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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 O_2 concentration in the sediment, which in turn triggers Ce regeneration.

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 Eu^{2+} and Ce^{4+}, 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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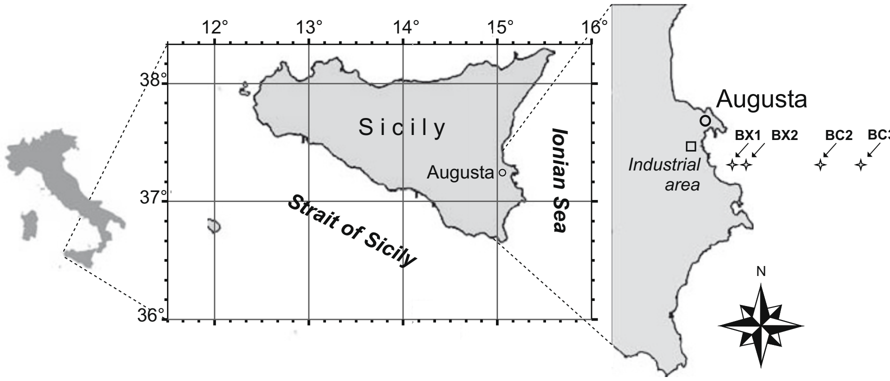

Core number	BX1	BX2	BC2	BC3
Latitude (N)	37° 09′ 00	37° 09′ 00	37° 08′ 98	37° 09′ 01
Longitude (E)	15° 16′ 00	15° 19′ 00	15° 33′ 99	15° 43′ 99
Water depth (m)	62	145	2223	2416
Core length (cm)	12	23	21	19
Nautical miles	2.15	4.29	16.73	25.10

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 (0.02–1.67 μg 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 °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 °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 μg g^{-1} for Eu and 0.1 μg 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 $Ce/Ce^* = 2(Ce_n)/(La_n + Pr_n)$ and $Gd/Gd^* = Gd_n/(0.33\ Sm_n + 0.67\ Tb_n)$, 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 alumino-silicates and quartz associated to biogenic carbonate, which becomes more abundant in the shallower sediments; in the sites BX2, BC2 and BC3 dominant phases are alumino-silicates 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 μg 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 $La_n/Yb_n = (La_{sample}/La_{shale})/(Yb_{sample}/Yb_{shale})$. 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