct from that of the crust, with large enrichments in La, Ce, Nd, and Sm, as detected in offshore sediments by Olmez et al. (1991).

In contrast to the uniform concentrations of MREEs and HREEs throughout the investigated Augusta cores, the LREEs exhibit a large range of concentrations. However, the REE patterns appear to be moderately enriched in LREEs relative to the average shale (Fig. 2). Even if sporadic LREE enrichments over the shale are registered by some sediment layers of BX2, BC2 and BC3, coastal and offshore sediments of the Augusta area do not provide evidence of a chemical signature of petrochemical and refining operations.

In the coastal core BX1 the Gd/Gd* ratio is 1.3 at the bottom sediments dated, taking into account errors on the core dating, as ca 1940–1950 and becomes as high as 1.53 at the topcore. The increase of the positive Gd/Gd* anomaly in surface sediments, that matches high Hg concentrations (more than 30 times the background value), potentially toxic PAH concentrations and a significant incidence of various morphological abnormalities in the foraminiferal tests (Di Leonardo et al., 2007), could be interpreted as proxy for input of anthropogenic Gd. However, owing to the coincidence with an enrichment in carbonate from benthic and planktonic shells which was presumably precipitated in equilibrium with seawater, it cannot be excluded that these anomalies are natural Gd/Gd* anomalies. In fact, uncontaminated seawater displays slight positive Gd anomaly (Gd/Gd*: 1.2–1.6; De Baar et al., 1985; Kim et al., 1991). On the other hand, the fact that Gd/Gd* ratios of core BX2 exhibit a similar trend of upcore increasing values argues in favour of the hypothesis of a recent anthropogenic Gd input in the Augusta area. Intriguingly, cores BX2, BC2 and BC3 display slightly positive Gd/Gd* anomalies at the same depth where negative Ce/Ce* anomalies were found and concurrent with high TOC and Hg concentrations that, as above discussed, mark episodes of terrestrial contamination. These peaks in the Gd/Gd* profiles might be seen as anthropogenic Gd anomalies. The anthropogenic Gd might be supplied from sedimentary materials dredged during the 1980s in the Augusta Bay, a semi-closed basin strongly affected by anthropogenic disturbance, and repeatedly discharged offshore of the Augusta area.

5. Conclusions

This study reveals that REE + Y concentrations are mainly controlled by the contribution of detrital (geogenic) material to the sediment and by the proportion of fine particles (clay minerals and Fe-oxides). Consistently, Y/Ho ratios are close to the chondritic ratio and their variability is interpreted to represent heterogeneous provenance of sedimentary materials. REE + Y distribution patterns do not provide clear evidence of a chemical signature of human activities. However, repeated anthropogenic inputs of heavily con-

taminated materials, dredged from the Augusta Bay and discharged into the offshore area, have modified the REE distribution by producing slight positive Gd and negative Ce anomalies.

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