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Mineralogy and geochemistry of a clogged mining reservoir affected by historical acid mine drainage in an abandoned mining area

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A B S T R A C T

The present study is focused on a water reservoir that is under the influence of AMD in the historic mining area of Riotinto (SW Spain). Transport of particulate matter and chemical precipitation within the reservoir has caused its clogging. Hydrochemical, geochemical and mineralogical characterization allowed to assess the degree of contamination by trace elements.

The results indicate high average concentrations of metals and metalloids in water and sediments. The sediments are strongly enriched in As, Pb, Cu, and Zn, which occur with concentrations > 1000 mg/kg. Highest accumulation was observed for As and Pb, which gave enrichment factors in the range 358–471, indicative of extreme pollution. Geochemical trends show strong correlation between major elements, including Fe and Al, mobilized from the source material.

Mineralogy of the clogging material showed a short-range of spatial variability. Among the newly formed phases jarosite and goethite are the most abundant. They are especially concentrated in the clay size fraction. Combining results about chemistry of the sediments and mineral distribution suggests that As is being retained by both clay and iron-rich minerals. Furthermore, results indicate that jarosite forms directly from sulphide oxidation, whereas goethite may result from transformations undergone in the reservoir.

1. Introduction

One of the most serious problems of environmental contamination is the formation of acid mine drainage, globally known by the acronym AMD. The severity of the problem lies in its intensity and magnitude, associated with a generally irreversible character (Carro et al., 2011; Grande et al., 2013a). This process results from sulphide oxidation, in particular iron sulphides such as pyrite (FeS_2). The reactions occur when sulphide minerals are exposed to weathering, generating acidity and sulphates, together with the mobilization of trace elements. Detailed information about the complex chain of biotic and abiotic reactions that involve the oxidative dissolution of pyrite can be found in the classical references of McKibben and Barnes (1986), Evangelou and Zhang (1995), Nordstrom and Southam (1997), Nordstrom and Alpers (1999), and Keith and Vaughan (2000).

As a consequence of the global process, the affected water systems may present pH values less than 2.5 and very high concentrations of sulphate and metals, which lead to strong degradation of the environment (*e.g.*, Grande, 2011; Gray, 1996).

AMD is a global problem, with severe consequences in metallogenetic provinces with sulphides around the world. It represents a dangerous type of contamination with consequences for health, especially if it reaches water reservoirs. The presence of high contents of metals and arsenic is a typical problem that can be found in many abandoned mining areas world widely (Borba and Figueiredo, 2003; Cheng et al., 2009; Iskandar et al., 2012).

In the SW of Europe, major problems occur in the Iberian Pyrite Belt (IPB) (Fig. 1), which is known worldwide by the intensity of the AMD processes, related with the exploitation of sulphides (Carro et al., 2011; Elbaz-Poulichet et al., 2001; Grande et al., 2013a; Sánchez-España et al., 2005). The climate conditions together with the geology and mining history have promoted a scenario where numerous water reservoirs have signs of contamination by AMD (Grande et al., 2013b). The present study was performed in one of these sites — the Marismillas reservoir, located in the Riotinto area (Fig. 1). It receives water from the Tinto River, known by its historical high levels of contamination by AMD. This river basin has been focus of much attention, with numerous studies dedicated to its hydrochemistry (*e.g.*, Cánovas et al., 2008; de la Torre et al., 2009; Grande et al., 2011; Nieto et al., 2013; Sánchez-Rodas et al., 2005; Sarmiento et al., 2009; Sobron et al., 2007; Vicente-Martorell et al., 2009), to sediment geochemistry, with works such as those by Galán et al. (2003), Ruiz et al. (2008), and Cáceres et al. (2013) as well

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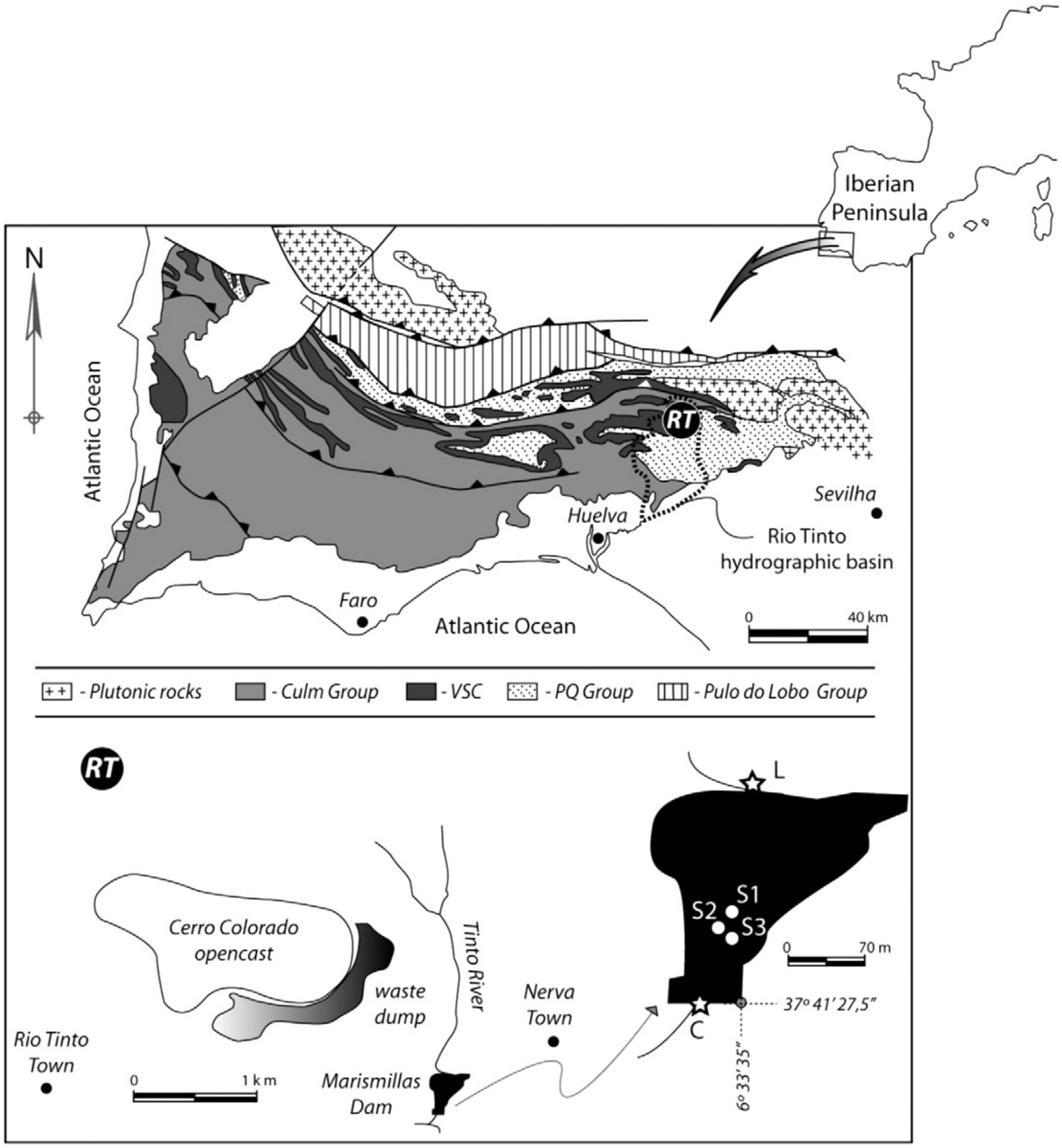

Fig. 1. Location of study site with identification of water samples (L and C) and sediment samples (S1, S2, and S3). Geological map adapted from Tornos (2006).

as soils (Fernández-Caliani et al., 2009). Also, due to its severe acidic contamination, microbe interactions and extreme ecology have been topics of research, as in the works of Fernández-Remolar et al. (2004), López-Archilla et al. (2004), Amils et al. (2007) and Stoker et al. (2008) among others.

The Marismillas reservoir has been receiving soluble contaminants as well as particulate matter for decades. Consequently, today, the reservoir is clogged by the accumulation of materials related with the evolution of AMD originated in the Riotinto complex.

Although there is an extensive bibliography on the subjects of Tinto River and Riotinto Mine, geochemical and mineralogical evolution undergone by water reservoirs submitted to extreme AMD and suffering clogging process remains a relevant topic of research. Therefore, the following specific objectives were defined for the present study: i) to describe the hydrochemistry of the acidic solution; ii) to understand the geochemical and mineralogical behaviour of the material that has been successively accumulated in the dam; and iii) to assess the relationship between the enrichment processes and the presence of secondary mineral phases. This integrated approach allows understanding the enrichment processes that may have environmental and even economic relevance in the IBP and other historical mining regions.

2. Site description

2.1. Geology and historic mining

The Marismillas reservoir is located just inside the Riotinto complex (RT), in the Iberian Pyrite Belt, SW Spain (Fig. 1). Here, metal mining has a long tradition, defining a world-class volcanogenic massive sulphide province, with more than 5000 years of mining history (Davis et al., 2000). Nowadays, several mining fields reopen and the economic interest lies on the base metals as well as precious and strategic metals as demonstrated by the intensive exploration activities (Adamides, 2013; Carvalho et al., 2011; De Oliveira et al., in press).

In the Riotinto mining district, the water and sediments will be strongly controlled by the geology of the ore deposits and host rocks. The local stratigraphic sequence comprises: i) slates and quartzites of the PQ group, ii) slates with interbedded basalt flows and volcanoclastic mafic rocks, iii) massive felsic rocks also interbedded with slate; and