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Geochemistry and behavior of REE in stream sediments close to an old Sn-W mine, Ribeira, Northeast Portugal

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ABSTRACT

The abandoned Sn-W Ribeira mine, northeast of Portugal, contained quartz veins with cassiterite, wolframite, scheelite, pyrite, arsenopyrite, sphalerite, chalcopyrite, manganocolumbite, bismuthinite, native bismuth, phosphates and carbonates. The exploration took place on the northern slope of the Viveiros stream, which is an affluent of the Sabor River. The waste-rock dumps and tailings were deposited on the hillside, close to the mine and are nowadays exposed to significant weathering and erosion, as they are not vegetated. The eroded material is transported by the Viveiros stream toward the Sabor River. A seasonal stream drains the tailings. The stream sediments samples were collected along the Viveiros stream, in the seasonal stream, in a seasonal spring at the bottom of the tailings, in the Sabor River and in other streams not affected by mine workings, following the mine influence along the Viveiros stream and in the Sabor River (1.2 km away from the mine workings). The data show that the degree of pollution increases along the Viveiros stream, especially in winter. The highest degree of pollution is for As, In, W, Sn and Bi. The sediments from the drainage of the main tailings are particularly polluted during winter, by Bi, In and Sn. The sedimentary precipitate from the spring is polluted in Cu, As, In, Sn, Ta, W, Bi, Zn, Nb, Ag, Sb and Ta. The sediments from the Sabor River are significantly polluted by As, Ag, In, Sn, W and Bi. The sediments from the regional streams, Viveiros stream and Sabor River have similar REE (NASC normalized) patterns (ΣREE = 131.7–185.9 mg/kg, $La_N/Lu_N = 1.23$–1.42 and $Eu/Eu^* = 1.02$), while those from the seasonal stream, crossing the main tailings, are enriched in REE (ΣREE = 250.3–283.6 mg/kg, $La_N/Lu_N = 1.6$–2.09 and $Eu/Eu^* = 0.96$). The general decrease in La_N/Lu_N values with increase in total Fe_2O_3 can be explained by the partitioning of HREE to the solid Fe-oxides phase. The sedimentary precipitate and coatings, which are mainly formed by Fe-oxy-hydroxides, but also contain jarosite, are impoverished in all REE. The impoverishment can be explained by the release of REE from the surface of the Fe-oxy-hydroxides, which occurs due to a local lowering of pH, caused by jarosite dissolution. During successive alternate cycles of wet and dry conditions, takes place the formation of Fe-oxy-hydroxides and jarosite in the sedimentary precipitate and coatings. The subsequent dissolution of jarosite releases acidity, thus promoting de-sorption of REE from the Fe-oxy-hydroxides mineral phases.

1. Introduction

Abandoned mine activities have produced vast quantities of waste-rock dumps containing low-grade ore and tailings in several regions of the world. Effluents of abandoned mine workings containing residual sulfides typically leads to acid mine drainage, eroded material from mine tailings and waste rocks. The abandoned mines sites continue to pose a potential or real threat to human safety and environmental damage (Ferreira da Silva et al., 2004).

The release and dispersion of potentially toxic elements (PTE) to the environment occurs through acid mine drainage (AMD), and the erosion of waste-rock dumps and tailings. AMD is produced in the mine wastes containing sulfides, which are easily oxidized in contact with air and water. AMD promotes high levels of dissolved potentially toxic elements, such as As, Cd, Cu, Fe, Mn, Pb, Zn, Sb, Sn and U (Pinto et al., 2004; Romero et al., 2010) in the regolith surrounding the mine site.

These elements are dispersed downslope and downstream from the mine-wastes by water and wind and thus are the source of stream sediments contamination (Grosbois et al., 2002). The extent and degree of PTE contamination around mine sites depends on mineralogical and geochemical characteristics, the content of sulfide minerals in the mine-wastes and its grain size and

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also on climatic and hydrological conditions. The leached PTE may be sorbed on solid phases, such as Fe, Al-oxy-hydroxides or Mn-oxides, precipitate as new phases, or may co-precipitate with solid phases (Lee et al., 2002). Secondary minerals on the surface of the waste rock attenuate the migration of PTE from high-sulfide wastes and tailings (Petrunic and Al, 2005). These reactions immobilize metals/semi-metals, and attenuate thereby the extent of contamination, until variations in pH or Eh promote their dissolution or desorption and incorporation in superficial and underground waters, which may became contaminated. Although metals released by sulfide oxidation are attenuated by precipitation, co-precipitation and sorption reactions (Berger et al., 2000) the content of elements in the environment also depends on their mobility and solubility from rocks and stream sediments.

REE abundance is high in acid mine drainage (Verplanck et al., 2004). Between pH 5.1 and 6.6 REEs partitioned into the solid phases whereby heavy REEs are preferentially removed. Laboratory experiments corroborated field data with the most solid-phase partitioning occurring in the water with the high pH (Verplanck et al., 2004).

In Portugal there are about ninety abandoned mine sites (Oliveira et al., 2002), with huge amounts of mine wastes and the subsequent accumulation of high concentrations of potentially toxic elements in the environment (Gomes and Favas, 2006; Carvalho et al., 2009, 2012; Gomes et al., 2010). A few of the most contaminated sites have been subjected to environmental remediation, including sealing, while a few of the others were subjected to some intervention to prevent erosion of the waste rock dumps and tailings. In the past the disposal of mine waste was often done into stream systems, near the operating mine.

Sampling and analysis of stream sediments is a technique largely used for mineral prospecting (Cohen et al., 2010), and geochemical cartography (Ferreira, 2000; Ferreira et al., 2001) because the active stream sediment composition gives an approximation of the chemical composition of materials derived from the catchment area upstream of the sampling site. Stream sediments analysis is also used in environmental monitoring because it allows the detection of regional contamination associated with mining activities (Schreck at al., 2005; Cohen et al., 2010).

The aim of this paper is to present the study of the geochemistry of stream sediments associated with the old Sn-W Ribeira mine. Particularly REE are of interest, because few data is available in Portugal and also worldwide. The variation and dispersion of potentially toxic elements and REE in stream sediments and the evaluation of their impact by mine workings, on the pollution of the stream system are presented, using data collected from November 2006 till August 2007. The behavior of REE in the stream sediments and coatings is discussed.

2. Geological and mineralogical setting

The Ribeira mine is located in the Northeast of Portugal (Fig. 1). It was a vein type Sn-W mine and the mining activity operated since 1813 till 1988, but with many interruptions. The mineralized quartz veins are thin (<1 m) and are located in the core of a Variscan antiform, cutting schistose quartzites and quartzophyllites, with quartzite intercalations of Middle Silurian age and dark-gray siliceous, carbonose phyllites with tuffites and lydites intercalations, of Upper Silurian age (Ribeiro and Pereira, 1982). About 5 km W to the mine site a Variscan two-mica porphyritc granite outcrops, which probably was the source of hydrothermal fluids. This granite shows an aplitic marginal facies which is similar to the aplitic dikes found at about −150 m, during the underground works of the mine (Thadeu, 1986). The mineralized quartz veins occur at −100 to −150 m and disappear near the aplitic dikes.

The mineralized quartz veins contain quartz, K-feldspar, albite, chlorite, tourmaline, zircon, cassiterite, ferberite, scheelite, pyrite, arsenopyrite, sphalerite, chalcopyrite, stannite, galena, magnetite, rutile, manganocolumbite, rarely bismuthinite, gananite and native bismuth, apatite, fluorite, fluorapatite, calcite and rarely dolomite (Lopes, 2008). The host metamorphic rocks were affected by muscovitization, silicification and turmalinization and the aplitic dikes were affected by greisenization, close to the quartz veins. The alteration minerals found in the mine dump materials are hematite, scorodite, vermiculite, kaolinite, Fe-oxy-hydroxides and jarosite.

3. Site description

The Ribeira mine was one of the biggest Sn-W mines in Portugal, during the forties and fifties of the XX century, and employed about two thousand workers. In 1954 the average monthly production was 21 tons of cassiterite, 9 tons of wolframite, plus 30 tons of mixed ore (wolframite + casssiterite) and in 1966 the production was 34.3 tons of cassiterite, 8.6 tons of wolframite plus 12.3 tons of mixed ore (Pereira, 2006). There are references of a total production of about 255 tons of cassiterite and 110 tons of wolframite (Pereira, 2006). The *tout venant* grade was 3.2 kg/ton, being 2.6 kg/ton of cassiterite and 0.6 kg/ton of wolframite (Pereira, 2006).

The area is mountainous, lies between 430 and 650 m altitude and is crossed by the Viveiros stream, an affluent of Sabor River. The climate is characterized by hot, dry summers and cold winters. For the 1981–2010 year period, the average temperature in August was 21.6 °C (the highest reached 39.5 °C) and it was 5.5 °C in December (the lowest reached −9.7 °C) (IPMA, 2013). The monthly precipitation was 140.0 mm in November 2006 and 21.8 mm in August 2007 (SNIRH, 2013). The hydraulic flux of Viveiros stream is low during the summer and its tributaries are already dry in May. In winter, the hydraulic flux of Viveiros stream and Sabor River are very high and the water flux is turbulent.

The waste-rock dumps and tailings consist of fragments of the country rocks, aplites and quartz, but grains of pyrite, arsenopyrite, sphalerite, chalcopyrite, calcite and dolomite were also observed. Thin films of widespread secondary Cu-carbonates, easily identified by the light-blue color, cover over the biggest boulders. The pyrite oxidation in the presence of water promotes acid conditions, causing the local dissolution of the other minerals. Coatings are also common and their identified minerals are Fe-oxy-hydroxides, Mn-oxides, scorodite, jarosite, hematite, chlorite/vermiculite, smectite and kaolinite.

The grain size of the tailings is about 1–2 mm. The waste-rock dumps and tailings were deposited in the hillside and in a seasonal stream valley, affluent of Viveiros stream (Fig. 1) close to the mine and are not vegetated, so they are subjected to intense erosion because the slope is high (46%). The eroded material is carried away to the Viveiros stream and then to the Sabor River, mostly during the raining periods. Mine tailings were identified in the river bed, 1.2 km away from the mine site. The mine site is now subject to some environmental rehabilitation specially to improve the safety conditions, as there were many ruined buildings, unguarded shafts, galleries, sinkholes and rock falls.

4. Methodology

4.1. Sampling and sample preparation

Samples of stream sediments were collected along the Viveiros stream (S3-D), (S3-H), (S6-H), (S6-D), (S8-H) and (S8-D), in its seasonal affluent that crosses the main tailings (S18a-D), (S18b-D), (S9-H), along the Sabor River (S12-D) and (S12-H), and also at three points (S1-H), (S20-D) and, (S21-D), near the mine, but upstream