REE behavior during evaporative precipitation in a severely affected-AMD creek (SW Spain)

Manuel Olías, Carlos R. Cánovas, Rafael Pérez-López, Francisco Macías, Julia Riera, José Miguel Nieto

Department of Earth Sciences, Faculty of Experimental Sciences, University of Huelva, Campus El Carmen s/n, 21071 Huelva, Spain
manuel.olias@dgyp.uhu.es, carlos.ruiz@dgeo.uhu.es, rafael.perez@dgeo.uhu.es, francisco.macias@dgeo.uhu.es, nieto@uhu.es

Abstract

The Iberian Pyrite Belt (IPB) covers a vast part of the SW of Spain and Portugal. This region is rich in sulfide deposits which have been exploited intensively. As a consequence, there is a large number of sources of acid mine drainages, characterized by very extreme pH conditions and high pollution load. Waters affected by acid mine drainage (AMD) can contain high concentrations of rare earth elements (REE) which have a great interest from the scientific and economic point of view. This work is focused on the REE behavior during evaporative concentration during the summer along the Agrio River, a small stream deeply affected by AMD coming from the Río Tinto mines. The pH varied from around 2.8 to 1.5 and the electrical conductivity from 5.8 to 15 mS/cm. Concentration of ∑REE varied from around 1.3 mg/L to around 5.3 mg/L at the end of the summer. In September, with the lowest discharges, most elements showed an increase along the reach (Al 12%, Zn 8%, Cu 4%) due to evaporation. REE also showed an enrichment, which varied from 7% (La to Nd) up to 10-11% (Ho to Lu), which seems to indicate a slightly higher affinity of the evaporative salts for LREE in relation to HREE. Although REE concentrations varied widely between the different samplings, the NASC-normalized patterns are very constant, showing a negative Eu anomaly together with the enrichment of MREE typical of AMD-affected waters. The amount of dissolved ∑REE transported by this small river was surprising, varying between 9 kg/day in September and 26 kg/day in May.

Key words: sulphides, rare earth elements, acid mine drainage, Iberian Pyrite Belt

Introduction

Nowadays, there is a great interest in studying the behavior of rare earth elements (REE) in acid mine drainage (AMD)-affected rivers with two main goals: 1) the possibility of recovery of these elements (Ayora et al., 2015) and 2) its use as tracers of hydrogeochemical processes (Noack et al., 2014). The Iberian Pyrite Belt is rich in sulphide deposits which have been exploited intensively since the mid-nineteeth century (Olías y Nieto, 2015), generating a huge problem of river contamination by AMD with highly-toxic concentrations of metals and metalloids.

Although the behavior of REE during Fe and Al oxyhydroxysulphates precipitation has received considerable attention (e.g. Gimeno et al., 2000; Delgado et al., 2012) their behavior during evaporative salt precipitation has been less studied. The main goal of this work is to study the variations of REE contents in a severely affected-AMD stream.

Methods

We have sampled four points along a small stream (~5 km long) deeply affected by AMD, the Agrio River coming from the Río Tinto mines, during spring and summer (March, May, July and September) 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+.

Results and conclusions

The river discharge decreased from approximately 200 L/s in March to 18 L/s in September. Concomitantly, the pH varied from around 2.8 to 1.5 and the electrical conductivity from 5.8 to 15 mS/cm (Fig. 1). Maximum concentrations were reached in September (up to 2048 mg/L of Al, 395 mg/L of Zn, 173 mg/L of Cu, etc.), except for Fe, whose maximum values (up to 693 mg/L) were reached in July. Concentration of ∑REE varied from around 1.3 mg/L (March) to around 5.3 mg/L (September), when there was a strong precipitation of evaporative salts over the river banks.

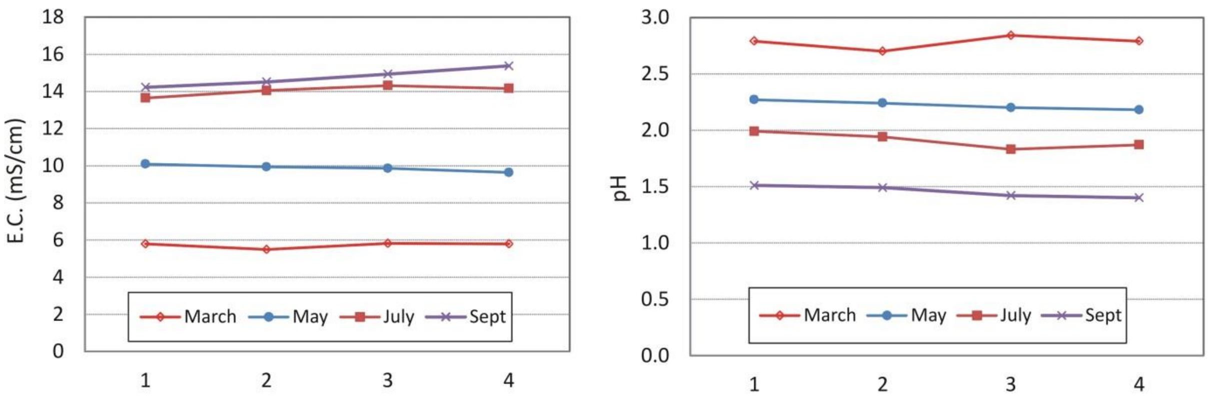

Figure 1 *Variation of electrical conductivity (E.C.) and pH along the reach from upstream (point 1) to downstream (point 4)*

From March to July, concentration of most elements, including REE, remained constant along the reach, showing a conservative behavior. However, Fe concentration diminished 17% in March, 10% in May and 12% in July indicating Fe precipitation. Arsenic also showed a decrease along the reach due to coprecipitation/adsorption processes.

In September, with the lowest discharges, most elements showed an increase along the reach (Al 12%, ∑REE 8%, Zn 8%, Cu 4%) due to evaporation. Concentration of Fe and As did not vary along the reach, showing a balance between precipitation and evaporative concentration. REE also showed an enrichment in waters, which varied from 7% (La to Nd) up to 10-11% (Ho to Lu), which seems to indicate a slightly higher affinity of the evaporative salts for LREE in relation to HREE. On the other hand, the amount of dissolved REE transported by this small river was surprising, varying between 9 kg/day in September and 26 kg/day in May.

Although REE concentrations varied widely between the different samplings, the NASC-normalized patterns are very constant (Fig. 2). It can be seen a negative Eu anomaly together with the enrichment of MREE typical of AMD-affected waters (Pérez-López et al., 2010).

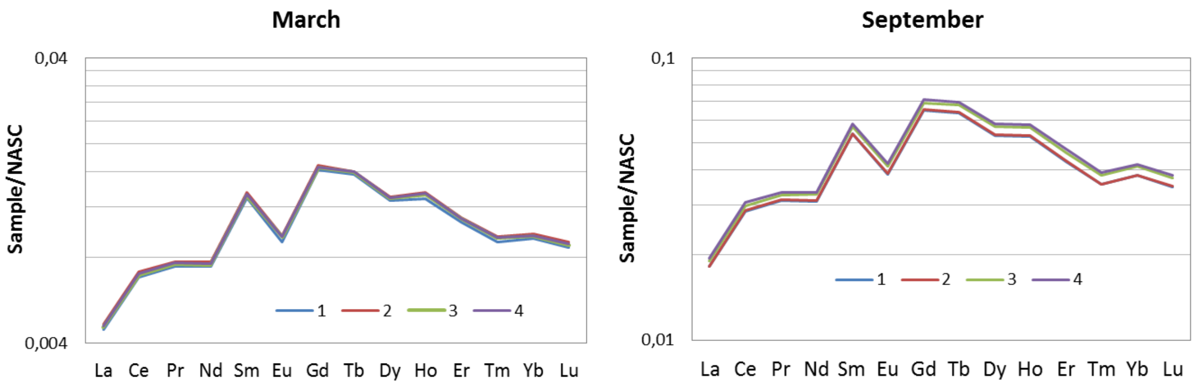

Figure 2 *NASC-normalized REE patterns of two samplings along points nº1 (upstream) to nº4 (downstream). Note the different Y-scale.*

The study on the mineral precipitation pathways that control REE mobility in AMD environments is of paramount importance in the search for possible sustainable and beneficial resources.In this sense, the high REE loads observed in this study and the longevity of AMD processes turn this polluted water course into a promising resource.

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References

Ayora C, Torres E, Lozano A, Macías F, Carrero S, Pérez-López R, Nieto JM (2015) Acid Mine Drainage: a possible source of Rare Earth Elements. Goldschmidt 2015 (Praga, Rep. Checa). Abs. vol., p. 153

Delgado J, Pérez-López R, Galván L, Nieto JM, Boski T (2012) Enrichment of rare earth elements as environmental tracers of contamination of acid mine drainage in salt marshes: A new perspective. Mar. Pollut. Bull. 64: 1799-1808

Gimeno MJ, Auqué LF, Nordstrom DK (2000) REE speciation in low-temperature acidic waters and the competitive effects of aluminium. Chem. Geol. 165: 167-180

Noack CW, Dzombak DA, Karamalidis AK (2015) Rare earth element distributions and trends in natural waters with a focus on groundwater. Environ Sci Technol 48: 4317-4326

Olías M, Nieto JM (2015). Background conditions and mining pollution throughout history in the Río Tinto (SW Spain). Environments 2: 295-316

Pérez-López R, Delgado J, Nieto JM, Marquez-García B (2010). Rare earth element geochemistry of sulphide weathering in the Sao Domingo mine area (Iberian Pyrite Belt): A proxy for fluid rock-interaction and ancient mining pollution Chem Geol 276: 29-40