Rare-earth-element fractionation patterns in estuarine sediments as a consequence of acid mine drainage: A case study in SW Spain

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ABSTRACT

Processes of seawater dilution and acid neutralization cause significant effects upon REE fractionation between the aqueous solution and sediments. This study describes the results of a recent investigation into such processes in the sediments of the Tinto and Odiel estuary. The results show differences in behaviour between light REEs (LREEs) and middle and heavy REEs (MREEs and HREEs). A relative depletion in La is observed as a consequence of the low pH values, which prevents the separation of LREEs from solution to the suspended matter. When acid neutralization occurs, on the other hand, an increase in the La content is related to the preferential separation of LREEs compared to MREEs and HREEs. Under these conditions three main fractionation patterns were distinguished: the first shows a slightly MREE-enriched shape in sediments deposited in the fluvial zone; the second displays significant depletion in LREEs and a nearly flat tendency in MREEs and HREEs towards the estuarine mixing zone; and the third is enriched in total REEs and shows a relative increase in LREEs and MREEs. The evolution of these patterns reveals that pH is the key variable controlling REE fractionation in environments affected by acid mine drainage.

Key words: acid and saline mixing, estuary, mining, rare-earth elements, sediments

Patrones de fraccionamiento de tierras raras en sedimentos estuarinos como consecuencia del drenaje ácido de mina: estudio del SW de España

RESUMEN

Los procesos de dilución de agua de mar y de neutralización ácida causa efectos evaluables en el fraccionamiento de tierras raras (REE) y han sido estudiados en los sedimentos del estuario de los ríos Tinto y Odiel. Se puede observar un comportamiento diferente entre las tierras raras ligeras (LREE) en relación con las tierras raras medias (MREE) y pesadas (HREE). Un relativo empobrecimiento de La se observa como consecuencia de la influencia de los bajos valores de pH que impide la transferencia de LREE en solución hacia la materia en suspensión. Por otro lado, cuando la neutralización ácida ocurre hay un aumento en el contenido de La, relacionado con el empobrecimiento preferencial LREE sobre MREE y HREE. En tales condiciones, se han distinguido tres modelos de fraccionamiento principales. El primero muestra un ligero enriquecimiento de MREE en sedimentos depositados en la zona fluvial. El segundo muestra una disminución significativa de LREE y una tendencia casi plana de MREE y HREE hacia la zona de mezcla estuarina. El tercero es el enriquecimiento en la totalidad de REE y muestra un enriquecimiento relativo de LREE y MREE. Mirando la evolución de este modelo, el pH es la variable clave que controla el fraccionamiento de REE en entornos afectados por el drenaje ácido de mina.

Palabras clave: estuario, mezcla de agua ácida y salina, minería, sedimentos, tierras raras

Introduction

It is well known that REEs are sensitive to changes in environmental conditions. Consequently they have been widely used as tracers of geochemical processes in a large variety of sedimentary environments (Elderfield, 1988; Goldsttein and Jacobsen, 1988; German and Elderfield, 1989; Elderfield *et al.,* 1990; Smedley, 1991; Klinkhammer *et al.,* 1994; Sholkovitz, 1995; Johannesson *et al.,* 1996; Van Middlesworth and Wood, 1998; Zhang *et al.,* 1998; Johannesson and Zhou, 1999; Leybourne *et al.,* 2000; Nozaki *et al.,* 2000; Haley *et al.,* 2004). Most studies dealing with partitioning between dissolved and particulate phases have been made in rivers and estuaries (Hoyle *et al.,* 1984; Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Elderfield *et al.,* 1990; Sholkovitz, 1993, 1995; Nozaki *et al.,* 2000; Sholkovitz and Szymczak, 2000; Lawrence and

Kamber, 2006) because these systems exhibit a considerable separation of REEs, which occurs due to mixing processes involving water bodies with different characteristics (fluvial, estuarine and ocean waters). Studies into deposited sediments in these environments are less common, and only in a few cases do they focus on the behaviour of REEs in estuarine sediments (but see Elderfield *et al.,* 1990; Gouveia *et al.,* 1993; Ramesh *et al.,* 1999; Borrego *et al.,* 2004, 2005).

The geochemical features of estuarine sediments are highly influenced not only by the water mixing processes but also by the environmental conditions that prevail where they are deposited. From a general point of view, estuaries display two kinds of sediments: (i) those produced on site by means of flocculation and precipitation, and (ii) those deriving from dynamic processes (fluvial input and tide). The former record the geochemical features prevailing at the site where they are deposited, whilst the latter show the geochemical signs of their source, with or without modifications. This must be born in mind when establishing new sampling strategies designed to allow the collection of only those sediments that characterize the study conditions.

The peculiarity of the Tinto and Odiel estuary is that not only does saline mixing take place on site, as in other estuaries, but also that acid mixing processes are superimposed upon these conditions due to the high acidity (pH < 3) of the river waters (Borrego, 1992; Braungardt *et al.,* 2003). The Tinto and Odiel estuary has been studied from many points of view, mainly related to the importance of its polluting load, because it is one of the most polluted systems in the world (Nelson and Lamothe, 1993; Borrego *et al.,* 2002; Sáinz *et al.,* 2004). Therefore, the large heavy-metal content of the waters and sediments of this estuary is relatively common knowledge (Nelson and Lamothe, 1993; Van Geen *et al.,* 1997; Hudson-Edwards *et al.,* 1999; Leblanc *et al.,* 2000; Borrego *et al.,* 2002; Braungardt *et al.,* 2003; López-González *et al.,* 2006). In addition, the facies have been analysed in detail and the Holocene evolution of the sedimentary filling from the last pulse of the Flandrian transgression (6,000 years ago) has been widely studied (Borrego *et al.,* 1995; Pendón y Morales, 1997; Borrego *et al.,* 1999; Dabrio *et al.,* 2000). Few papers, on the other hand, have been published concerning the behaviour of REEs in this system, except those dealing with water and suspended matter by Elbaz-Poulichet and Dupuy (1999) and surficial and Holocene sediments by Borrego *et al.* (2004 and 2005).

The main aim of this study was to determine the REE fractionation pattern related to acid–saline mixing processes by characterizing the surficial sediments deposited in different environmental conditions along the Tinto and Odiel estuary. Our results constitute the first study into estuarine sediments where saline mixing and acid neutralization processes come together in a natural system affected by acid mine drainage (AMD).

Regional setting

The estuary of the Tinto and Odiel Rivers flows into the northwest of the Gulf of Cadiz in the Atlantic Ocean (Fig. 1A). The estuary has a strong tidal influence that controls water mixing processes within the system. Tidal wave propagation follows a weak hypersynchronic model with a mean range of 2.10 m, ranging from 1.63 m (average neap tides) to 2.90 m (average spring tides) (Borrego *et al.,* 1995). The landward estuarine limits are established at the towns of Gibraleon (Odiel estuary) and Niebla (Tinto estuary), where the tidal effect is insignificant (Borrego, 1992; Braungardt *et al.,* 2003).

The Tinto and Odiel River basins drain the volcanogenic massive sulphide deposits of the Iberian Pyrite Belt (IPB) within the southernmost part of the Iberian Variscan Massif (SW Spain). The IPB is one of the largest metallogenic provinces in the world (Leistel *et al.,* 1998; Sáez *et al.,* 1999) and has been mined for the last 5,000 years (Davis *et al.,* 2000). The natural alteration of these sulphide masses and the acid mine drainage (AMD) deriving from these zones, over centuries determine the hydrochemical features of both rivers, which have an extremely low pH (< 3) and high contents of sulphates, Fe and metals such as Al, Mn, Cu, Zn, Cd, and Pb (Nelson and Lamothe, 1993; Van Geen *et al.,* 1997; Elbaz-Poulichet *et al.,* 1999; Davis *et al.,* 2000; Achterberg *et al.,* 2003; Braungardt *et al.,* 2003; Sáinz *et al.,* 2004; Olías *et al.,* 2004; Cánovas *et al.,* 2007). The fresh-water inflow from these rivers reflects both significant seasonal and yearly variations. The marked seasonality of this inflow is characterized by a rainy season from October to March, which can reach up to 100 Hm³ per month, and a dry period from May to September, with an average monthly volume of less than 5 Hm³ (Borrego, 1992).

Method

Sediment traps

Sampling was conducted in February 2004 from sediment traps placed in December 2003 at 10 points along the Tinto and Odiel estuary. These traps were distributed as follows (Fig. 1A): four at the Tinto estuary (S2, S3, S4, and S5), four at the Odiel estuary (S6, S7, S8, and S9), one at the confluence channel of
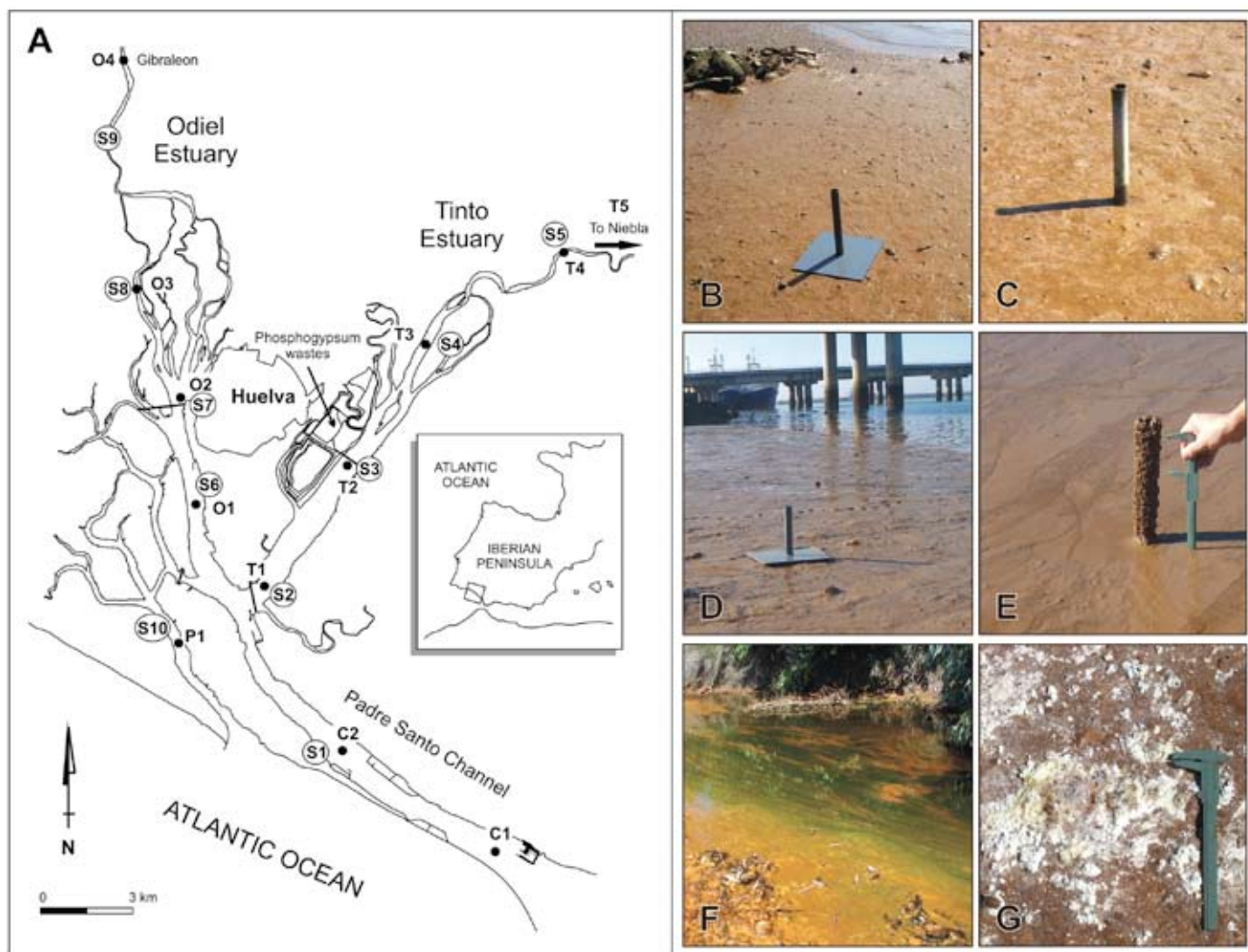
Figure 1. (A) General setting of the Tinto and Odiel estuaries with indications of the water sampling sites (Padre Santo Channel: C1 to C2, Tinto estuary: T1 to T5, Odiel estuary: O1 to O4, and Punta Umbría Channel: P1) and the sediment traps (Padre Santo Channel: S1, Tinto estuary: S2 to S5, Odiel estuary: S6 to S9, and Punta Umbría Channel: S10), (B) sediment trap at site S3 and (C) the trap at the moment of sampling, (D) sediment trap at site S7 and (E) the trap at the moment of sampling, (F) algal plants at the Tinto channel, and (G) sulphate-salt precipitates.
Figura 1. (A) Localización general del estuario de los ríos Tinto y Odiel con indicación de las muestras de agua (Canal del Padre Santo: C1 a C2, Estuario del Tinto: T1 a T5, Estuario del Odiel: O1 a O4, y Canal de Punta Umbría: P1) y las trampas de sedimento (Canal del Padre Santo: S1, Estuario del Tinto: S2 a S5, Estuario del Odiel: S6 S9, y Canal de Punta Umbría: S10), (B) trampa de sedimentos en el sitio S3, y (C) trampa en el momento del muestreo, (D) trampa de sedimentos en el sitio S7 y (E) trampa en el momento del muestreo, (F) algas en el canal del Tinto, y (G) sulfatos precipitados.

both estuaries (S1) and the last one at a point with no fluvial input, where tidal water was the main source of the sediments (S10). To ensure that the sediments collected belonged to recent deposition a group of 50 cm² PVC-square sediment traps were constructed and placed along the intertidal zone (Fig. 1B-E). The traps were placed in an active sedimentation zone located within the four hydrochemical zones that characterize the system (Carro *et al.,* 2011) so that the collected sediments should represent these hydrochemical conditions. The traps were fixed to the substrate by 20-cm-long cylindrical supports. The uppermost oxic sedimentary layer deposited on these traps was carefully removed with a plastic spoon and stored in acid-washed polypropylene bottles before being taken straight to the laboratory and kept at 4 °C. Only the oxic area of the sediment was analysed because it is this one which is in contact with the water and therefore the one that directly collects the environmental conditions during deposition.

Water pH and chlorinity

The hydrochemical features considered in this study were pH and chlorinity (used as salinity). Both parameters were measured ten times at 9 points located

close to the sediment traps (Fig. 1A). In addition, 3 water-sampling points were systematically measured at the Tinto (T5) and Odiel (O4) fluvial and marine (C1) end-members to characterize the water inputs reaching the estuary. A Crison pH-meter calibrated with pH 4 and 7 buffer solutions was used to determine pH values. Water chlorinity (Cl) was measured by means of ionic chromatography in the Central Research Services of the University of Huelva.

Grain size analysis

The particle-size distribution of the collected sediments was studied using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) belonging to the Geology Department of the University of Huelva. Particle diameters ranged between 0.02 µm and 2,000 µm, including sand (< 2000 – 63 µm), silt (63 – 4 µm) and clay (< 4 µm) groups. Each sample was measured in triplicate for 30 seconds, 10 seconds breaking and between 10% to 20% obscuration under moderately high pump and stirrer settings (1500 – 2000 rpm).

Geochemical analysis

The sediment samples for geochemical analysis were pre-dried at 60 °C in an oven until they reached a constant weight and then powdered in an agate mortar.

Chemical extraction and analysis

The sediment samples were subjected to "near total", or four-acid, digestion in the Activation Laboratories Ltd. (Actlabs) of Canada. This acid attack is the most vigorous used in geochemistry and is capable of decomposing most minerals, although certain heavy minerals such as zircon, sphene and magnetite may not be completely dissolved. Powdered sediment splits of 0.5 g were digested with HF (hydrofluoric), $HClO_4$ (perchloric), HNO_3 (nitric), and HCl (hydrochloric) acids. The solution was analysed by ICP-MS using a Perkin Elmer SCIEX ELAN 6100. International certified reference materials USGS GXR-1, GXR-2, GXR-4, and GXR-6 were analysed at the beginning and end of each batch of samples. Internal control standards were analysed every ten samples and a duplicate was run for every ten samples. Reference standards were within 10% of certified values. The precision of all analyses was always within 5%.

Organic carbon and sulphur

Duplicate samples of 0.2 g were used for organic carbon (C_{org}) and sulphur (S) determinations by means of dry combustion in an elemental analyser (LECO CNS2000, Central Research Services of the University of Huelva). Every duplicate sample was acidified with 1:1 HCl in excess until effervescence was not observed. The remaining acid was removed by the addition of 1 ml Milli-Q water and the sample was then heated to dryness at 50 °C. Intermediate standards of S and $CaCO_3$ were used every five samples, obtaining a standard deviation of < 0.6 for the whole process.

Results and discussion

Hydrochemical zonation of the estuary

The Padre Santo Channel (CPS) shows a decreasing trend in chlorinity from 14.49 g l^{-1} (point C1) to 9 g l^{-1} towards samples T1 (Tinto) and O1 (Odiel). This reach corresponds to a channel shared by the Tinto and Odiel estuaries and can be denoted as the marine (saline) estuary. From this zone to the inner estuary, there is a significant gradient evidenced by a sharp drop in Cl values from about 9.5 g l^{-1} to less than 3 g l^{-1} near to samples O3 and T3 (Fig. 2). These areas correspond to the estuarine (low-salinity brackish?) mixing zone. The zones above O3 and T3 show only slight marine influence and have nearly constant Cl values of less than 2 g l^{-1}. The water characteristics of these reaches depend considerably upon the fluvial inputs and can be denoted as the fluvial (riverine) estuary.

The estuarine zonation based on variations in pH accords well with that observed in the chlorinity gradients (Fig. 2). Thus, the marine estuary is characterized by homogeneous pH values ranging from 8 to 7.5, typical of marine conditions. The two estuarine mixing zones display a steep pH gradient reaching a minimum of 4.5. The pH of the Odiel fluvial estuary can drop to 4.24 (O4), whereas in the Tinto a pH of 3 is reached at the inner point of the fluvial estuary (T5).

In short, the Tinto and Odiel River estuaries display typical estuarine zonation based on chlorinity gradients. These allow the system to be divided into zones subject to fluvial and marine influence, together with those of intermediate estuarine features due to water mixing. In addition, another zonation based on pH gradients could be established, resulting from interactions between the acid fluvial water and slightly basic marine water.

Sedimentary features

According to the textural charts proposed by Folk (1954), the sediment deposited in the Padre Santo Channel (sample S1) was silty sand (Table 2). The ave-
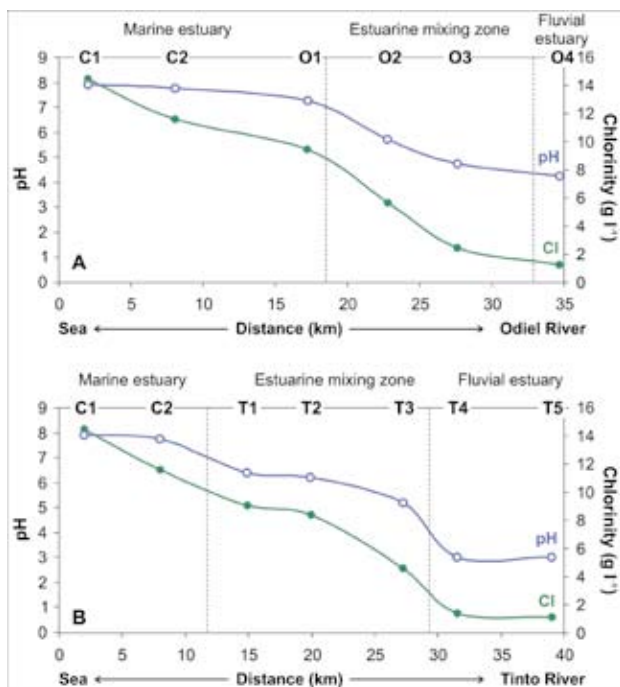
Figure 2. Estuarine zonation based on pH (open circle) and chlorinity (black circle) values (data from Table 1). (A) Odiel estuary, and (B) Tinto estuary.

Figura 2. Zonación estuarina basada en los valores de pH (círculo abierto) y clorinidad (círculo negro) (datos procedentes de la Table 1). (A) Estuario del Odiel, y (B) Estuario del Tinto.

Water samples	pH	Chlorinity (g l⁻¹)
C1	7.92	14.49
C2	7.74	11.62
T1	6.39	9.09
T2	6.22	8.40
T3	5.20	4.60
T4	3.02	1.39
T5	3.00	1.12
O1	7.26	9.45
O2	5.71	5.69
O3	4.75	2.48
O4	4.24	1.29
P1	7.54	12.71

**Table 1.** Average pH and chlorinity values in the estuarine water samples.
Tabla 1. Valores medios de pH y clorinidad de las muestras de agua del estuario.

rage sediment texture in the Tinto estuary was sandy silt, whereas in the Odiel estuary it ranged between sandy silt and silty sand. The higher sand contents co-

	CPS S1	Tinto estuary S2	S3	S4	S5	Odiel estuary S6	S7	S8	S9	Punta Umbría S10
Sedimentary features (%)										
Organic carbon	0.95	2.11	2.10	2.77	3.68	2.35	2.31	1.55	2.87	0.29
Sulphur	0.40	0.80	0.77	0.80	1.14	0.61	0.84	1.10	0.82	0.17
Clay	7.40	26.61	23.97	22.22	15.62	11.23	12.37	9.83	5.90	4.31
Silt	30.47	58.83	63.20	52.63	43.33	50.26	46.62	41.24	22.47	15.30
Sand	62.13	14.56	12.83	25.15	41.05	38.51	41.01	48.93	71.63	80.39
Rare earth content (ppm)										
La	18.84	10.40	8.50	3.34	11.75	30.12	5.13	8.94	12.86	7.61
Ce	28.32	23.36	17.58	8.80	22.96	49.30	13.25	18.43	26.96	11.94
Pr	4.82	4.11	3.09	1.73	3.64	8.29	2.62	3.47	4.47	1.80
Nd	18.65	18.42	13.05	7.78	15.41	33.27	12.26	13.86	17.61	6.87
Sm	3.90	4.83	3.25	2.17	3.54	7.70	3.66	3.66	4.48	1.29
Eu	0.82	1.10	0.66	0.49	0.71	1.56	0.78	0.64	0.75	0.30
Gd	3.73	4.88	3.14	2.16	2.75	7.71	3.99	3.17	3.56	1.24
Tb	0.49	0.79	0.49	0.39	0.42	1.12	0.68	0.47	0.52	0.15
Dy	2.81	4.41	2.93	2.31	2.28	6.28	3.85	2.89	3.04	0.77
Ho	0.61	1.02	0.63	0.50	0.48	1.33	0.84	0.54	0.57	0.16
Er	1.55	2.63	1.65	1.37	1.29	3.48	2.34	1.58	1.69	0.41
Tm	0.23	0.43	0.27	0.23	0.20	0.54	0.37	0.24	0.26	0.01
Yb	1.66	2.81	1.81	1.60	1.30	3.66	2.46	1.94	1.92	0.43
Lu	0.24	0.46	0.27	0.26	0.21	0.56	0.39	0.26	0.27	0.01
Total REE	86.66	79.64	57.32	33.11	66.94	154.91	52.60	60.10	78.98	32.97
(La/Gd)$_{NASC}$	0.82	0.35	0.44	0.25	0.70	0.64	0.21	0.46	0.59	1.00
(La/Yb)$_{NASC}$	1.10	0.36	0.45	0.20	0.87	0.80	0.20	0.45	0.65	1.73

Table 2. Sedimentary features (organic carbon and sulphur in wt% and textural characteristics in vol%) and rare-earth elements (in ppm) in the sediments of the estuarine system.
Tabla 2. Características sedimentarias (carbón orgánico y azufre en % peso y características texturales en %volumen) y tierras raras (en ppm) en los sedimentos del sistema estuarino.
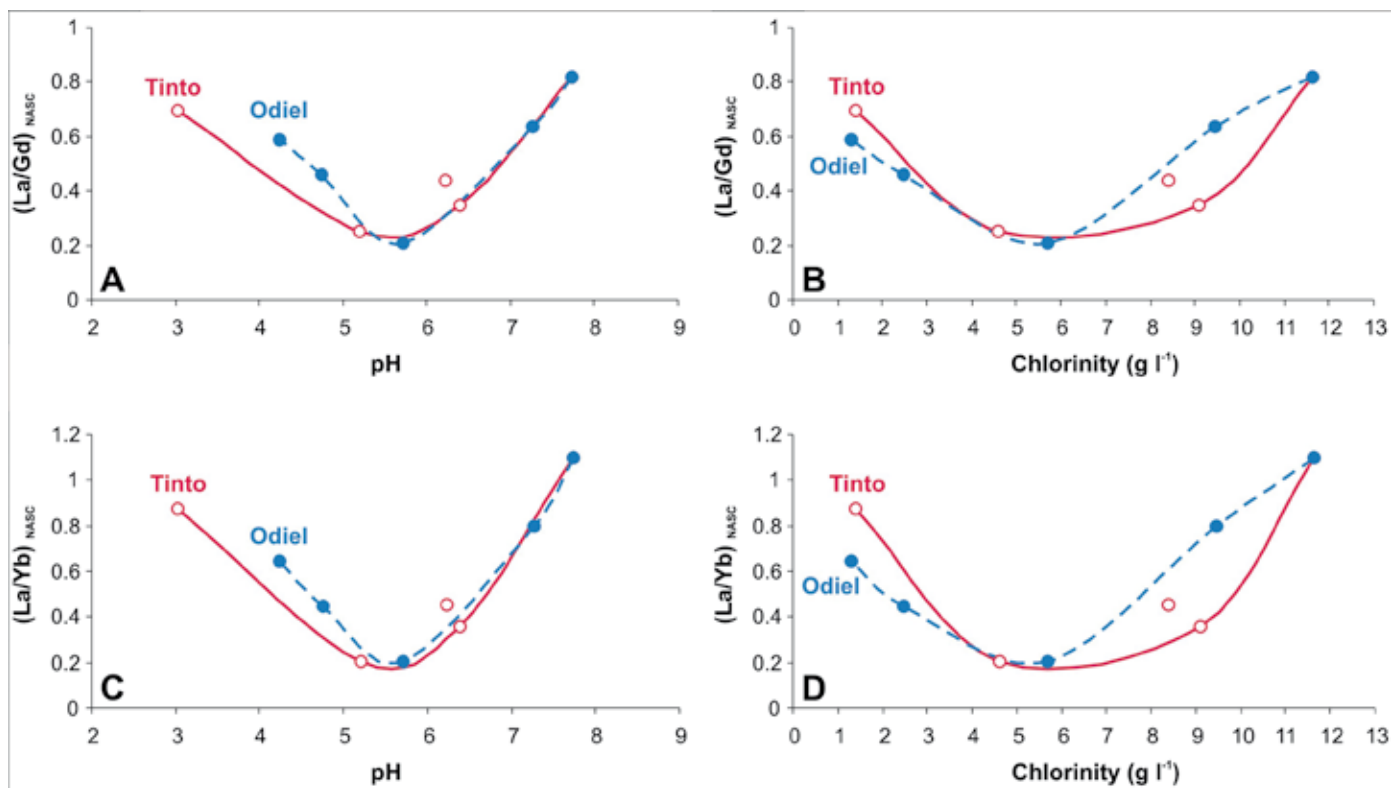
Figure 3. Plots of (La/Gd)$_{NASC}$ and (La/Yb)$_{NASC}$ ratios *vs* pH and chlorinity values for the Tinto and Odiel estuaries (NASC, North American Shale Composite, Taylor and McLennan, 1985). Sample S3 is represented by a single open circle (see text for explanation).
Figura 3. *Ratios de (La/Gd)$_{NASC}$ y (La/Yb)$_{NASC}$ vs. valores de pH y clorinidad para los estuarios de los ríos Tinto y Odiel (NASC, Taylor and McLennan, 1985). La muestra S3 se representa mediante un círculo abierto.*

rresponded to the fluvial and marine end-members, i.e. zones linked to fluvial (samples S5 and S9) and coastal (S1) inputs according to the bipolarity of the sedimentary contributions. Thus, high contents of fine-grained sediments were detected at the mixing zones of both estuaries, where saline mixing and acid neutralization processes take place.

The average content of organic carbon (C$_{org}$) and sulphur (S) in the River Tinto estuary is 2.66 ± 0.6 wt% and 0.86 ± 0.14 wt% respectively. They both display a similar trend of increasing concentration upstream towards the inner estuary. The C$_{org}$ and S contents of the Odiel River estuary, on the other hand, show an almost opposite tendency, with slightly lower values (C$_{org}$: 2.27 ± 0.79 wt% and S: 0.84 ± 0.18 wt%) than those observed in the Tinto estuary. This distinct evolution of the S and C contents probably results from textural differences. The highest C$_{org}$ concentration occurs in the sediments of the fluvial zone of both rivers (Table 2) and derives from the accumulation of algal debris developed during the spring and summer seasons (Fig. 1F). In turn, these zones show the highest S contents (Fig. 1G) where extensive sulphate salt precipitation usually takes place (Sanchez-España *et al.,* 2005). Conversely, the minimum S contents are found in the marine estuary (S1).

Hydrochemical influence on REE fractionation

The NASC-normalized (North American Shale Composite; Taylor and McLennan, 1985) ratios of La/Gd and La/Yb versus pH and Cl are shown in Figure 3. These two ratios have been selected as indicators of the relative enrichment or depletion between the LREE (La), MREE (Gd) and HREE (Yb) groups (Elderfield *et al.,* 1990; Borrego *et al.,* 2005). Thus, when these ratios are equal to unity it implies that there is no REE fractionation.

According to our results, most fractionation takes place at pH values of between 5.0 and 6.0 in the inner estuary of the Tinto and Odiel rivers, where the La/Yb < La/Gd indices (Fig. 3A and 3C) are less than 0.25. The least REE fractionation is observed, on the other hand, when pH is above 7.5 and below 4 (both ratios > 0.7), at the marine and fluvial estuary respectively, with the order where of La/Yb > La/Gd. The transitional sectors (the zones between pH values of 4-5 and 6-7) show fractionation indices ranging from 0.3 to 0.7 in both estuaries.

These same relationships have been observed with regard to the Cl range of the estuary (Fig. 3B and 3D). Thus, the lowest ratios occur where Cl varies from 4 to
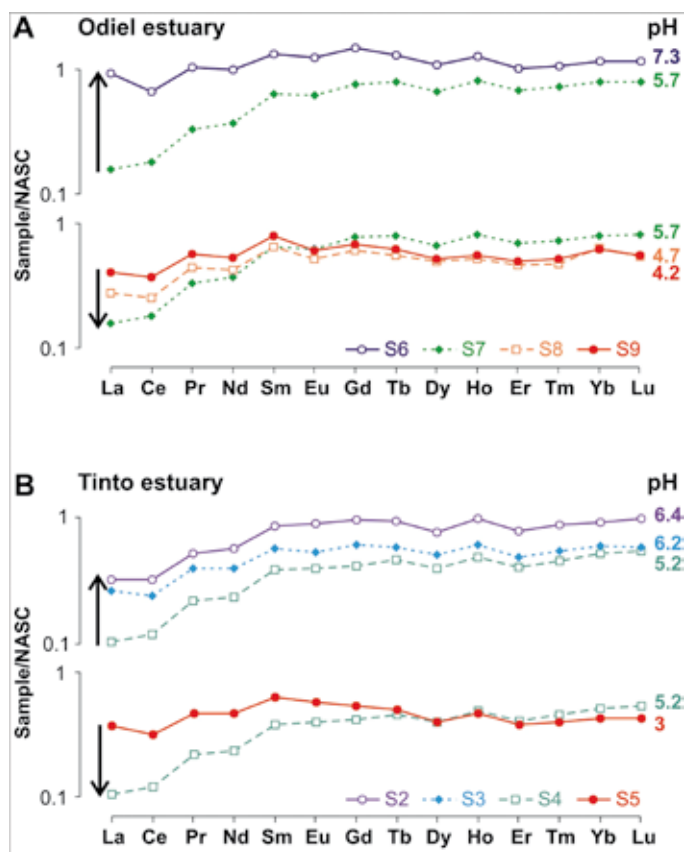
Figure 4. REE NASC-normalized pattern of the sediments from the Tinto (B) and Odiel (A) estuarine system together with the corresponding pH values. Arrows indicate how REE patterns evolve with increasing pH.

Figura 4. Patrón de REE NASC-normalizados de sedimentos procedentes del Tinto (B) y Odiel (A) sistema estuarine junto con los correspondientes valores de pH. Las flechas indican cómo evolucionan los patrones de REE con el incremento de pH.

8 g l^{-1}, at the inner estuarine mixing zone, where La/Yb < La/Gd. In the marine and fluvial estuary, where Cl is above 8 g l^{-1} and below 4 g l^{-1} respectively, minor REE fractionation occurs with La/Yb > La/Gd.

The anomalous high indices observed in sediments deposited at site S3 (Fig. 3, single open circle) are due to the influence of LREE-enriched waters coming from phospho-gypsum wastes dumped nearby (Borrego *et al.,* 2004). Nevertheless, although these sediments have a higher LREE content than that expected for this area, they still fall into the predicted pH and chlorinity range for the REE fractionation indices.

Discrepancy in REE fractionation patterns

On the application of geochemical indices, REE fractionation is clearly evidenced by the NASC-normalized pattern of the sediments (Fig. 4).

At the fluvial estuary of the Tinto and Odiel rivers (S5 and S9), where the lowest pH and Cl values occur,

the NASC-normalized patterns display a nearly flat but slightly MREE-enriched shape. These inner sediments should be denoted as riverine end-members, assuming that they have not undergone any fractionation, because REEs behave conservatively at pH 3–4, even when fresh Fe precipitates are present (Verplanck *et al.,* 2004), and there is no fractionation of REEs due to SO$_4$-complexes (Bozau *et al.,* 2004) either.

Towards the estuarine mixing zone these patterns change to one of significant depletion in LREEs and an almost flat tendency in MREEs and HREEs. LREE depletion in these sediments probably reflects their being retained preferentially in the dissolved phase when pH is lower than 6, whilst the MREEs, and to a lesser extent HREEs, are removed preferentially from the solution to the suspended matter and thence to the sediments due to their greater affinity for the solid phase (De Carlo *et al.,* 2000; Verplanck *et al.,* 2004). This phenomenon may also include the selective precipitation of MREEs and HREEs together with Fe oxydroxides, which occurs especially during the initial stages of acid neutralization (Carro *et al.,* 2011). In other well-studied estuaries unaffected by AMD, the dissolved LREEs are removed during estuarine mixing, mainly in the low-salinity brackish? zones (Elderfield *et al.,* 1990; Sholkovitz, 1995; Sholkovitz and Szymczak, 2000; Lawrence and Kamber, 2006). In this study, however, the influence of pH was found to cause this anomalous behaviour in LREE separation in the low-chlorinity zones.

When the water is completely neutralized (pH ~ 7) most of the MREEs and HREEs have already been included in the sediments. Most LREE separation occurs at pH > 7 (Lee *et al.,* 2002, De Carlo and Wen, 1998) by means of adsorption onto freshly formed Mn oxyhydroxides and so the downstream sediments deposited at the outer (S6) and the marine estuary display a nearly flat NASC-normalized pattern due to steady LREE enrichment.

The sediments collected at the nearest coastal area without fluvial influence (trap S10, see Fig. 1) show near-marine conditions (water point P1, pH of 7.54 and Cl of 12.71 g l^{-1}) and thus could be denoted as the marine end-member for this area. The REE features of these sediments are characterized by a NASC-normalized pattern slightly enriched in LREEs and MREEs, which accords with other near-shore sediments reported by Elderfield and Sholkovitz (1987) and Elderfield *et al.* (1990).

Conclusions

As a consequence of the acid fluvial waters that reach the estuary, this sedimentary environment does not
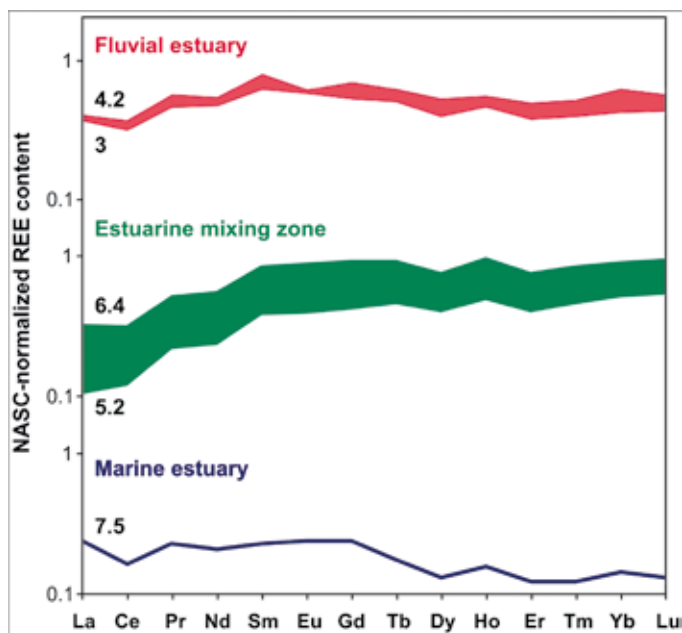
Figure 5. Three main NASC-normalized patterns of the Tinto and Odiel estuarine sediments according to the environmental conditions prevailing when they were deposited.
Figura 5. Tres patrones principales NASC-normalizado de los sedimentos del estuario del Tinto y el Odiel de acuerdo con las condiciones ambientales que prevalecían cuando fueron depositados.

behave in the way described in other estuaries that are unaffected by acid mine-drainage pollution. The fluvial and marine water mixing causes significant pH and chlorinity gradients inside the estuary, which involve two main processes: (i) dilution of the saline marine water, and (ii) acid neutralization of the fluvial water. This peculiarity leads to noticeable effects upon REE fractionation, which are evidenced in the sediments.

REE fractionation in the sediments of the Tinto and Odiel estuary can be synthesized in three NASC-normalized patterns according to the environmental conditions prevailing in the areas where they were deposited (Fig. 5):

— The fluvial estuarine sediments deposited under pH < 4 and Cl < 2 g l^{-1} conditions show a slightly MREE-enriched NASC-normalized pattern.

— The estuarine mixing zone involves steep gradients characterized by pH values ranging from 5 to 7 and chlorinity from 2 to 10 g l^{-1}. Under these conditions the sediments display a fractionation pattern of LREE depletion and a nearly flat trend for MREE and HREE.

— Once acid neutralization has finished at the outer estuary and pH increases to above 7 and chlorinity to above 10 g l^{-1}, the sediments of the marine estuary show a LREE and MREE-enriched pattern

with a slightly negative Ce anomaly typical of marine conditions (Elderfield *et al.,* 1990; Nath *et al.,* 1997; Lawrence and Kamber, 2006).

The close relationship between pH and REE content indicates that pH is the key variable controlling REE geochemistry in estuarine systems affected by acid mine drainage. Recognition of these patterns in the sedimentary record could help in the identification of acid-dominated periods in environments related with acid waters.

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References

Achterberg, E.P., Herzl, V.M.C., Braungardt, C.B. and Millward, G.E. 2003. Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. *Environmental Pollution,* 121, 283-292.

Borrego, J. 1992. *Sedimentología del estuario del río Odiel (Huelva, SO España).* Ph. D. Thesis, University of Sevilla.

Borrego, J., López-González, N., Carro, B. and Lozano-Soria, O. 2004. Origin of the anomalies in light and middle REE in sediments of an estuary affected by phosphogypsum wastes (south-western Spain). *Marine Pollution Bulletin,* 49, 1045-1053.

Borrego, J., López-González, N., Carro, B. and Lozano-Soria, O. 2005. Geochemistry of rare-earth elements in Holocene sediments of fan acidic estuary: Environmental markers (Tinto River Estuary, South-Western Spain). *Journal of Geochemistry Exploration,* 86, 119-129.

Borrego, J., Morales, J. A., De la Torre, M.L. and Grande, J.A., 2002. Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). *Environmental Geology,* 41, 785-96.

Borrego, J., Morales, J.A. and Pendón, J.G. 1995. Holocene estuarine facies along the mesotidal coast of Huelva, south-western Spain. In: W.F. Flemming, A. Bartholoma, Tidal Signatures in Modern and Ancient Sediments. *International Association of Sedimentologists, Special Publication,* 24, 151-170.

Borrego, J., Ruiz, F., González-Regalado, M.L., Pendón, J.G. and Morales, J.A. 1999. The Holocene transgression into the estuarine central basin of the Odiel River mouth (Cadiz Gulf SW Spain): lithology and faunal assemblages. *Quaternary Science Rev,* 18, 769-788.

Bozau, E., Leblanc, M., Seidel, J.L. and Stärk, H.J. 2004. Light Rare Earth Elements enrichment in an acidic mine

lake (Lusatia, Germany). *Applied Geochemistry,* 19, 261-271.

Braungardt, C.B., Achterberg, E.P., Elbaz-Poulichet, F. and Morley, N.H. 2003. Metal geochemistry in a mine-polluted estuarine system in Spain. *Applied Geochemistry,* 18, 1757-1771.

Cánovas, C.R., Olías, M., Nieto, J.M., Sarmiento, A.M. and Cerón, J.C. 2007. Hydrogeochemical characteristics of the Tinto and Odiel Rivers (SW Spain). Factors controlling metal contents. *Science of the Total Environment,* 373, 363-382.

Carro, B., Borrego, J., López-González, N., Grande, J.A., Gómez, T., De la Torre, M.L. and Valente, T. 2011. Impact of acid mine drainage on the hydrogeochemical characteristic of the Tinto-Odiel Estuary (SW Spain). *Journal of Iberian Geology,* 37, 87-96.

Dabrio, C.J., Zazo, C., Goy, J.L., Sierro, F.J., Borja, F., Lario, J., González, J.A. and Flores, J.A. 2000. Depositional history of estuarine infill during the last postglacial transgression (Gulf of Cadiz, Southern Spain). *Marine Geology,* 162, 381-404.

Davis, R.A., Welty, A.T., Borrego, J., Morales, J.A., Pendón, J.G. and Ryan, J.G. 2000. Rio Tinto estuary (Spain): 5000 years of pollution. *Environmental Geology,* 39, 1107-1116.

De Carlo, E.H. and Wen, X.Y. 1998. The influence of redox reactions on the uptake of dissolved Ce by suspended Fe and Mn oxide particles. *Aquatic Geochemistry,* 3, 357-389.

De Carlo, E.H., Wen, X.Y. and Cowen, J.P. 2000. Rare earth element fractionation in hydrogenetic Fe-Mn crusts: the influence of carbonate complexation and phosphatization on Sm/Yb ratios. In: C.R. Glenn, L. Prevot-Lucas, J. Lucas. *Marine Authigenesis: From Global to Microbial. SEPM Special,* 64, 271-285.

Elbaz-Poulichet, F. and Dupuy, C. 1999. Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). *Applied Geochemistry,* 14, 1063-1072.

Elbaz-Poulichet, F., Morley, N.H., Cruzado, A., Velasquez, Z., Achterberg, E.P. and Braungardt, C.B. 1999. Trace metal and nutrient distribution in an extremely low pH (2.5) river–estuarine system, the Ría de Huelva (south-west Spain). *Science of the Total Environment,* 227, 73-83.

Elderfield, H. 1988. The oceanic chemistry of the rare-earth elements. *Phil. Trans. Royal Society London A,* 325, 105-126.

Elderfield, H. and Sholkovitz, E.R. 1987. Rare earth elements in the pore waters of reducing nearshore sediments. *Earth and Planetary Science Letters,* 82, 280-288.

Elderfield, H., Upstill-Goddard, R. and Sholkovitz, E.R. 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta,* 54, 971-991.

German, C.R. and Elderfield, H. 1989. Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin. *Geochimica et Cosmochimica Acta,* 53, 2561-2571.

Goldstein, S.J. and Jacobsen, S.B. 1988. REE in the Great-Whale river estuary, northwest Quebec. *Earth and Planetary Science Letters,* 88, 241-252.

Gouveia, M.A., Araújo, M.F.D. and Dias, J.M.A. 1993. Rare earth element distribution in sediments from the Minho river and estuary (Portugal) – a preliminary study. *Chemical Geology,* 107, 379-383.

Haley, B.A., Klinkhammer, G.P. and McManus, J. 2004. Rare earth elements in pore waters of marine sediments. *Geochimica et Cosmochimica Acta,* 68, 1265-1279.

Hoyle, J., Elderfield, H., Gledhill, A. and Greaves, M. 1984. The behaviour of the rare earth elements during mixing of river and sea waters. *Geochimica et Cosmochimica Acta,* 48, 143-149.

Hudson-Edwards, K.A., Schell, C. and Macklin, M. 1999. Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. *Applied Geochemistry,* 14, 1015-1030.

Johannesson, K.H., Lyons, W.B., Yelken, M.A., Gaudette, H.E. and Stetzenbach, K.J. 1996. Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: complexation behaviour and middle rare-earth element enrichments. *Chemical Geology,* 133, 125-144.

Johannesson, K.H. and Zhou, X. 1999. Origin of middle rare earth element enrichments in acid waters of a Canadian High Artic lake. *Geochimica et Cosmochimica Acta,* 61, 153-165.

Klinkhammer, G.P., Elderfield, H., Edmond, J.M. and Mitra, A., 1994. Geochemical implications of rare earth element patterns in hydrothermal fluids from mid-ocean ridges. *Geochimica et Cosmochimica Acta,* 58, 5105-5113.

Lawrence, M.G. and Kamber, B.S. 2006. The behaviour of the rare earth elements during estuarine mixing – revisited. *Marine Chemistry,* 100, 147-161.

Leblanc, M., Morales, J.A., Borrego, J. and Elbaz-Poulichet, E. 2000. 4,500-Years-Old mining pollution in southwestern Spain: long-term implications for modern mining pollution. *Economic Geology,* 95, 655-662.

Lee, G., Bigham, J.M. and Faure, G. 2002. Separation of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry,* 17, 569-581.

Leistel, J.M., Marcoux, E., Thiéblemont, D., Quesada, C., Sánchez, A., Almodóvar, G.R., Pascual, E. and Sáez, R. 1998. The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt - Review and preface to the Thematic Issue. *Mineralium Deposita,* 33, 2-30.

Leybourne, M.I., Goodfellow, W.D., Boyle, D.R. and Hall, G.M. 2000. Rapid development of negative Ce anomalies in surface waters and contrasting REE patterns in groundwaters associated with Zn-Pb massive sulphide deposits. *Applied Geochemistry,* 15, 695-723.

López-González, N., Borrego, J., Morales, J.A., Carro, B. and Lozano-Soria, O. 2006. Metal fractionation in oxic sediments of an estuary affected by acid mine drainage (south-western Spain). *Estuarine Coastal and Shelf Science,* 68, 297-304.

Martin, J.M. and Meybeck, M. 1976. Elemental mass-balance of material carried by major world rivers. *Marine Chemistry,* 7, 173-206.

Nath, B.N., Bau, M., Rao, B.R. and Rao, C.M. 1997. Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone. *Geochimica et Cosmochimica Acta,* 61, 2375-2388.

Nelson, C.H. and Lamothe, P.J. 1993. Heavy metal anomalies in the Tinto and Odiel river and estuary system, Spain. *Estuaries,* 16, 496-511.

Nozaki, Y., Lerche, D., Alibo, D.S. and Snidvongs, A. 2000. The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. *Geochimica et Cosmochimica Acta,* 64, 3983-3994.

Olías, M., Nieto, J.M., Sarmiento, A.M., Cerón, J.C. and Cánovas, C. 2004. Seasonal water quality variations in a river affected by acid mine drainage: The Odiel River (South West Spain). *Science of the Total Environment,* 333, 267-281.

Pendón, J.G. and Morales, J.A. 1997. Facies deposicionales Holocenas en la Costa de Huelva: Propuesta de nomenclatura para litofacies estuarinas. *Cuadernos de Geología Ibérica,* 22, 165-190.

Ramesh, R., Ramanathan, A.L., James, R.A., Subramanian, V., Jacobsen, S.B. and Holland, H.D. 1999. Rare earth elements and heavy metal distribution in estuarine sediments of east coast of India. *Hydrobiologia,* 397, 89-99.

Sáez, R., Pascual, E., Toscano, M. and Almodóvar, G.R., 1999. The Iberian Type of volcano-sedimentary massive sulphide deposits. *Mineralium Deposita,* 34, 549-570.

Sáinz, A., Grande, J.A. and De la Torre, M.L. 2004. Characterisation of heavy metal discharge into the Ria of Huelva. *Environment International,* 30, 557-566.

Sánchez-España, J.S., Pamo, E.L., Santofimia, E., Aduvire, O., Reyes, J. and Barettino, D. 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry,* 20, 1320-1356.

Sholkovitz, E.R. 1993. The geochemistry of rare-earth elements in the Amazon River estuary. *Geochimica et Cosmochimica Acta,* 57, 2181-2190.

Sholkovitz, E.R. 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquatic Geochemistry* 1, 1-34.

Sholkovitz, E.R. and Elderfield, H. 1988. The cycling of dissolved rare-earth elements in Chesapeake Bay. *Global Geochemical Cycles,* 2, 157-176.

Sholkovitz, E.R. and Szymczak, R. 2000. The estuarine chemistry of rare earth elements: comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. *Earth and Planetary Science Letters,* 179, 299-309.

Smedley, P.L., 1991. The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. *Geochimica et Cosmochimica Acta,* 55, 2767-2779.

Taylor, S.R. and McLennan, S.M. 1985. *The Continental Crust: Its Composition and Evolution.* Blackwell, Oxford.

Van Geen, A., Adkins, J.F., Boyle, E.A., Nelson, C.H. and Palanques, A. 1997. A 120 yr record of widespread contamination from mining of the Iberian pyrite belt. *Geology,* 25, 291-294.

Van Middlesworth, P. E. and Wood, S.A. 1998. The aqueous geochemistry of the rare earth elements yttrium: Part 7. REE, Th and U contents in thermal springs associated with the Idaho batholith. *Applied Geochemistry,* 13, 861-884.

Verplanck, P.L., Nordstrom, D.K., Taylor, H.E. and Kimball, B.A. 2004. Rare earth element partitioning between hydrous ferric oxides and acid mine water during iron oxidation. *Applied Geochemistry,* 19, 1339-1354.

Zhang, C., Wang, L., Zhang, S. and Li, X. 1998. Geochemistry of rare earth elements in the mainstream of the Yangtze River, China. *Applied Geochemistry,* 13, 451-462.