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Temporal variations of REE in several AMD sources of the Odiel River (SW Spain)

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Abstract

Waters affected by acid mine drainage (AMD) can contain high concentrations of rare earth elements (REE) which have a great interest not only by its application as tracers in hydrogeochemical processes but also as a potential economic resource. The Iberian Pyrite Belt (IPB) is rich in sulfide deposits which have been exploited intensively since ancient times, generating numerous AMD discharges. This work studies the REE content in five different AMD sources located in the upper reach of the Odiel River (SW Spain). The concentration of REE in these sources ranged from 113 to 7208 ppb. Differences in NASC-normalized REE patterns were observed among AMD sources that remained constant along the year despite the variability in REE concentrations, being lower during the rainy season due to dilution processes.

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Keywords: Iberian Pyrite Belt (IPB); sulphides; rare earth elements (REE)

1. Introduction

The Iberian Pyrite Belt (IPB) constitutes one of the most important metallogenic provinces of the world, with giant and supergiant polymetallic massive sulphide deposits, which have been exploited intensively since ancient times, generating a huge problem of water resources contamination by acid mine drainage (AMD) with highly-toxic concentrations of metals and metalloids.

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The Odiel River basin (SW Spain) drains partially materials belonging to the IPB and is deeply affected by AMD. At its source, the river is clean but along a 7 km-long reach receives five discharges of acid mine waters: Concepción, San Platón, Esperanza, Poderosa and the Agrio River coming from the Riotinto mines, causing the progressive deterioration of the river^{1,2}.

There is a great interest in studying the behavior of rare earth element (REE) in acid mine sources in order to investigate: 1) the possibility of recovery of these elements and 2) its use as tracers of hydrogeochemical processes³. The present work is focused on the REE content and NASC-normalized patterns of these acid discharges, as well as their seasonal variations.

2. Methodology

From March 2014 to February 2016 several samplings were performed in the acid discharges of the mines: Concepción, San Platón, Esperanza, Poderosa and Riotinto. The highest number of observations corresponds to the Agrio River (n=13) which collects drainage from Riotinto while the lowest were obtained from Poderosa mine (n=8). The samples were filtered (through 0.2 µm), acidulated to pH <2 and refrigerated until analysis by ICP-AES for main elements and ICP-MS for trace elements and REE. Temperature, pH, electrical conductivity and oxidation-reduction potential (ORP) were measured in situ using an equipment CRISON model MM40+. North-American Shale Composite (NASC)-normalized REE patterns⁴ were obtained and the Ce- and Eu-anomalies were calculated from the expressions (1) and (2), where the subscript 'SN' indicates shale-normalised values.

$$Ce / Ce^* = Ce_{SN} / \sqrt{La_{SN} Pr_{SN}} \quad (1)$$

$$Eu / Eu^* = Eu_{SN} / \sqrt{Sm_{SN} Gd_{SN}} \quad (2)$$

3. Results and discussion

Values of pH in AMD sources showed low variability (between 1.48 and 3.51). The Agrio River showed the highest discharge values (average close to 200 L/s) and highest level of contaminants (concentrations up to 2048 mg/L of Fe, 622 mg/L of Al, 324 mg/L of Zn, etc.). The rest of AMD sources showed lower average discharge values (between 0.5 and 10 L/s). Average values of electrical conductivity, that reveals the polluting potential of each discharge, ranged from 2.1 mS/cm in Concepción mine to 10.2 mS/cm in the Agrio River. A more detailed information about hydrochemical characteristics of each AMD source can be found². Concerning REE concentrations, the highest average value (3974 ppb) was observed in San Platón mine, although the maximum value was recorded in the Agrio River (7208 ppb). High REE concentrations were also observed in Poderosa mine (average of 2073 ppb), while noticeably lower values were recorded in drainages from Concepción and Esperanza mines (close to 400 ppb, Table 1).

Table 1. Mean values and range (between parenthesis) obtained in the sampling points

		ΣREE (ppb)	(La/Gd) _{SN}	(Gd/Yb) _{SN}	(La/Yb) _{SN}	Ce/Ce*	Eu/Eu*
Concepción	A	388 (113 - 986)	0.60 (0.53-0.69)	1.82 (1.63--1.95)	1.09 (0.93-1.31)	1.02 (0.98-1.09)	0.67 (0.57-0.81)
San Platon	C	3974 (3339-4730)	0.54 (0.50-0.57)	4.67 (4.20-5.12)	2.54 (2.24-2.76)	0.96 (0.94-1.00)	0.79 (0.61-0.89)
Esperanza	D	402 (129-697)	0.31 (0.24-0.39)	1.68 (1.55-1.85)	0.51 (0.40-0.72)	0.96 (0.92-1.00)	0.67 (0.61-0.87)
Poderosa	E	2073 (822-4620)	0.38 (0.35-0.40)	2.90 (2.63-3.15)	1.11 (1.00-1.25)	0.99 (0.96-1.09)	0.59 (0.48-0.69)
Agrio	F	3329 (979-7208)	0.28 (0.24-0.36)	1.69 (1.54-1.82)	0.48 (0.41-0.65)	1.16 (1.10-1.26)	0.79 (0.66-0.95)

As with main elements², REE concentration follows a seasonal pattern with higher values during the dry season while dilution by runoff is observed during the rainy season. Nevertheless, AMD from San Platón mine showed a

low variability due to the proximity of sampling point to the AMD emergence while the rest are much further away and thus, more influenced by mixing processes with runoff (Fig. 1).

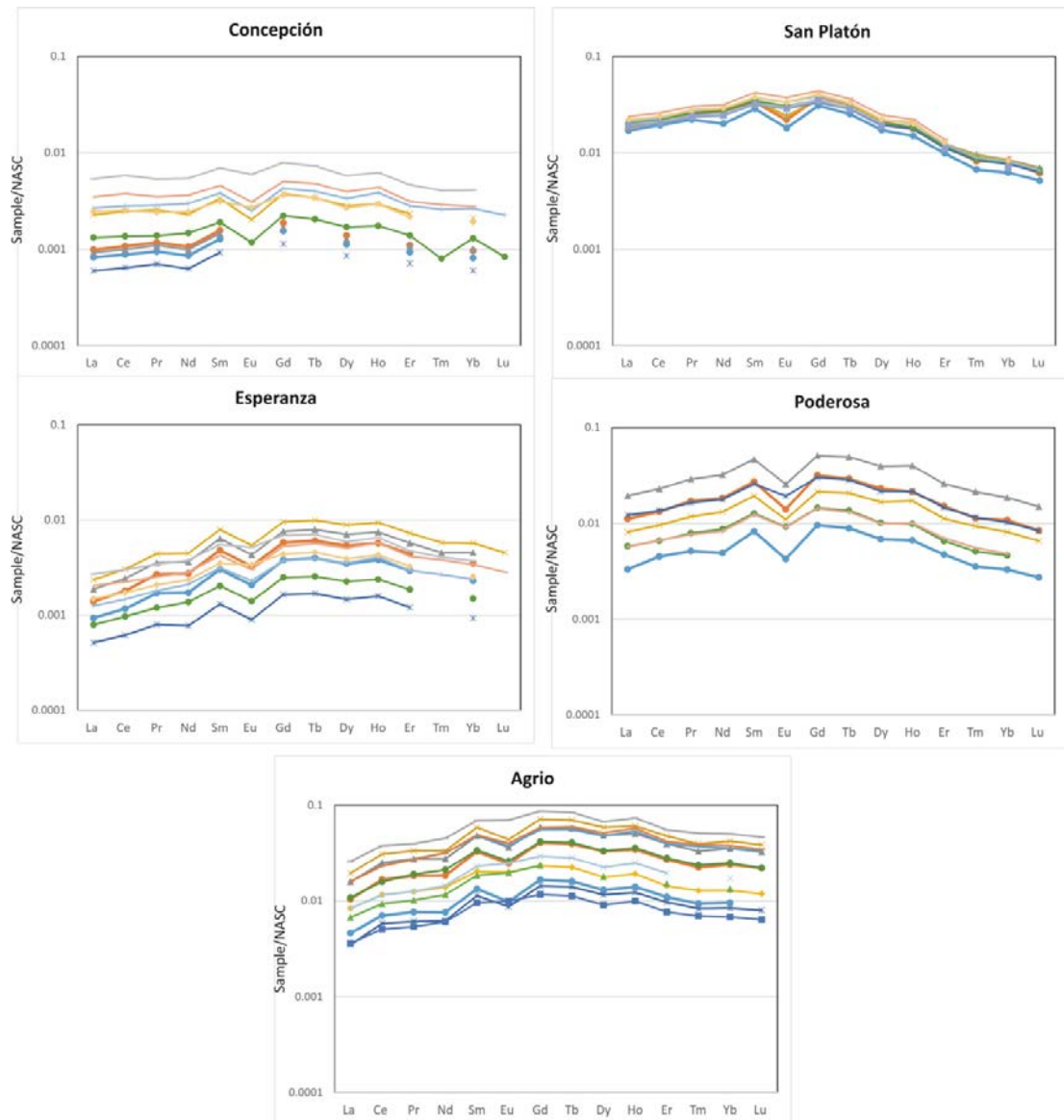


Fig. 1. NASC-normalized REE patterns for each sampling point

All AMD sources showed enrichment in middle REE (MREE), commonly observed in AMD waters⁵, although some differences can be observed among them (Fig. 1). Thus, AMD from Concepción mine stand out for displaying a lower MREE enrichment, with an average value of the $(La/Gd)_{SN}$ of 0.60 and a slightly lower heavy REE (HREE) content than that observed for light REE (LREE), with a $(La/Yb)_{SN}$ ratio of 1.09. In addition to the low variability observed, AMD from San Platón is also notable by its low HREE content (Fig. 1), with a $(Gd/Yb)_{SN}$ ratio of 4.67. The NASC-normalized REE pattern observed in Poderosa mine is quite similar to that recorded in Concepción although a greater enrichment in MREE is observed as evidenced by the lower value of the $(La/Gd)_{SN}$ ratio and the higher $(Gd/Yb)_{SN}$ one (Table 1). In the same way, AMD from Poderosa displayed the greater negative Eu anomaly

(Eu/Eu* of 0.59). Finally, the NASC-normalized REE pattern observed in Esperanza mine is comparable to that observed in the Agrio River, although the latter can be distinguished by a greater positive Ce anomaly (Ce/Ce^* de 1.16).

On the other hand, it is striking the absence of changes in the NASC-normalized REE patterns of each sampling point despite the seasonal variations observed in the AMD sources. Figure 2 evidences that $(Gd/Yb)_{SN}$ and Ce/Ce^* ratios hardly change despite the increasing REE concentrations. This fact suggests that REE behave conservatively in this environment, at least in the pH range studied (below 3.5) and seem to be only affected by dilution processes during the rainy season.

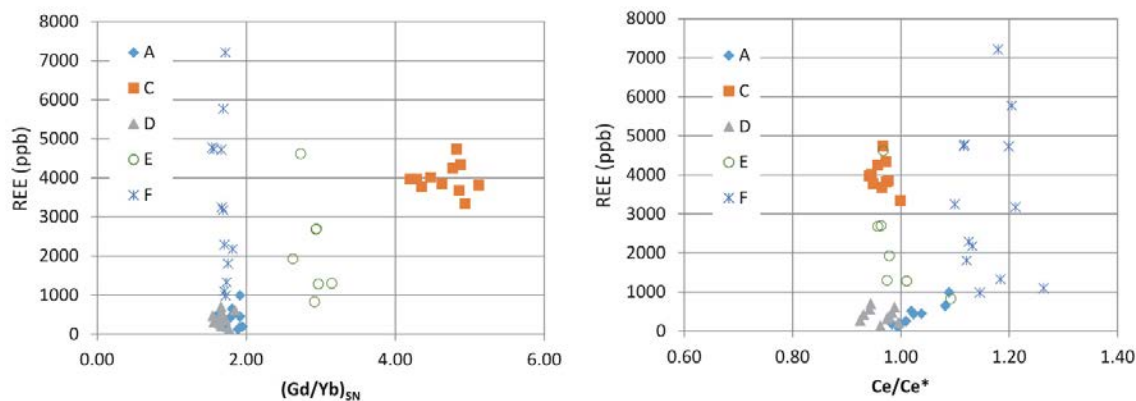


Fig. 2. Variation of the ratios $(Gd/Yb)_{SN}$ and Ce/Ce^* versus $\sum REE$ concentrations (A: Concepción, C: San Platón, D: Esperanza, E: Poderosa and F: Agrio River)

4. Conclusions

The different AMD sources that deteriorate the quality of the Odiel River headwaters show significant REE concentrations, ranging from 113 to 7208 ppb. The highest average values are recorded in San Platón mine although the highest level of pollutants is observed in the Agrio River. Differences in NASC-normalized REE patterns were observed among AMD sources and remained constant along the year, although a decrease in concentration is observed during the rainy season. This seems to indicate that REE behave conservatively in the pH range studied (below 3.5), and dilution during the rainy season turns to be the only process that affect its concentration.

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