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The role of cassiterite controlling arsenic mobility in an abandoned stanniferous tailings impoundment at Llallagua, Bolivia

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HIGHLIGHTS

- Acid leachates generated from tin tailings have low Sn, As and Pb concentrations.
- Cassiterite, jarosite and plumbojarosite control the mobility of Sn, As and Pb.
- The mechanism of As retention on cassiterite had not been described so far.

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ABSTRACT

The surface water contamination by potentially toxic elements (PTE) leached from mine tailings is a major environmental concern. However, the formation of insoluble solid phases can control the mobility of PTE, with subsequent decrease of the risk that tailings suppose to the environment. We characterized the tailings from a tin inactive mine in Llallagua, Bolivia in order to assess the risk for surface water quality. These tailings contain high concentrations of PTE, with up to 94,344 mg/kg Fe, 9135 mg/kg Sn, 4606 mg/kg As, 1362 mg/kg Cu, 1220 mg/kg Zn, 955 mg/kg Pb and 151 mg/kg Cd. Oxidation of sulfide minerals in these tailings generates acid leachates ($pH = 2.5–3.5$), rich in SO_4^{2-} and dissolved PTE, thereby releasing contaminants to the surface waters. Nevertheless, the concentrations of dissolved Sn, As and Pb in acid leachates are low ($Sn < 0.01$ mg/L; $As = 0.25–2.55$ mg/L; $Pb < 0.05$ mg/L). This indicates that, for the most part, Sn, As and Pb are being retained by the solid phases in the impoundment, so that these elements are not reaching the surface waters. Fe-bearing cassiterite—an insoluble and weathering-resistant oxide mineral—is abundant in the studied tailing deposits; it should be the main solid phase controlling Sn and As mobility in the impoundment. Additionally, jarosite and plumbojarosite, identified among the secondary minerals, could also play an important role controlling the mobility of As and Pb. Taking into account (a) the low solubility constants of cassiterite ($Ksp = 10^{-64.2}$), jarosite ($Ksp = 10^{-11}$) and plumbojarosite ($Ksp = 10^{-28.66}$), and (b) the stability of these minerals under acidic conditions, we can conclude that they control the long-term fate of Sn, As and Pb in the studied tailings.

1. Introduction

Historically, mining activities have produced vast quantities of inactive sulfide-bearing mine tailings in several regions around the world. The inactive tailings constitute potential environmental pollution sources due to the oxidation of sulfide minerals, which may result in the generation of acidic mine drainage (AMD) usually containing high concentrations of dissolved potentially toxic elements (PTE) and SO_4^{2-} (Talavera et al., 2004). However, when the neutralization capacity of tailings—essentially provided by carbonate and aluminosilicate minerals—exceeds their acid generation potential, protons released by sulfide oxidation are balanced by acid consumption and, consequently, concentrations of dissolved PTE in tailing leachates are kept relatively low.

Upon the changes in pH conditions in the tailings impoundment, secondary solid phases may precipitate as amorphous, poorly crystalline and well-crystallized products (Sracek et al., 2010). Secondary solid phases reported in mine wastes include (e.g. Roussel et al., 2000; Hammarström et al., 2005; Valente and Leal Gomes, 2009): Fe-oxyhydroxides (goethite, lepidocrocite, akaganeite, maghemite, and ferrihydrite), hydroxysulfates (jarosite, plumbojarosite, beudantite and argentojarosite), sulfates (gypsum, barite, anglesite, bassanite,

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melanterite, goslarite, hexahydrite, siderotil, rozenite and copiapite), carbonates (cerussite, smithsonite), arsenates (scorodite) and clay minerals (kaolinite, smectite etc.). Among these groups of minerals, sulfates, Fe-oxyhydroxides and hydroxysulfates deserve further attention in view of their geochemical behavior. Metal-sulfate salts serve as storage of metals and acidity during dry periods (Seal II et al., 2002) although, due to their high solubility they can be readily dissolved during rain storms, thus releasing metals and protons to the surrounding watershed. In the same way, Fe-oxyhydroxides and hydrosulfates play an important role in metal sequestration in surface environments, since they have a large capacity for retention of As and metals. For example, arsenate may be sorbed onto Fe-oxyhydroxides (McGregor et al., 1998), and either can substitute the sulfate anion in the crystal structure of hydrosulfates as jarosite (Foster et al., 1998). Therefore, Fe-rich secondary precipitates are the main solid phases controlling the mobility of PTE in mine tailings (Dold and Fontbote, 2001; Levy et al., 1997; Moncur et al., 2005). From an environmental standpoint, Fe-oxyhydroxides and hydroxysulfates may be an effective way of removing PTE from AMD, especially if compared with engineered designs (Levy et al., 1997).

In addition to Fe-oxyhydroxides and hydroxysulfates, the secondary precipitation of scorodite, beudantite, anglesite, plumbojarosite and Pb-bearing barite may play an important role on the attenuation of As and Pb in mine tailings, because all these minerals have very low solubility under acidic conditions (Roussel et al., 2000; Paktunc et al., 2004; Romero et al., 2010).

In order to develop an effective management strategy for AMD, it is important to understand the geochemical processes occurring in the tailings. For this purpose, it is necessary to identify the effects of solid phases on the mobility of metals and metalloids in the tailings, taking into account that the control exerted on the PTE dispersion depends on the environmental conditions (Hudson-Edwards and Edwards, 2005).

The study of the role of solid phases as a control of the mobility and retention of PTE has been done mainly in gold, nickel and base metal tailings. On the other hand, the solid phases governing the PTE mobility in tin tailings remains largely unexplored, and there is little knowledge on the behavior of trace elements in this particular environment (Lottermoser and Ashley, 2006; Salvarredy-Aranguren et al., 2008). Hence, our contribution aims to characterize the solid phase controls on the mobility of heavy metals and metalloids at the stanniferous tailings from the Siglo XX mine, the most important of the Llallagua mining district, which belongs to the world-class tin province of Bolivia.

2. Materials and methods

2.1. Study site

The studied tailings were generated by the exploitation of tin deposits from the Llallagua mining district, which is located at an altitude of 3706–3805 m above sea level. Influenced by this high altitude, the climate is cool and semi-arid with average annual temperature of 9 °C, and average annual rainfall between 400 and559 mm. The study site is drained by the Catavi River (Fig. 1), a tributary of the Andavilque River that flows into the Rio Grande, being part of the Amazon River basin.

Llallagua is a major tin district of the Bolivian Altiplano (i.e. plateau), and is located in the northern part of the Department of Potosi, approximately 300 km SE of the City of La Paz and 80 km SW of Oruro. The ore mineralization mostly consists of cassiterite (SnO_2), accompanied by quartz, tourmaline and pyrite; lesser amounts of marcasite, pyrrhotite, wolframite, bismuthinite, stannite, sphalerite, siderite, kaolin, franckeite, apatite, vivianite, paravauxite and vauxite complete the paragenesis (Sugaki et al., 1981).

Ores occur principally as veins and veinlets, commonly anastomosed, hosted by a Tertiary quartz–diorite porphyry stock, locally brecciated, that intrudes Silurian greywackes. Additionally, the mineralization forms disseminations of cassiterite within the porphyritic rock. The mineralization is largely controlled by fractures, faults and by the distribution of brecciated intrusive rocks. Haloes of pervasive hydrothermal alteration (i.e. tourmalinization, silicification, kaolinization and sericitization) are found around the ore-bearing structures (Sillitoe et al., 1975).

Mining activity began in the study area by the year 1900, with the exploitation of high-grade ores (12–15 wt.% Sn). According to historical information, the tin grade was declining drastically down to 0.53% in 1965 and to 0.32% in 1986. Currently, it is assumed that the tin ores associated to the porphyritic stocks are virtually exhausted.

The mining activity in the study area generated tailings, which were deposited in a large elevated impoundment covering an area of approximately 100 ha (Fig. 1). The tailing impoundment is estimated to contain 20,739,300 tons averaging 0.31% Sn (Zambrana, 2011), whereby they are currently reprocessed by the *Cooperativa Multiactiva* "*Catavi Siglo XX Ltda.*". This process is carried out in the Plant "C-4" (Fig. 1) throughout gravimetric sorting, and a cassiterite concentrate is produced. Up to 250 tons of tailings are reprocessed daily, with a recovery of about 48%. Final wastes derived from this activity are discharged as a pulp into the Catavi River.

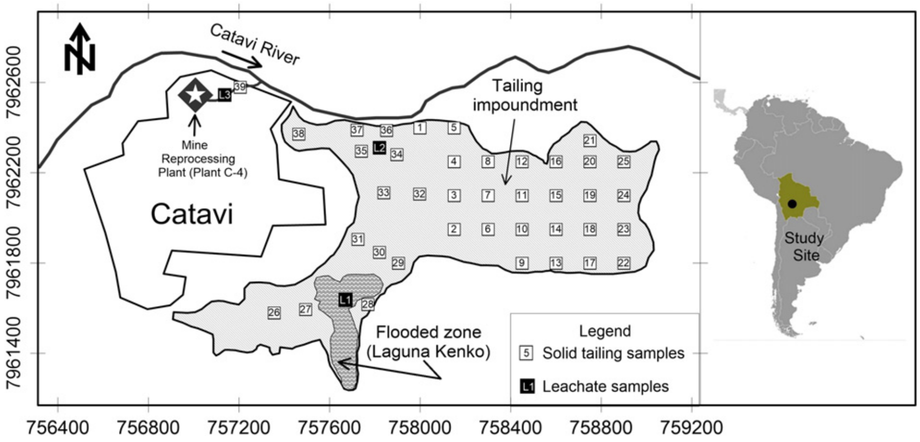

Fig. 1. Sampling location of solid tailings and leachates.