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Mobility and speciation of rare earth elements in acid minesoils and geochemical implications for river waters in the southwestern Iberian margin

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ABSTRACT

This paper discusses the abundance, fractionation and chemical speciation of the rare earth elements (REE) released during two contrasting water–soil interactions, using acid sulfate and circumneutral soil samples from an abandoned mine land watershed in SW Spain. Our simulative experiment shows that the REE mobility is strongly dependent on the soil solution acidity. The acid solution extracts (pH = 3.1–3.7) extracted from the minesoils display overall REE concentrations much higher (up to three orders of magnitude) than those of the near-neutral soil extracts. The middle REE (MREE) were preferentially removed when compared to light REE ($La_N/Sm_N = 0.07$) and heavy REE ($Gd_N/Yb_N = 2.49$). The origin of this MREE-enriched signature is attributed to dissolution and/or solid–liquid exchange reactions involving iron oxy-hydroxides particles and surface coatings.

The REE were found to behave conservatively under the strong acid conditions of the soil solutions, with sulfate complexes (mainly $LnSO_4^+$) being the largely dominant aqueous species (75–80%) despite the competitive effects of aluminium. Free metal ions (Ln^{3+}) accounted for most other species in solution (12–16%). All other ligands analysed (phosphate, nitrate, chloride, fluoride and bicarbonate) were not predicted to be significant complexers of REE, according to speciation calculations.

The results of this study have implications for the REE geochemistry of the rivers draining the mine sites of the Iberian Pyrite Belt. The acid sulfate soils represent a major readily leachable MREE reservoir for the Tinto–Odiel fluvial system, which reflect the geochemical signature of the soil–water interaction in the mine lands watersheds.

1. Introduction

The geochemistry of rare earth elements (REE) in rivers and estuaries that receive acid mine drainage (AMD) has gained considerable prominence over the last decade (e.g. Elbaz-Poulichet and Dupuy, 1999; Verplanck et al., 1999; Worrall and Pearson, 2001; Verplanck et al., 2004; Borrego et al., 2005; Gammons et al., 2005; Wood et al., 2006; Zhao et al., 2007). This increasing interest is based on the fact that the REE patterns can be used as tracers of water–rock interactions in watersheds impacted by mining activities, and might provide a tool for understanding processes involved in AMD generation. REE distributions are also useful in monitoring flow paths of contamination and processes important in remediation actions, including reactive transport and transfer of heavy metals from soil to biota (Merten et al., 2005).

Previous studies have revealed that the acid waters contain high concentrations of dissolved REE in comparison with those of the river freshwaters, and show normalised REE patterns indicative of middle REE (MREE) enriched signatures (e.g. Johannesson and Zhou, 1999, and references therein). However, MREE enriched patterns have been observed under non-acidic conditions such as coarsely filtered waters (Hoyle et al., 1984); river waters with relatively high concentration of colloids and organic matter (Elderfield et al., 1990), and in Mediterranean river waters sampled at high flow (Cidu and Biddau, 2007).

The origin and mechanisms controlling the MREE enrichments are still a matter of debate, and it is not sufficiently clear whether the REE patterns relate to the aqueous processes or are source-related (e.g. Verplanck et al., 1999). The development of MREE enrichments observed in naturally and anthropogenically acidified waters may be due to: a) dissolution of MREE-bearing minerals and/or amorphous mineral surface coatings (Johannesson and Zhou, 1999); b) fractionation by colloid-borne REE (Elderfield et al., 1990); c) solid–liquid exchange reactions involving adsorption/desorption and/or cation exchange between acid waters and MREE enriched minerals or suspended particles (Gosselin et al., 1992; Sholkovitz, 1995); or d) a consistent combination of the aforementioned mechanisms. Therefore, composition of the weathered bedrock in the watershed and solution chemistry, including the presence and concentration of complexing agents, can play important roles in determining the

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dissolved REE signature (Goldstein and Jacobsen, 1988; Johannesson et al., 1996b).

Abandoned mine land watersheds are well-suited for investigating the many processes that potentially control REE behaviour in acidic waters (Verplanck et al., 1999). The minesoils are usually developed on overburden materials and show properties that differ dramatically from the original soil, such as strong acidity and elevated concentrations of sulfates and heavy metals, thus limiting their quality, functions and capability to support vegetation (Sencindiver and Ammons, 2000). The mobility of REE in acid minesoils is theoretically much higher than in natural soils from adjacent areas unaffected by mining activities, because the low pH of the soil solution enhances the REE removal through the aforementioned mechanisms. The occurrence of acid sulfate soils is, therefore, a major factor controlling the concentration of REE in stream waters (Aström, 2001). However, few studies have investigated the fate and fractionation of the REE during acid minesoil drainage.

This paper focuses on determining the readily leachable fraction, distribution pattern and chemical speciation of REE released during two contrasting water–soil interactions, using acid sulfate soil and natural near-neutral soil samples from an abandoned mine land watershed. This experimental simulation was intended to provide a better understanding of REE mobility and behaviour at the mining catchments of the southwestern margin of Iberia, and their influence on the REE geochemistry of the regional AMD systems.

2. Study area

The southwestern corner of the Iberian peninsula (South-West Spain and South Portugal) is marked by the presence of a large number (over 80) of volcanic-hosted massive sulphide deposits, within the Iberian Pyrite Belt (Leistel et al., 1998, and references therein), that historically have been a major focus of mining and ancillary industries.

There is abundant archaeometallurgical evidence suggesting that mining dates back to about 5000 years ago and continued during Tartessian and Roman times, principally for copper, gold and silver from the gossan caps and underlying supergene enrichment zones of exposed ore bodies (Salkield, 1987). However, the large-scale and intensive mining, mineral processing and smelting activities did not begin until the end of the nineteenth century, owing to the great demand for pyrite as a raw material for sulphuric acid production in Europe. During the past century, up to 60 mines were operating for pyrite, and base-metals when present, leaving a legacy of uncountable sulphide-bearing waste rock piles, spoil heaps and tailings impoundments that currently constitute major sources of acid mine drainage.

In SW Spain, the vast majority of the mine sites are located at the catchment areas of the Odiel and Tinto rivers, a fluvial system severely polluted with the acid discharges emanating from surface and underground mine workings, mine wastes and minesoils (e.g. Nelson and Lamothe, 1993; Galán et al., 2003; Sánchez-España et al., 2005; Olías et al., 2006). As a result, the river waters have a long-standing acidity, with a pH ranging between 2 and 4, and contain elevated concentrations of dissolved sulfate, metals and metalloids, particularly Fe, Mn, Cu, Zn, Pb, As and Cd, thus contributing largely to the trace metal enhancement in both waters and sediments of the Huelva estuary and adjacent Atlantic shelf (e.g. Fernández-Caliani et al., 1997; Van Geen et al., 1997; Elbaz-Poulichet et al., 1999; Ruiz, 2001; Sáinz et al., 2004).

Leptosols (classification according to the system of FAO, 1999) are by far the most extensive group of soils in the region. They are poorly developed and very shallow soils, with an AC profile of less than 25 cm depth, occurring over a wide variety of parent rocks, mainly metasediments and acid volcanic-sedimentary materials. The mine land surfaces and soils developed from anthropogenic mine waste materials cover more than 4200 ha (Fernández-Caliani et al., 2008). Contamination arising from the abandoned mine lands watersheds not only affects water quality but also involves soil degradation around the mining areas (Fernández-Caliani et al., 2005; Chopin and Alloway, 2007a,b; Fernández-Caliani et al., 2008; López et al., 2008).

The minesoils studied are located in the vicinity of sulphidic waste dumps of the Filón Norte open pit, at the Tharsis mines (Fig. 1), one of the oldest and most outstanding mining districts in the Iberian Pyrite Belt. The minesoils developed in sulphide-bearing overburden

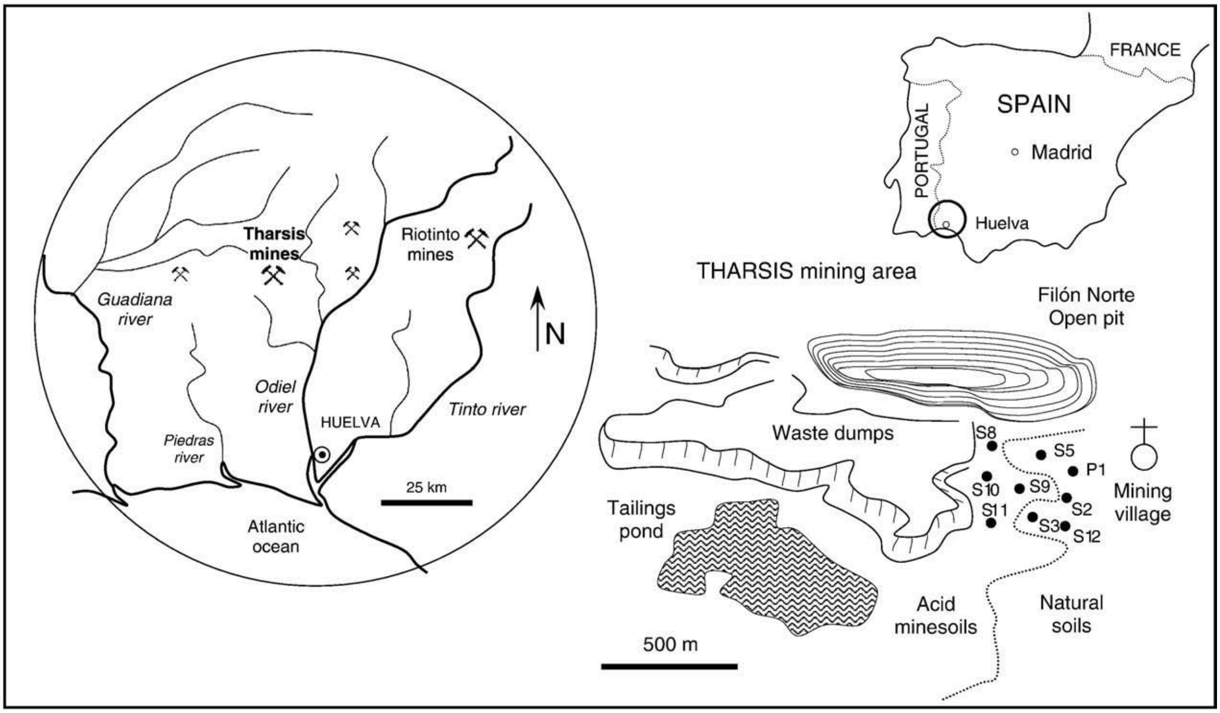

Fig. 1. Schematic depiction of the Tharsis mining area in SW Spain showing the major sources of acid mine drainage and the location of the soil samples considered in this study (filled circles).