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Geochemical comparison of waters and stream sediments close to abandoned Sb-Au and As-Au mining areas, northern Portugal

Paula C.S. Carvalho[a,*], Ana M.R. Neiva[a], Maria M.V.G. Silva[a], Eduardo A. Ferreira da Silva[b]

[a] Geosciences Centre and Department of Earth Sciences, University of Coimbra, 3000-272 Coimbra, Portugal
[b] University of Aveiro, Geosciences Department, GeoBioTec Research Centre, Campus de Santiago, 3810-193 Aveiro, Portugal

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ABSTRACT

Waters from abandoned Sb-Au mining areas have higher Sb (up to 2138 μg L^{-1}), As (up to 1252 μg L^{-1}) and lower Al, Zn, Li, Ni and Co concentrations than those of waters from the As-Au mining area of Banjas, which only contain up to 64 μg L^{-1} As. In general, Sb occurs mainly as SbO_3^- and As $H_2AsO_4^-$. In general, waters from old Sb-Au mining areas are contaminated in Sb, As, Al, Fe, Cd, Mn, Ni and NO_2^-, whereas those from the abandoned As-Au mining area are contaminated in Al, Fe, Mn, Ni, Cd and rarely in NO_2^-. Waters from the latter area, immediately downstream of mine dumps are also contaminated in As. In stream sediments from Sb-Au and As-Au mining areas, Sb (up to 5488 mg kg^{-1}) and As (up to 235 mg kg^{-1}) show a similar behaviour and are mainly associated with the residual fraction. In most stream sediments, the As and Sb are not associated with the oxidizable fraction, while Fe is associated with organic matter, indicating that sulphides (mainly arsenopyrite and pyrite) and sulphosalts containing those metalloids and metal are weathered. Arsenic and Sb are mainly associated with clay minerals (chlorite and mica; vermiculite in stream sediments from old Sb-Au mining areas) and probably also with insoluble Sb phases of stream sediments. In the most contaminated stream sediments, metalloids are also associated with Fe phases (hematite and goethite, and also lepidocrocite in stream sediments from Banjas). Moreover, the most contaminated stream sediments correspond to the most contaminated waters, reflecting the limited capacity of stream sediments to retain metals and metalloids.

1. Introduction

Plumlee and Nash (1995) defined a geoenvironmental model for a mineral deposit, where the main purpose was to establish cause and effect between geologic characteristics of a deposit and its environmental setting, mining history and environmental behaviour. The low-sulphide Au-quartz veins are the most widespread type of Au deposits around the world (Ashley, 2002; Pašava et al., 1995). The geoenvironmental characteristics of low-sulphide Au-quartz veins have been studied for several authors (e.g. Ashley, 2002; Craw et al., 2004; Wilson et al., 2004; Desbarats et al., 2011; Carvalho et al., 2012; Beauchemin et al., 2012). In Sb-Au and As-Au deposits, As and Sb are the most abundant metalloids retained in ore minerals. Therefore, it is important to study the behaviour of these metalloids in mining areas. Some studies have reported the As and Sb concentrations in different mining sites (e.g. Ashley et al., 2003; Casiot et al., 2007; Craw et al., 2004; Wang et al., 2011). However, the environmental behaviour of Sb is much less known than that of As in gold mining areas (Milham and Craw, 2009; Filella et al., 2009).

The geoenvironmental characteristics of a deposit provide information to prevent future environmental impacts if it is exploited. Some of those environmental impacts extend over decades after mining closure, as sulphides were not totally weathered and/or toxic elements retained by the environment may be released. Even after large periods of mining closure, it is of special interest to know the proportion of metals and metalloids which can be mobilized to the environment.

A large number of gold deposits occurred associated with the Valongo anticline (northern Portugal). These Au deposits are classified as Sb-Au and As-Au types. Initially, at Roman times, they were exploited for Au, but later, Sb and As were also exploited intermittently, until the end of nineteenth century. The mine wastes, widespread over the area, are deposited in or close to streams. The two types of deposits have a distinct mineralogical paragenesis and occurred in different geological units.

The geochemical characteristics of the mineral deposit type and the mineralogy and geochemistry of the host rock determine the geochemical signature of surrounding soils, stream sediments and waters (Plumlee and Nash, 1995). The host rock type also influences mineralogy of stream sediments and geochemistry of waters. This study provides the metals and metalloids distributions in waters and stream sediments close to abandoned gold mines, one of

* Corresponding author. Tel.: +351 239860500; fax: +351 239860501.
E-mail address: paulacscarvalho@gmail.com (P.C.S. Carvalho).

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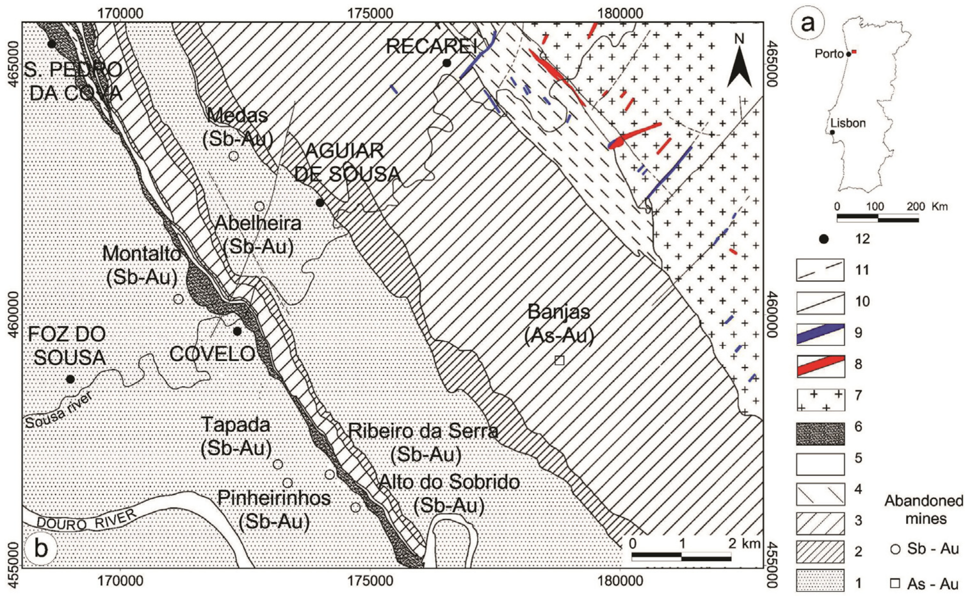

Fig. 1. (a) Location of the study area on the map of Portugal; (b) geological map of the study area and location of abandoned Sb-Au mines of Medas, Abelheira, Montalto, Tapada, Ribeiro da Serra, Pinheirinhos, Alto do Sobrido and old As-Au mine of Banjas; 1 – Cambrian schist–greywacke complex, 2 – Arenigian quartzites with intercalated shales, 3 – Llandeilian–Llanvirnian schists, greywackes, quartzites, 4 – Silurian schists, greywackes and quartzites 5 – Devonian shales and quartzites, 6 – carboniferous conglomerates, arkoses and schists, 7 – medium- to coarse-grained porphyritic biotite > muscovite, 8 – aplite, aplite–pegmatite, pegmatite veins, 9 – quartz veins, 10 – fault and overthrust, 11 – probable faults and 12 – villages.

Sb-Au and another of As-Au in Valongo, northern Portugal. Metals and metalloids contents in quartz veins are different in the two mines. The main purpose of this study is to assess the chemical behaviour, mobilization and attenuation of metals and metalloids in mine waters and stream sediments at these two different abandoned mining areas. Moreover, the geochemistry of Sb and As in stream sediments and waters is compared, in order to find out the behaviour of these metalloids in the two old mining areas.

2. Geology setting

The Valongo study area is located about 18 km at east of Porto, northern Portugal (Fig. 1a).

The study area is characterized by mountainous relief derived from quartzite ridges at both limbs of the Valongo anticline. These elevations reach up to 376 m and the lowest altitudes are below 200 m in core and western limb of the anticline. Several farms are spread over old Sb-Au mining areas and in Montalto and Banjas a farm is developed over a dump.

The climate of this area is characterized by a maritime temperate climate with temperatures ranging from 25 to 30 °C in dry and warm summers. The wet season starts in October and lasts until May and the mean annual temperature is 14.6 °C and the annual precipitation ranges from 1148 to 1771 mm/year (SNIRH). The year of 2008 was characterized by anomalous rainfall events. February (57.5 mm), March (68.8 mm), October (46.1 mm) and November (70.0 mm) had low monthly rainfall compared to normal hydrological years. However in April (235.7 mm) and May (118.5 mm) the month rainfall was higher than in typical hydrological years (SNIRH, 2012).

The Valongo anticline is an elongated asymmetric structure which is limited at southwest by the Douro-Beira Shear Zone and at northeast by variscian granites. It comprises Cambrian to Carboniferous metasediments. The Cambrian schist-greywacke complex predominates in the area and is composed of alternating phyllites and greywackes containing metaconglomerate and marble lenses. It crops out in the western anticline limb and core (Fig. 1b). The schist-greywacke complex is overlain at angular discordance by the Arenigian quartzites with intercalated shales. The Llandeilian–Llanvirnian black slates with graphite crop out at both limbs of the anticline. The Devonian consist of schist, sandstones and quartzites. The Silurian is composed of metapelites, black slates and greywackes with quartzites intercalations. The Carboniferous crops out at the western limb, consist of basal sedimentary breccias, shales, sandstones, quartzites and is in contact with the schist greywacke complex by an overthrust (Vallance et al., 2003).

The As–Au quartz veins crop out in the eastern limb of the Valongo anticline, filling N 10–30° W faults. They are up to 2 m thick and 200 m long, hosted by Ordovician slates and were exploited at the Banjas mine. The As–Au quartz veins consist of quartz, arsenopyrite, pyrite, pyrrhotite, pyrargyrite, sphalerite, chalcopyrite, galena, glaucodote, boulangerite, tetrahedrite, bournonite, freibergite, electrum, gold, siderite, scorodite, covellite and jacobsite. The Sb–Au quartz veins crop out mainly in the western limb of the Valongo anticline and rarely in the core of the anticline, filling N–S, N 10–75° E, N 30–50° W and E–W faults and are hosted by Cambrian phyllites and metagreywackes (Fig. 1b). They are up to 2.5 m thick and 200 m long. The ore exploitation took place at Medas, Abelheira, Montalto, Tapada, Alto do Sobrido, Ribeiro da Serra and Pinheirinhos mines, mainly in the late nineteenth century. The Sb–Au quartz veins consist of quartz, arsenopyrite, pyrite, pyrrhotite, marcasite, sphalerite, chalcopyrite, galena, boulangerite, jamesonite, electrum, tetrahedrite, fülöppite, zinkenite, berthierite, stibnite, gold, native antimony, ankerite, siderite, calcite, dolomite and also schafarzikite, apuanite, valentinite and cervantite.

Mining activity in the Valongo anticline dates back to roman times. Gold and antimony were exploited in the western limb of Valongo anticline in several deposits. The most important explorations of gold and antimony took place at Montalto and Tapada mines (Fig. 1b) and gold was also exploited at Banjas. Between 1864 and 1888, the most important period of mining activity at Montalto, 27,500 tonnes of material was exploited, containing 0.58 tonnes of gold and 732 tonnes of antimony. Between 1880 and 1890, at Tapada-Ribeiro da Serra, 360,000 tonnes of material was exploited, containing 14,400 tonnes of antimony (Parra et al., 2002). At