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Baseline

Distribution of rare earth elements in marine sediments from the Strait of Sicily (western Mediterranean Sea): Evidence of phosphogypsum waste contamination

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ABSTRACT

Concentrations of rare earth elements (REE), Y, Th and Sc were recently determined in marine sediments collected using a box corer along two onshore–offshore transects located in the Strait of Sicily (Mediterranean Sea). The REE + Y were enriched in offshore fine-grained sediments where clay minerals are abundant, whereas the REE + Y contents were lower in onshore coarse-grained sediments with high carbonate fractions. Considering this distribution trend, the onshore sediments in front of the southwestern Sicilian coast represent an anomaly with high REE + Y concentrations (mean value 163.4 $\mu g\ g^{-1}$) associated to high Th concentrations (mean value 7.9 $\mu g\ g^{-1}$). Plot of shale-normalized REE + Y data of these coastal sediments showed Middle REE enrichments relative to Light REE and Heavy REE, manifested by a convexity around Sm–Gd–Eu elements. These anomalies in the fractionation patterns of the coastal sediments were attributed to phosphogypsum-contaminated effluents from an industrial plant, located in the southern Sicilian coast.

1. Introduction

The rare earth elements (REE), including yttrium, are a group of 15 elements characterized by similar chemical properties principally due to the same electronic configuration. They are mainly trivalent, with the exception of Ce and Eu which are also stable in the tetra and divalent oxidation states. The REE exhibit decreasing ionic radii with increasing atomic number from La to Lu (lanthanide contraction; Henderson, 1984) causing different fractionation patterns in various phases during geochemical processes. They are usually denoted as HREE (heavy rare earth elements) and LREE (light rare earth elements) (Dubinin, 2004).

The REE have been intensively studied as natural tracers of biogeochemical processes (Oliveri et al., 2010) and of water mass circulation in the marine environment (Elderfield and Greaves, 1982; De Baar et al., 1985; De Baar, 1991; Piepgras and Jacobsen, 1992; German et al., 1995; Bau and Dulski, 1996; Zhang and Nozaki, 1996; Jeandel et al., 1998; Alibo and Nozaki, 1999, 2000) and they are widely used to investigate weathering processes (Nesbitt, 1979; Sawka et al., 1986; Banfield and Eggleton, 1989; Marsh, 1991; Braun et al., 1993; Gouveia et al., 1993; Prudencio et al., 1993; Boulangé and Colin, 1994; Ohlander et al., 1996; Leybourne et al., 2006). Due to their coherent behaviour the REE are widely used as tracers of sources and processes controlling trace element distribution in marine sediments (Piper, 1974; Sholkovitz, 1990; Toyoda et al., 1990; Murray et al., 1991; Piper et al., 2007; Censi et al., 2010). The REE distribution in sediments is largely controlled by scavenging processes, in particular by Fe–Mn–oxides (Elderfield and Greaves, 1982; Whitfield and Turner, 1987; Elderfield, 1988; Haley et al., 2004), by redox conditions of the overlying water column (Liu et al., 1988), by composition of the terrigenous source (Chaudhuri and Cullers, 1979; Taylor and McLennan, 1985) and by potential anthropogenic inputs (Olmez et al., 1991).

Bau and Dulski (1996) reported the first evidence of an anthropogenic REE source in natural systems (Gd anomaly), after which different works reported on anomalous REE concentrations in terrestrial waters (Möller et al., 2000; Protano and Riccobono, 2002; Zhu et al., 2004; Grande et al., 2000; Kulaksiz and Bau, 2007; Rabiet et al., 2009) and in river and marine sediments (Olmez et al., 1991; Ravichandran, 1996; Yusof et al., 2001; Borrego et al., 2004; Oliveira et al., 2007) caused by unnatural liquid or solid inputs derived from human activities (e.g. industrial plants, acid mine drainage, agricultural activities).

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This paper is the first to report on the REE composition of onshore–offshore marine sediments from the Strait of Sicily, the connection gateway between the large western and eastern Mediterranean basins (Lermusiaux and Robinson, 2001; Gasparini et al., 2004).

The aim of this work was to study the REE distribution in sediments from the coastal to the pelagic zone in the Strait of Sicily and to assess industrial effluents as sources of anomalous REE concentrations near the Sicilian coastline. In this area the geochemistry of recent sediments is poorly investigated; in particular, data of REE composition in sediments from the Strait of Sicily not have been reported in literature until now. At light of these data lacking, this work should represent a baseline dataset in the study of REE in marine sediments from this zone of the Mediterranean Sea and in the environmental pollution assessment. The anthropogenic influences on the studied sediments were previously reported by Tranchida et al. (2010). These authors suggested that elements as Sb, As, Pb and Hg accumulated in sediments near the coastline to a higher degree with respect to their natural background value due to the intensification of industrial activity on the southern Sicilian coast since the 1960s.

2. Sampling and analytical methods

The studied sediments were collected in the Strait of Sicily along two transects, Sciacca-Pantelleria (SP hereafter) and Pozzallo-Malta (PM hereafter), perpendicular to the southern coast of Sicily (Fig. 1). The sediments were sampled using a USGS-modified NEL-box corer aboard the R/V *Urania* during oceanographic cruises in the summers of 2001, 2002 and 2003. The locations of all studied sediment cores are shown in Fig. 1.

The samples were stored in polyethylene liners and kept frozen (at −20 °C) until chemical analysis. In the laboratory, the defrosted cores were cut at 1–2 cm intervals with a stainless steel bandsaw and dried at 50 °C.

For the chemical analysis, bulk sediment samples were digested with aqua regia in Teflon bombs using a microwave mineralizer (CEM MSD 2000); this method is widely used in environmental geochemistry studies (Chan et al., 1998; Rubio et al., 2001; among others). The obtained solutions were analysed by inductively-coupled plasma mass spectrometry (ICP-MS) using an ELAN 6000 Perkin–Elmer. All calibration standards and blanks were prepared in the same acid matrix used for the sediment samples. Extreme caution was used in preparing and analysing the samples to minimize any possible ambient contamination. The reagents used were all of Suprapur quality. The differences between the results of duplicate samples (about 10% of total sample) were minor, at 10%, and between blank concentrations (about 20% of the samples) were at least an order of magnitude lower than the sample concentrations, and the precision of the analytic method was routinely between 2% and 8%. The accuracy of the analytical technique was evaluated by measuring the reference materials Soil 7 (IAEA) which

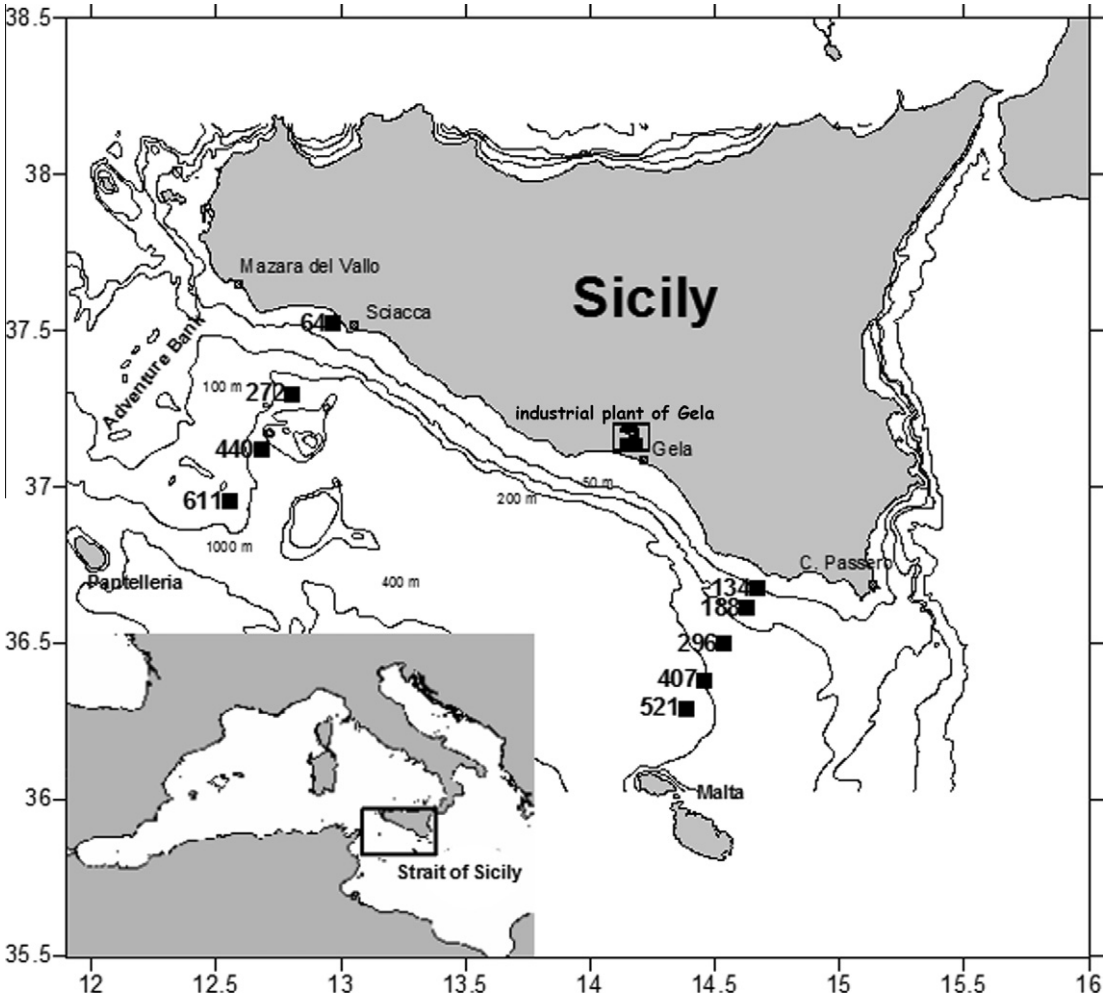

Fig. 1. Location of sampling stations in the Strait of Sicily.