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Enrichment of rare earth elements as environmental tracers of contamination by acid mine drainage in salt marshes: A new perspective

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ABSTRACT

Rare earth elements (REE) were analyzed in surface sediments from the Guadiana Estuary (SW Iberian Pyrite Belt). NASC (North American Shale Composite) normalized REE patterns show clearly convex curvatures in middle-REE (MREE) with respect to light- and heavy-REE, indicating acid-mixing processes between fluvial waters affected by acid mine drainage (AMD) and seawater. However, REE distributions in the mouth (closer to the coastal area) show slightly LREE-enriched and flat patterns, indicating saline-mixing processes typical of the coastal zone. NASC-normalized ratios (La/Gd and La/Yb) do not discriminate between both mixing processes in the estuary. Instead, a new parameter (E_{MREE}) has been applied to measure the curvature in the MREE segment. The values of $E_{MREE} > 0$ are indicative of acid signatures and their spatial distribution reveal the existence of two decantation zones from flocculation processes related to drought periods and flood events. Studying REE fractionation through the E_{MREE} may serve as a good proxy for AMD-pollution in estuarine environments in relation to the traditional methods.

1. Introduction

Estuarine environments are known to receive huge amounts of contaminants and are considered among the most sensitive areas to the accumulation of toxic compounds. In the estuaries, sediment particles play a key role in the transport of trace elements from the continent to the ocean since they can act as a source or sink to the interstitial water. The estuarine processes controlling the flux and the behavior of trace elements are the salinity-induced coagulation of colloids and the adsorption or desorption from the particulate material (Edmond et al., 1985). Rare earth elements (REE, from La to Lu) are a coherent group of trace elements whose chemical behaviors, though similar to each other, systematically change along the series. Both limited mobility and fractionation capacity of the REE during weathering and sedimentation make to this element group an ideal tool for evaluating the estuarine processes through the study of sediments.

Concentration and fractionation patterns of REE in estuarine sediments are controlled by the fluvial discharge composition and the water mixing conditions in the system (Byrne and Sholkovitz, 1996). Acid mine drainage (AMD) results from oxidation of sulfides by run-off waters draining abandoned mining areas, and often affects to surrounding estuarine systems (e.g. Olías et al., 2006; Nieto et al., 2007). REE fractionation has been shown to be very useful for identifying salt-mixing processes in non-polluted estuaries with mixing between circum-neutral river and seawater, or acid-mixing processes in estuaries receiving fluvial courses impacted by AMD (e.g., Elbaz-Poulichet and Dupuy, 1999; Borrego et al., 2005). Mixing processes are often quantified according to REE patterns and (La/Yb) and (La/Gd) ratios. In order to be better able to observe fractionation processes, it is customary to normalize absolute REE concentrations to those in some naturally occurring material such as North American Shale Composite (NASC), which is usually used in the marine geochemistry (Haskin et al., 1968).

In estuarine environments not affected by acid discharges, light-REE (LREE) are preferentially adsorbed on the solid particles, while middle-REE (MREE) and heavy-REE (HREE) preferentially remain in solution (e.g. Elderfield et al., 1990; Sholkovitz et al., 1992; Sholkovitz, 1993, 1995; Sholkovitz and Szymczak, 2000; Lawrence and Kamber, 2006). When normalized against NASC, the sediments present a sub-parallel REE fractionation pattern, with often a relative LREE enrichment with respect to MREE and HREE. The enrichment in LREE relative to HREE is reflected by $(La/Yb)_{NASC}$ ratios above 1 and indicates estuaries only affected by saline mixing processes.

However, the distribution of REE in AMD discharges often shows NASC-normalized convex patterns with an evident enrichment of MREE with respect to LREE and HREE (e.g. Johannesson

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and Lyons, 1995; Verplanck et al., 1999; Gimeno et al., 2000; Gammons et al., 2005; Olías et al., 2005; Ferreira da Silva et al., 2009). The preferential sorptive removal of MREE by precipitation of poorly crystalline iron oxyhydroxides, typical of AMD-affected environments, favors that fluvial sediments also preserve NASC-normalized patterns with convex MREE-signatures (Bau, 1999; Johannesson and Zhou, 1999). In AMD-affected estuarine environments, MREE-enriched signatures in sediments are often quantified by $(La/Gd)_{NASC}$ ratios <1 and indicates estuaries affected by acid mixing processes, and hence, likely metal-polluted (Elbaz-Poulichet and Dupuy, 1999; Borrego et al., 2004, 2005). Consequently, REE patterns could be used to identify water–rock interactions that govern the composition of acidic discharges from sulfide-mining wastes and as a tool to assess contamination by AMD in environmental systems.

We report hence a comprehensive study of the REE content in surface sediments of the Guadiana river estuary (SW Iberian Peninsula). This estuary is controversial because some authors have classified it as a non-polluted sedimentary environment (e.g., Ruiz, 2001; González-Pérez et al., 2008), while other authors noted metal concentrations in excess of background values due to AMD discharges (Delgado et al., 2010). Hence, applying the REE fractionation would be a useful proxy for assessing the impact of sulfide mine-related pollution. In this study, spatial variation of $(La/Gd)_{NASC}$ ratios in the surface sediments of this estuary was analyzed to recognize REE patterns enriched in MREE, and thus, AMD-affected environments. The results were compared with a new parameter, so-called E_{MREE} index, recently proposed by Pérez-López et al. (2010) as a more sensitive environmental tracer especially designed for systems affected by AMD pollution.

The main aims of this work are: (1) to characterize concentration and spatial distribution of REE along the estuary, (2) to understand the processes controlling the REE behavior in non-natural estuarine systems where seawater mixes with acidic river water and, (3) to assess the possibility of using the methodology devised by Pérez-López et al. (2010) as a geochemistry tool to trace contamination by AMD in estuarine systems.

2. Environmental setting

The study area is located in the Iberian Pyrite Belt (IPB), which is the largest sulfide metallogenic province in the world with an intense mining activity dating back to Third Millennium BC (Sáez et al., 1999; Nocete et al., 2005; Delgado et al., 2012). Thenceforth, this massive sulfide belt has been a source of wealth but also of pollution. Part of the courses of the Tinto, Odiel and Guadiana rivers run over the IPB and drain huge contributions of AMD from oxidation of sulfide-rich mining wastes spread over more than a hundred abandoned mines around the region (Cánovas et al., 2007; Sarmiento et al., 2009; Delgado et al., 2009). Tinto and Odiel rivers converge in a common estuary that receives large amounts of contaminants to the extent that is considered one of the most polluted aquatic systems in the world (Nieto et al., 2007). So, recent studies suggest that both rivers transport enormous quantities of dissolved contaminants: $7900\ t\ a^{-1}$ of Fe, $5800\ t\ a^{-1}$ Al, $3500\ t\ a^{-1}$ Zn, $1700\ t\ a^{-1}$ Cu, $1600\ t\ a^{-1}$ Mn and minor quantities of other metals. These values represent 60% of the global gross flux of dissolved Zn transported by rivers into the ocean, and 17% of the global gross flux of dissolved Cu (Olías et al., 2006). Mining pollution can even be dated from vertical sedimentary records using metal concentration (López-González et al., 2006) and REE fractionation (Borrego et al., 2005).

The Guadiana river basin also drains the IPB, concretely the western part of the region and its corresponding estuary is open to the Atlantic Ocean at approx. 50 km from the Tinto–Odiel estuary. The main course has 810 km of length, of which the last 200 km constitute the natural border between Portugal and Spain. This river is the main system responsible for the transport and diffusion of the pollution, from São Domingos mine in the Portuguese sector and Herrerías and Thasis mines in the Spanish sector, to its estuary (Delgado et al., 2009). However, compared to the Tinto–Odiel system, the lower influence of mining effluents and the existence of some water reservoirs attenuating the metal concentration by dilution, favor that fluvial and estuarine sediments present a less significant contamination.

3. Materials and methods

3.1. Sampling points

A total of 89 samples of shallow surface sediments were collected with a manual drill in the channels of the Guadiana River Estuary. Sampling was conducted in the lower estuary within 30 km of the shoreline, coinciding with the marine influence according to Morales et al. (2006). Sampling points were located in the main channel of the Guadiana River and the five secondary tidal channels forming the wetland area: Carrasqueira and Castro Marim in Portugal, and Canela, San Bruno, Carreras in Spain (Fig. 1). Henceforth, to differentiate the samples closest to the coastal line (samples S3, S4, S6 and S7) we will use the term mouth, which describe the part practically open to the sea in the estuary.

3.2. Analytical procedures

Sediment samples (around 2 kg for each sample) were ground, oven-dried at 40 °C until complete dryness, homogenized and sieved (<2 mm) for mineralogy, grain size study and geochemical analysis. Given that physical–chemical properties of water strongly influence REE geochemistry of surface sediments, some parameters such as temperature, pH and electrical conductivity using portable meters, and salinity determined from chloride concentration, were also measured at 13 points of water quality control (Fig. 1) at the time of sample collection (details above the methodology have been described by Delgado et al., 2009).

Major minerals present in the samples were identified by X-ray diffraction (XRD), and minor phases were detected and identified by means of scanning electron microscopy equipped with an energy dispersive system for microanalysis (SEM–EDS). The grain size study of the sediments was performed using a particle size analyzer Malvern Mastersizer 2000. Bulk composition was carried out by Acme Analytical Laboratories Ltd. (Vancouver, Canada), accredited under ISO 9002, through its Italian affiliate (ERS Srl, Napoli). Sediment samples were digested by $LiBO_2$–$Li_2B_4O_7$ fusion/dilute nitric and the resulting solutions analyzed. The major and trace elements (including the REE) of solutions were analyzed by ICP–AES (inductively coupled plasma–atomic emission spectroscopy; Jarrell Ash model Atomcomp 975) and ICP–MS (inductively coupled plasma–mass spectrometry; Perkin Elmer model Elan 6000), respectively. Volatile phases were calculated by loss on ignition (LOI), and total carbon and sulfur by LECO (SC-144DR model).

To demonstrate the reproducibility and accuracy of the results, the analysis sequences consisted of Acme's in-house reference materials (DS7 and SO-18), Canadian certified reference materials project (TILL-4 and LKSD-2), other certified reference materials analyzed as an unknown (STSD-1 and STSD-2, standard from stream sediments), method blanks and replicated samples. For detailed information of the results on the quality control, the reader is referred to previous works in this matter (Delgado et al., 2010).