TECHNICAL ARTICLE

Geochemistry and Mineralogy of Mill Tailings Impoundments from the Panasqueira Mine (Portugal): Implications for the Surrounding Environment

Paula F. Ávila · Eduardo Ferreira da Silva · Ana R. Salgueiro · J. A. Farinha

Abstract Selected geochemical results are presented from a study of the Panasqueira mine (Sn–W mineralization), which is one of the Portuguese test sites for the e-EcoRisk project (http://www.e-ecorisk.info/). These data permit a better understanding of the dynamics inherent to leaching, transport, and accumulation of some elements (mainly As, but also Cu, Pb, Zn, and Cd) in different sampling media and their environmental relevance. Stream sediment and water samples were found to be contaminated by the stored waste material in the tailing ponds; this effect could be observed for a considerable distance downstream.

Keywords Acid mine drainage · e-EcoRisk · Environmental geochemistry · Mine wastes · Panasqueira mine

Introduction

Mining, like other industrial activities, can negatively affect the surrounding environment. Mineral extraction and processing produce crushed and milled waste rock and tailings that cause a potential risk to the environment when exposed to weathering (Dold and Fontboté 2001; Nordstrom and Alpers 1999). In particular, mine wastes containing high sulphide concentrations are notorious for their potential production of acid mine drainage (AMD) and leaching of contaminants during and after mining, often resulting in pollution of waters, stream sediments, and soils. These consequences can be particularly problematic when the mining and ore treatment occur in populated areas. Soil and water can be easily contaminated by metals (and metalloids) (Alloway 1993; Forstner and Wittmann 1983). Understanding the geochemical processes that control precipitation and dissolution of secondary minerals in abandoned or active sulphide mines is crucial for the elaboration of models to predict the environmental impact of such sites (Gieré et al. 2003).

The regional enterprise network information management and decision-support system (*e-EcoRisk*) is a major contributor to the decision-making process of environmental and civil protection agencies charged with the responsibility for assessing, preventing, mitigating, and controlling the potential and actual effects of large-scale industrial spills on the environment. The primary goal of environmental risk and emergency management is to reduce environmental and civil risk by choosing a risk prevention or reduction plan from a set of options (e-EcoRiskDoW 2001), based on-site characterization and knowledge of the geochemical mechanisms, to facilitate site remediation and help alert authorities whenever a spill occurs.

The Panasqueira Sn–W mine was one of the two Portuguese test sites studied in the scope of the e-EcoRisk project. This mine is a group of interconnected room and pillar underground mines that initially took their names

P. F. Ávila (✉)
Lab S Mamede Infesta INETI, 4466-956,
S. Mamede de Infesta, Portugal
e-mail: paula.avila@ineti.pt

P. F. Ávila · E. F. d. Silva
Dept de Geociências, GeoBioTec, Univ de Aveiro,
Campus de Santiago, 3810-193 Aveiro, Portugal

A. R. Salgueiro
CERENA, Natural Resources and Environment Centre,
IST, Av Rovisco Pais, 1049-001 Lisbon, Portugal

J. A. Farinha
Dept Prospecção Minerais Metálicos INETI,
2720 Alfragide, Portugal

from the villages or other geographic features where the mining began. The most important of these sections are: Panasqueira, Barroca Grande, Corga Seca, Rebordões, Seladinho, Fonte das Lameiras, Vale das Freiras, Vale da Ermida, and Cabeço do Pião (Fig. 1).

Panasqueira was chosen by the consortium to be an e-EcoRisk test site due to several factors: (a) it is an active mine; (b) there are huge tailings piles and dams; the Rio tailings ($\approx 1{,}200{,}000$ m^3) has one mud dam ($\approx 731{,}034$ m^3) and the Barroca Grande ($\approx 7{,}000{,}000$ m^3) has two mud dams ($\approx 1{,}193{,}885$ m^3); (c) small villages, S. Jorge da Beira (694 inhabitants—INE Censos de 2001 in http://www.ine.pt.), Panasqueira, Barroca Grande (200 workers and their families), and Aldeia de S. Francisco de Assis (692 inhabitants) are near the mine site; (d) the Zêzere river crosses the area and feeds the Castelo do Bode dam (located 90 km downstream), the main water supply source for Lisbon; and (e) the local population strongly depends on the use of land and water for their subsistence (water supply, agriculture, cattle breeding, fishing, and forestry).

The main goal of this geochemical research was to characterize the anomalous distribution of some heavy metals and to understand their mobility and transfer mechanisms to the secondary geochemical environment at the Panasqueira site, as part of the e-EcoRisk Project.

Site Description

The Panasqueira mine is located in the municipalities of Covilhã and Fundão (Castelo Branco district, Central Portugal). The mining district is situated between the
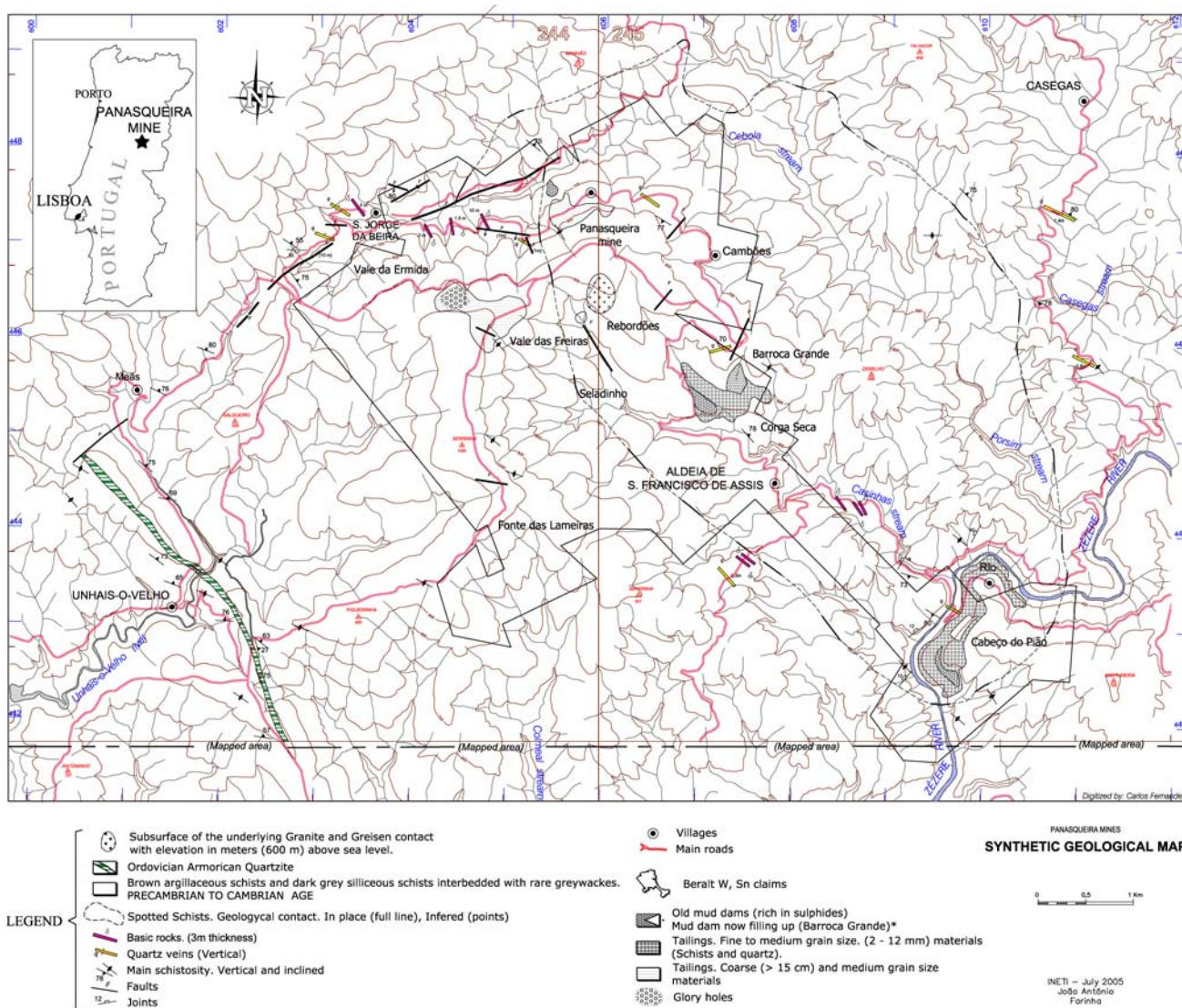

Fig. 1 Synthetic map showing the location of Panasqueira mining area and the main geological units (Farinha 2005)

Gardunha and S. Pedro de Açor mountains, to the west of the Central Portugal depression Cova da Beira (Beira Baixa province). The topography ranges in altitude from 350 to 1,080 m (Reis 1971), with deep valleys. The streams are generally dry in the summer and flooded in the winter. Climate, which can be an important instability factor, is aggressive in the Panasqueira region, with hot and dry conditions during the summer and very cold, rainy, and windy conditions in the winter. The average annual rain precipitation in the region is 1,200–1,400 mm; snow fall is frequent, particularly above the altitude of 700 m. The average annual temperature is $\approx 12°C$, ranging from $\approx 0°C$ during the winter to about $\approx 30°C$ in summer. The evapotranspiration in this region is around 1,080 mm (source http://www.inag.pt).

Geology and Mineralization

According to the paleogeographic and tectonic zoning established for the Hercynian Chain of the Hesperic massif (Julivert et al. 1974; Lotze 1945), this deposit is included in the Central Iberian Zone (CIZ, Fig. 1). As a result of the regional metamorphism, the sediments changed to biotite-chlorite schists and phyllites, and the more arenaceous units converted to dark, fine-grained quartzites. The Panasqueira deposit lies in a folded metasedimentary sequence, the Beira-Schist Formation of upper Precambrian-Cambrian age. The Beira-Schist Formation was subjected to lower greenschist grade regional metamorphism during the early compressive stages of the Hercynian Orogeny. The Beira-Schist Formation is composed of a several thousand meter thick sequence of lower marine flyschoid schists, greywackes, lenticular, thinly bedded mudstones, shales, and arenites (Bloot and de Wolf 1953; Cavey and Gunning 2006; Conde et al. 1971; Kelly and Rye 1979).

The dominant lithological unit hosting the tin–tungsten concessions of the Beralt Tin & Wolfram Company was of Cambrian to Upper Cambrian age, and forms an outcrop of about 35 km^2; however, brown argillaceous schists and dark grey siliceous schists interbedded with rare greywackes were also identified in the area. Few mafic rocks (dolerites) were observed, particularly near S. Jorge da Beira (NW–SE subvertical). Some quartz veins disposed parallel to the principal schistosity were also mapped. An important 4-m thick, N65°E vertical fault, the Ribeira da Cebola fault, was observed between the villages of S. Jorge da Beira and Panasqueira. It is characterized as a sinistral fault that caused a horizontal displacement of about 95 m to the schist formation.

The Panasqueira ore deposit is a typical example of a Sn–W hydrothermal mineralization associated with the Hercynian plutonism. The mineralized zone has an average length of 2,500 m, ranges in width from 400 to 2,200 m

and extends at least 500 m in depth (Cavey and Gunning 2006). The Panasqueira has been in production for over 100 years and is one of the largest economic vein deposits in the world. During the period 1947–2001, over 27 million tonnes of rock were mined, from which approximately 92,800 t of tungsten concentrate, 4,800 t of tin concentrate, and 28,600 t of copper concentrate were produced (Smith 2006).

The granitic intrusion is thought to be the principal source of the mineralizing fluids responsible for the economic wolframite vein system. The most dominant and important structural feature at Panasqueira mine is a flat open joint system that is prevalent throughout the mine workings. The remobilized ore-bearing fluids migrated from the intrusion into these flat joints to form the stacked quartz vein system being mined today. A second set of non-wolframite bearing quartz veins (veins contain minor chalcopyrite, galena, and pyrite) also exists at the Panasqueira deposit, and are aligned with the vertical foliation and cut by the later tungsten-bearing hydrothermal vein system (Cavey and Gunning 2006).

The Panasqueira deposit consists of a series of stacked, sub-horizontal, hydrothermal quartz veins intruding into the Beira schists and shales. The paragenesis is complex. Four stages of mineral formation are generally accepted by most of the authors who have studied this deposit: (1) the oxide–silicate phase (quartz, wolframite; cassiterite); (2) the main sulphide phase (pyrite, arsenopyrite, pyrrothite, sphalerite, chalcopyrite); (3) the pyrrothite alteration phase (marcasite, siderite, galena, Pb–Bi–Ag sulphosalts); and (4) the late carbonate phase (dolomite, calcite) (Breiter 2001; Corrêa de Sá et al. 1999; Correa and Naique 1998; Noronha et al. 1992). At Panasqueira, more than 65 minerals, including sulphides, sulphosalts, oxides, carbonates, silicates, phosphates, and tungstate minerals, have been identified (Kelly and Rye 1979).

In general, the most common minerals in addition to quartz are: wolframite, pyrite, pyrrhotite, arsenopyrite, chalcopyrite, cassiterite, beryl, mica, and fluorite. The Panasqueira mine has many rare minerals that can only be observed microscopically, making it a site of specific scientific importance.

Mining Activity and Potential Environmental Considerations

Historical data shows that Romans worked the area for tin. The first prospecting licence was granted in 1886 and the first reference to wolframite mineralization in Panasqueira mine reportedly dated to 1888 (Cavey and Gunning 2006).The Panasqueira mining concession covers an area of more than 2,000 ha and developed through the amalgamation of a Portuguese company. In 1928, the

concession was taken over by Beralt Tin & Wolfram Lda. (Corrêa de Sá et al. 1999; D'Orey 1967). The first underground drifts were opened at Cabeço do Pião (Rio), but mining decreased there as richer veins were discovered at the Panasqueira site.

The exploitation was extended to other areas, the most important being Barroca Grande, Corga Seca, Panasqueira, Rebordões, and Vale da Ermida. The economic exploitation mainly focused on wolframite, cassiterite, and chalcopyrite, the last two as by-products. On average the "tout-venant" contains 0.3% WO_3; the three final concentrates contain 75% WO_3, 72% SnO_2, and 22% Cu together with significant amounts of Ag. At the present time, exploitation is focused at Barroca Grande.

The long history of exploitation and ore treatment operations are testified by the presence of tailings and other debris disposed of in the Vale de Ermida. The site is characterized by the presence of old infrastructures as well as large tailings piles from the earliest years of production (late 1890s–1927) that were abandoned when the new plant was constructed at Rio (Cavey and Gunning 2006). At that time, the ore was transported from Barroca Grande along a 4-km cableway to the concentration plant located in Rio. The Rio plant and tailings disposal area were deactivated in 1996; nowadays, the waste rock is still placed in the Barroca Grande tailings area.

During the mining process, two types of mine waste are generated: coarse aggregates derived from rock blasting, most of which is disposed of in the tailings, though minor quantities have been used in hot bituminous mixtures, and waste mud coming from the plant and conveyed by pipelines into lagoons built specifically for that purpose (several million tonnes have been deposited and almost 100 t are being added each day).

The ore treatment process begins with heavy media separation (HMS) for the coarse fractions of material. In a second phase, cyclones are used to produce ore concentrates with high metal content, and tables are used to treat the sands. These pre-concentrates contain all the existent heavy minerals, such as wolframite, cassiterite, sulphides, and siderite. Until 1996, these pre-concentrates were transported to the Rio plant, but today, the final separation procedures are carried out exclusively in Barroca Grande. James flotation tables are used to float the pre-concentrates; the floated sulphides constitute the steriles, which feed the copper circuit. Copper concentrates are recovered after differential flotation in Denver cells (Corrêa de Sá et al. 1999; Reis 1971; Rodrigues and Gonzalez 1973). It must be emphasized that arsenopyrite (the main sulphide present) is rejected with the tailings, which contain about 30% As.

The Rio tailing site, located near and draining directly to the Zêzere River, is a large site where tailings have been disposed of for approximately 90 years. This deposit has an average height of 90 m and has slopes of about 35°. The grain size of the materials is variable, due to successively finer grinding procedures, and are classified as: coarse sterile material from the mine, coarse tailings (sterile material) from the heavy media separation, sand, mud, and slush. The three-first types of materials are disposed of in the tailings, while the mud and slush are discharged into a pond that was intentionally created for that purpose, in the SE section of the tailings site. The existing pond at the Rio tailings dam is an open-air impoundment and contains 731,034 m^3 of rejected ore concentrates with high metal levels. At the far other end of the tailings, an arsenopyrite stockpile with 9,400 m^3 had been deposited in the past, and remained exposed until June 2006, when the pile was capped with geotextile and layers of clay (e-EcoRisk 2007). There are several slippage zones evident in the tailings, indicating a risk of collapse. In this scenario, the arsenopyrite stockpile will enter directly into the Zêzere River. When this pile was exposed (prior to June 2006) to the atmosphere and rain water, the oxidized materials generated AMD.

The Barroca Grande site includes underground mine and portals, a processing plant, mine offices, and employee housing, in addition to the active tailings disposal areas and the Salgueira water treatment plant (Cavey and Gunning 2006). A huge tailings pile and two mud dams exist at this site. One of the dams is old and deactivated, although stabilized in geotechnical terms, while the other (smaller and disposed over the tailings) is still being fed with steriles (some rich in sulphides) obtained from the ore dressing operations. These tailings and impoundments are exposed to atmospheric conditions. Surface runoff and water percolation leach the tailings and form AMD. The tailings piles at Barroca Grande are adjacent to the small, but perennially flowing, Casinhas Stream, which drains to the Zêzere River. The Salgueira water treatment plant receives surface water from the old tailing pond area, water from the new tailings pond, mine drainage water, and seepage from the base of the tailings. These waters are mainly treated with lime. The precipitated sludge is pumped to the tailings pond while the treated water is pumped into holding tanks for later use in the mill, or discharged to a creek channel adjacent to the plant, and thus into the Zêzere River.

Materials and Methods

In order to assess the dynamics of leaching, transport, and accumulation of some selected metals and metalloids, different media (stream sediments, alluvium, surface waters, impoundment materials, iron coatings, arsenopyrite stockpile material, and ferruginous crust) were sampled. These media are considered to be the most representative of the

surface environment, and are commonly used in environmental geochemical investigations. All the sample sites were located by GPS and geo-referenced to UTM coordinates.

Sampling

Tailings and dams: The main tailings were mapped and characterized (particularly the Rio and Barroca Grande

tailings) based on the granulometric and mineralogical characteristics of their forming materials and the observed geotechnical and hydrological patterns (stability, landslides, formation of ravines, erosion, water circulation at the surface, resurgences, etc.). Two kilograms of samples were collected from the two Barroca Grande dams (active dam, AD1 to AD9; old dam, OD1 to OD5; Fig. 2b) below the oxidized layer at about 40 cm depth. Three superficial
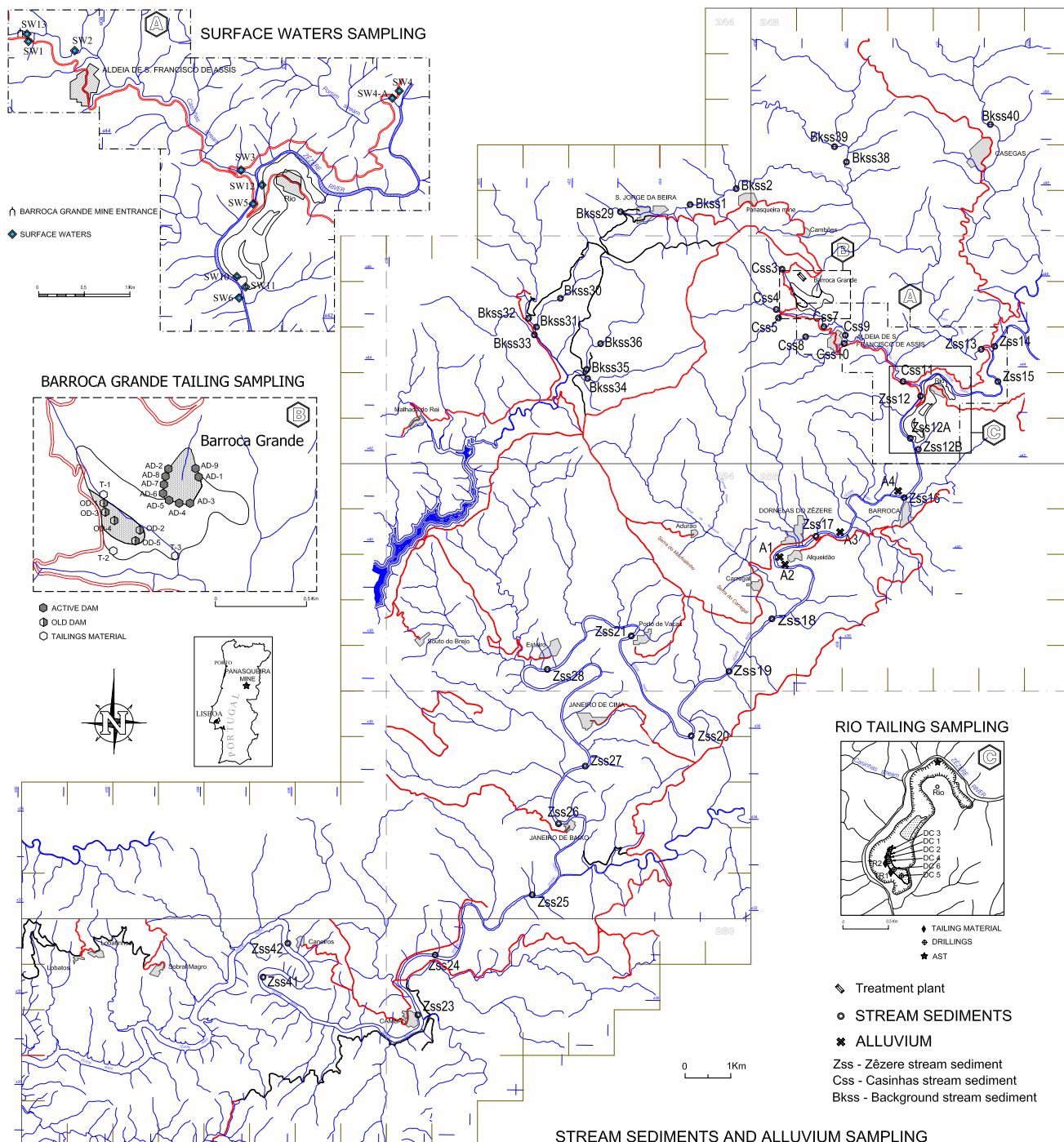

Fig. 2 Regional map of Panasqueira study area with sampling location of stream sediments, alluvium, surface waters, tailings and dams

tailing samples were also collected from the Barroca Grande tailings (T1, T2, and T3; Fig. 2b). The Rio tailings were characterized using selected samples from six available drill cores (DC1 to DC6; Fig. 2c) collected to Beral tin company by IGM (Instituto Geológico e Mineiro) in 2002 for geotechnical studies (Dinis da Gama 2002). All of the cores except DC2 reached the bedrock, with the following lengths: 24.08, 43.58, 26.77, 21.95, 34.63, and 40.13 m, respectively. All the remaining sampling was carried out by INETI in the scope of the e-Ecorisk project in 2005.

Stream sediments and alluvium samples: In order to evaluate the extent of contamination, 41 stream sediments samples (composite samples of 3 sub-samples collected from several places at the sample site, generally along 10 m of the active stream channel) were collected for 50 km downstream of the Barroca Grande tailings along the Zêzere River (Fig. 2, samples representative of the local geochemical background, BKss1, BKss2, BKss29, upstream Barroca Grande; BKss30 to BKss40, samples taken in a different watershed not affected by mining, industrial, or agricultural activities; samples collected in Casinhas stream, Css3 to Css11; samples collected in the Zêzere River, Zss12 to Zss28, Zss41, and Zss42; Fig. 2). The alluvium samples (A1, A2, A3, and A4; Fig. 2) were collected in some mapped alluvium areas located in the Zêzere River and sieved in loco in order to retain the fine material for later analysis.

One iron coating sample was collected in the Zêzere River, immediately downstream of the Rio tailings (near stream sediment sample Zss12A) and a ferruginous crust sample in the basement of Rio tailings (near surface water SW10).

Surface water samples: A total of 11 samples were collected along the Casinhas Stream and Zêzere River: SW1, SW2, and SW3 were collected in the Casinhas downstream of the Barroca Grande tailings; samples SW4 and SW4A were collected from the Zêzere, upstream of the Rio tailings (local background samples); sample SW5 was collected in Zêzere river after its confluence with Casinhas stream; SW6 was collected from the Zêzere but downstream of both tailings areas (Barroca Grande and Rio); samples SW10, SW11, and SW12 are seepage waters collected at the base of the Rio tailings dam, and sample SW13 from the mine entrance at Barroca Grande (Fig. 2a). Samples were collected from each selected site using a clean 1-L acid-washed polyethylene bottle and stored at 4°C until analyzed.

Sample Preparation

The stream sediment, alluvium, tailings, and drilling core samples were oven dried before dry sieving at 40°C, mixed, homogenized, and sieved through a <200 mesh

screen for chemical analysis. In order to analyze the dissolved phases, 250 mL of surface waters from each sample was filtered on-site through 0.45-μm Millipore membrane filters using an all-plastic pressurized filtering system (ASTM 1984). Samples for metal analysis were immediately preserved after collection in the field, with pH reduction to 2.0 using HNO_3, avoiding Fe hydroxide precipitation. All the water samples were stored at 4°C pending further analysis.

Sample Analysis

Physico-chemical parameters: temperature, pH, and electric conductivity (SC) of the surface waters were recorded at each site. The pH was measured with a HI 8424 microcomputer pH meter, previously calibrated. Conductivity was measured using a HI 8633 microcomputer electric conductivity meter. All SC measurements are referenced to 25°C. The concentrations of HCO_3 were determined in situ by volumetric titration on filtered unacidified samples.

Chemical analyses: The homogenized stream sediments, tailings, and dam samples were analyzed in the S. Mamede de Infesta INETI accredited lab. For trace metal analysis, a 0.5-g split was leached in hot (95°C) aqua regia (HCl–HNO_3–H_2O) for 1 h. Although not all minerals are decomposed during aqua regia digestion, for the purposes of the study, the results obtained for heavy metals in the aqua regia extraction are considered as total concentrations, due to the fact that hot aqua regia totally decomposes sulphides, which are the major sources of these elements. After dilution to 10 mL with deionized water, the solutions were analyzed for Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, V, Y, and Zn (by conductive plasma emission spectrometry). The Sn and W were analyzed separately by X-ray fluorescence (XRF); the high stability of the XRF system generally allows the analysis of Sn and W with high precision. The detection limits (Table 1) were based on three times the standard deviation of a reagent blank that was analyzed ten times. The accuracy and analytical precision were determined by analysis of reference materials (SO1, SO2, SO3, SO4, FER1, FER2, FER3, and FER4 from the Canadian Centre of Mineral and Energy Technology; PACS-1 from NRS26 CNRC; and 2711 from NIST) and duplicate samples in each analytical set. The results were within the 95% confidence limits of the recommended values given for this certified material. The relative standard deviation was between 5 and 10%.

Mineralogy: The mineral constituents in selected solid media samples (including efflorescences) were identified by X-ray diffraction at INETI. The mineralogical composition was determined using a Philips X'Pert MPD machine equipped with CuKa radiation, graphite monochromator,

Table 1 Range, median, and average concentrations of the analyzed chemical elements in tailings and dams samples from the Barroca Grande and Rio sites

Site		Ag	As	B	Ba	Cd	Co	Cu	Fe	Mn	Ni	P	Pb	Sb	Sn	V	W	Y	Zn
Barr. Grande active dam (n = 9)	Mean	27	56,111	885	228	563.6	25	3,662	9.6	991	61	978	109	29	413	71	3,182	430	4,024
	Median	21	2,2000	548	249	429	20	2,758	8.2	982	52	1,011	78	25	311	77	3,027	321	3,294
	Min	9	6,300	312	96	112	10	1,921	6	856	37	736	28	12	147	30	1,861	225	1,795
	Max	68	200,000	2,378	348	1,813	67	6,800	19	1,257	110	1,189	267	45	877	102	5,192	798	7,300
Barr. Grande old dam (n = 5)	Mean	65	22,905	1,157	287	361.4	11	4,690	7.6	719	65	1,027	269	47	526	91	3,736	553	3,223
	Median	16	6,100	695	277	105	10	3,977	5.8	662	59	1,225	123	23	198	107	1,936	476	3,615
	Min	8	2,715	461	69	41	5	1,755	4.5	620	36	384	57	14	160	41	1,590	202	433
	Max	263	92,000	2,488	451	1,499	17	9,800	17	871	119	1,247	934	150	1,643	119	10,300	1,178	6,300
Barr. Grande tailings (n = 3)	Mean	40	7,142	3,323	168	56	6	2,501	8.7	730	29	1,866	172	62	679	58	5,400	208	1,689
	Median	38	4,715	3,312	182	79	5	3,548	7.3	641	34	1,880	171	39	702	81	2,434	168	460
	Min	37	4,711	2,780	127	2	5	214	7.1	571	7	1,722	64	29	453	3	1,766	33	384
	Max	45	12,000	3,878	195	87	10	3,741	11.6	979	45	1,995	282	118	882	89	12,000	422	4,224
Rio dam (n = 17)	Mean	32	73,649	1,573	163	1,227	17.2	2,494	12.5	924	52	1,111	215	39	525	60	4,068	295	6,843
	Median	19	19,000	1,520	229	207	11	1,895	7.4	852	41	1,077	132	34	433	74	3,486	224	2,776
	Min	10	3,094	443	12.5	28	4.5	78	5.3	419	6.5	439	73	13	216	3	2,050	9	142
	Max	83	240,000	3,260	300	4,028	48	7,200	28.8	1,605	97	2,452	821	77	875	106	8,676	848	27,000
Detection limit	–		1	20	8	25	4	9	1	0.2	50	13	30	16	12	6	6	6	1	5

Concentrations are expressed in mg kg^{-1}, except for Fe (%)

automatic divergence slit, and 0.5-receiving slit. A step size of 0.05° 2θ, a scan setting of 2–70° 2θ, and a 10 s counting time were chosen.

Surface water samples were analyzed without pre-concentration. The analyzed elements include major anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$), major cations (Ca, K, Na, and Mg), as well a suite of dissolved trace metals (Ag, Al, As, Bi, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, and Zn). Unacidified samples were analyzed using a Dionex 1000i ion chromatography (IC) Work33 station to determine the chloride, nitrate, and sulphate concentrations. Anisocratic elution with a sodium bicarbonate–sodium carbonate eluent was employed together with a Dionex AS4-SC column. Although standards were prepared containing only the above anions, other anions would have been detected if present at levels greater than ≈ 0.1 mg L^{-1}. For concentrated samples, dilution was required for reliable anion analysis. The concentrations of major cations and trace elements in acidified waters were determined using mass inductive plasma spectrometry (ICP-MS) at the same INETI accredited lab. Reagent blanks and duplicate samples were inserted into each batch for quality control (Ramsey et al. 1987). The geostandards AQUACHECK and EAA 4 were used to check the validity and reproducibility of the results. Typical uncertainties, including all error sources, are <6% for the trace elements, and between 2 and 7% for the major anions, depending on the concentration levels. The limit of detection for the analyzed trace metals is about 0.05–10 mg L^{-1}.

Data Analysis

Enrichment index calculation: One approach for comparing metal concentrations is to compute an index that averages the accumulation of each metal in a sample. To evaluate the degree of trace metal contamination, an Enrichment Index (EI) (Chon et al. 1995; Ferreira da Silva et al. 2005; Kim et al. 1998; Lee et al. 1998; Nishida et al. 1982) was computed by averaging the ratios of the element concentration (mg kg^{-1}) to the permissible level for each element, based on hazard criteria. In this study, six elements (As, Cd, Cu, Pb, Zn, Sb) were selected to calculate the enrichment factor in each sample. For the sediment and alluvium samples, the criteria used for the EI calculation was the Severe Effect Level (indicating the level at which pronounced disturbance of the sediment-dwelling community can be expected) fixed by the Ontario Sediment Quality Guidelines (As, 33 mg kg^{-1}; Cd, 10 mg kg^{-1}; Cu, 110 mg kg^{-1}; Pb, 250 mg kg^{-1}; Zn, 820 mg kg^{-1}) (Persaud et al. 1993). This index is useful in evaluating the degree of multiple element enrichment. An enrichment index over 1.0 indicates that, on average, metal concentrations are above the permissible level, though element enrichment may be from anthropogenic inputs or natural geological sources (Nimick and Moore 1991).

Principal component analysis (PCA): Multivariate statistical analysis of geochemical data can be effective in quantifying anthropogenic effects (i.e., Ali et al. 2006; Anazawa et al. 2004; Birke and Rauch 1993; de Carlo et al.

2005; Wu et al. 2007). PCA allows one to find associations between variables, thus reducing the dimensionality of the row data table. This is accomplished by diagonalization of the correlation matrix of the data, which transforms a large number of variables into a smaller number of orthogonal components (or factors). In this new reference system, the similarities between variables are highlighted, allowing one to interpret the contribution of geology versus the anthropogenic processes. The PCA analysis was applied to a data matrix of 41 stream samples by 18 variables.

Results and Discussion

Geochemistry and Mineralogy of the Tailings and Mud Dams

It is estimated that mining and ore processing at Panasqueira mining site have exposed ≈ 10 million m^3 of mining wastes to weathering. The tailings and mud dams (in Rio and Barroca Grande) contain significantly elevated levels of As, Cd, Cu and Zn (Table 1).

The Rio tailings samples (DC4 and DC6; Fig. 2c) contained abundant amounts of scorodite, sphalerite, wolframite, quartz, natrojarosite, montmorilonite, ilite-vermiculite, some silicates like kaolinite, and also sulphate minerals. Arsenopyrite breaks down through the actions of oxygen, water, and catalytic bacteria (e.g., ferrooxidans sp.) in the supergene environment, with scorodite ($FeAsO_4 \cdot 2H_2O$) being one of the major products (Boyle

and Jonasson 1973; Dove and Rimstidt 1985; Robins 1987). According to Dove and Rimstidt (1985), a typical reaction leading to destruction of arsenopyrite in the supergene environment is:

$$FeAsS + 14Fe^{3+} + 10H_2O \rightarrow 14Fe^{2+} + SO_4^{2-}$$
$$+ FeAsO_4 \cdot 2H_2O + 16H^+ \quad (1)$$
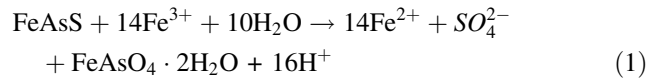
Acid drainage occurs at the base of the Rio tailings dam and the arsenopyrite stockpile. The sample collected from the stockpile (AST; Fig. 2c) has high concentrations of Ag (124 mg kg^{-1}), As (210,000 mg kg^{-1}), Cd (3,057 mg kg^{-1}), Cu (1,426 mg kg^{-1}), Fe (19.8%), Pb (1,450 mg kg^{-1}), W (5,166 mg kg^{-1}), and Zn (460 mg kg^{-1}).

In the Rio tailings dam, melanterite ($Fe^{2+}(SO_4) \cdot 7(H_2O)$) and minor amounts of rozenite ($Fe^{2+}(SO_4) \cdot 4(H_2O)$) and szomolnokite ($Fe^{2+}(SO_4) \cdot (H_2O)$) were observed (DRX identification).

Selected drill cores were macroscopically studied. The samples revealed vertical zonation, with the upper parts of the cores generally formed by fine dark grey mud while the lower parts (7–10 m from the bottom) were reddish, sometimes with greenish grey shades. Ferruginous crusts, 0.1–0.8 m thick, were observed in all of the drill cores. These crusts were yellow, red, and/or brown and are probably related to successive dry summers in the past. The selected trace element composition of the studied drill cores material is given in Table 2. The chemical analysis demonstrates the dominance of As (3,094–240,000 mg kg^{-1}), Cd (28–4,028 mg kg^{-1}), Cu (78–7,200 mg kg^{-1}), Fe (5.3–28.8%), and Zn (142–27,000 mg kg^{-1}).

Table 2 ICP-MS results for As, Cd, Cu, Fe, Mn, P, Pb, Sn, W, and Zn for core samples from the Rio tailings mud dam

Sample	Depth (m)	As	Cd	Cu	Fe	Mn	P	Pb	Sn	W	Zn
DC2/1	2.39	140,000	2,456	4,848	21.4	1,605	1,509	297	539	7,788	11,000
DC2/2	10.0	87,000	1,419	3,837	15.0	841	949	116	274	5,464	6,500
DC2/3	23.0	3,094	45	1,092	5.3	854	1,178	104	584	2,232	2,199
DC2/4	35.49	19,000	207	1,477	7.4	786	1,302	82	384	2,162	2,776
DC2/5	40.43	3,313	28	78	6.5	419	564	625	400	4,071	142
DC4/1	2.73	100,000	1,985	3,834	11.3	1,172	2,452	97	858	5,269	27,000
DC4/2	13.48	4,332	59	1,038	5.8	737	920	143	661	2,050	2,431
DC4/3	19.58	4,786	58	1,586	5.4	862	1,210	120	560	2,676	2,292
DC5/1	2.32	190,000	2,996	2,804	18.0	1,369	1,029	312	869	8,676	9,100
DC5/2	8.0	240,000	4,028	7,200	28.5	791	449	821	875	6,096	21,000
DC5/3	16.53	6,400	60	1,895	6.1	899	1,135	103	228	3,296	1,254
DC5/4	32.0	6,800	63	1,957	5.4	988	1,435	94	425	2,637	1,143
DC6/1	0.0	220,000	3,802	873	24.8	795	439	132	411	3,728	4,185
DC6/2	8.38	180,000	3,026	4,268	28.8	1,100	1,059	179	832	3,754	18,000
DC6/3	22.0	6,400	57	1,895	5.8	852	1,077	73	216	3,486	1,394
DC6/4	32.58	8,900	104	1,593	6.4	833	1,149	182	376	2,782	2,015
DC6/5	36.0	32,000	459	2,123	9.8	797	1,034	165	433	2,989	3,907

Concentrations are expressed in mg kg^{-1}, except for Fe (%)

The results show that arsenic is enriched, ranging from 8.7 to 24%, in all of the studied cores from the surface down to a depth of 13 m; below this depth, arsenic concentrations decrease to values near or below 1%. Cores DC2 and DC6 are exceptions in that in them the As content increases at 35–36 m.

The higher concentrations near the surface may be due to revised ore treatment process management in the plant, as the company used successively finer grinding procedures to liberate the ore more economically, giving rise to increasingly fine-grained rejected materials. Previously, the relatively coarse-grained sulphides, with coarse grain and high metal contents, were considered as sterile material and were rejected to the tailings. When the company began extracting copper from the associated "sterile" sulphides, the sulphides were also milled to a fine caliber to separate and recover the cooper from the chalcopyrite, while the others sulphides were rejected. The fine grain size made the reject materials much more reactive to weathering and leaching and, consequently, they have contributed to the increased metals content in the tailings and mud dams.

The Rio dam (DC6) consists predominantly of quartz, mica, feldspar, illite-vermiculite, arsenopyrite, marcasite, pyrite, pyrrhotite, and chalcopyrite. Other minerals, like scorodite and natrojarosite, are also present.

The Barroca Grande tailing piles have significantly elevated concentrations of As, Cd, Cu, Pb, Sn, W, and Zn. The mineralogy of these tailings was mainly quartz, muscovite, kaolinite, illite-montmorilonite, montmorilonite-vermiculite, and chlorite, and also arsenopyrite, wolframite, and natrojarosite. The dam materials from Barroca Grande also contain high concentrations of As (2715–200,000 mg kg^{-1}; Table 1) and Ag, Cd, Cu, Fe, Mn, P, W, and Zn. The old dam may pose a more significant potential threat due to the fine-grained nature of the materials and its location with respect to the Casinhas stream. The DRX analysis of the active dam sample (AD1) revealed the presence of scorodite, arsenopyrite, quartz, sphalerite, hematite, and muscovite while the sample from the old dam (OD1) contained quartz, pyrite, chalcopyrite, wolframite, and scorodite. All of the EI values show that the studied tailings and dams samples are metal-enriched at a level likely to be toxic to the ecosystem (the EI varies from 31.9 to 2251.1 for Rio and 30.4 to 1783.9 for Barroca Grande.

Geochemistry and Mineralogy of Stream Sediment and Alluvium

The conductive plasma results for the stream sediments samples analyzed are given in Table 3. It can be observed

Table 3 Average contents for selected chemical elements in stream sediments

	Css (n = 8)				Zss (n = 20)				Bkss (n = 13)			
	Mean	Med.	Min.	Max.	Mean	Med.	Min.	Max.	Mean	Med.	Min.	Max.
Ag	7.4	1.0	1.0	23.0	1.7	1.0	1.0	11.0	1.0	1.0	1.0	1.0
As	5,353	732	91	18,000	927	102	10	15,000	34	30	10	88
B	873	367	261	2,018	112	61	8	631	34	24	12	99
Ba	221	208	180	269	278	284	152	367	329	346	248	372
Cd	85.4	19.5	2.0	268.0	13.1	2.0	2.0	186.0	2.5	2.0	2.0	8.0
Co	42	27	12	120	21	16	5	104	19	16	5	43
Cu	1,711	1,153	116	4,561	293	215	13	895	64	39	20	207
Fe	5.23	4.55	3.60	8.10	3.18	3.05	2.20	4.80	3.82	3.80	2.70	4.70
Mn	1,515	806	300	3,638	841	528	333	4,777	540	502	180	875
Ni	70	56	31	125	19	15	7	64	30	28	7	64
P	1,019	1,039	745	1,142	1,188	1,158	742	1,800	881	836	452	1,572
Pb	46	31	19	117	23	20	8	83	28	25	20	44
Sb	18	6	6	51	8	6	6	32	6	6	6	6
Sn	206	172	51	394	94	36	21	764	114	13	6	735
V	91	91	75	114	52	52	19	98	99	101	70	113
W	1,392	318	101	4,103	312	65	17	2,876	59	20	3	301
Y	204	137	14	538	35	25	2	107	8	5	3	24
Zn	1,444	1,004	240	3,562	415	332	79	1,454	211	162	80	638

Concentrations are expressed in mg kg^{-1}, except for Fe (%)

Css Casinhas stream sediment samples, *Zss* Zêzere river sediment samples, *Bkss* stream sediment samples representative from local geochemical background

that some of the stream sediments are seriously contaminated compared to background levels (values obtained from samples taken in an upstream area not affected by the mine), despite some mitigation after the confluence with the Zêzere River. Comparing the mean values of Casinhas (Css) and Zêzere (Zss) with the mean values of the background stream sediments (Bkss samples), it is clear there is moderate to strong enrichment of As (157×; 26×), Cd (34×; 5×), Cu (27×; 5×), and Zn (7×; 2×). Given the toxicity of these elements, this represents a potentially harmful situation.

The estimated EI values for the sediments are elevated in both the Casinhas (3.9–41.5) and the Zêzere (1.0–10.6). All of the background samples had EI < 1.0. Comparison to the Ontario aquatic sediment quality guidelines (Persaud et al. 1993) indicates that the majority of the Casinhas samples exceed the severe effect level for As and Cu (100% of samples), Cd (90% of samples) and Zn (50% of samples) and so are deemed "grossly polluted". Correlation coefficients of data related to the Casinhas samples indicate an association of As–Fe (0.95), As–W (0.95), As–Cd (0.94), Cd–Cu (0.91), Cd–Zn (0.92), W–Sb (0.92), and Cd–W (0.91), in keeping with the mineralogy. The Casinhas stream sediment sample from near Barroca Grande (Css9; Fig. 2) contains arsenopyrite, wolframite, quartz, pyrite, chalcopyrite, and illite/kaolinite.

The stream sediments sampled downstream of the Rio tailings (Zss12A e Zss12A; Fig. 2), after the Casinhas stream and Zêzere River confluence, contains wolframite, ilmenite, cassiterite, mica, chlorite, quartz, feldspar, kaolinite, chlorite-vermiculite, and hematite. This mineral assemblage is typical of the local mineralization and confirms that the contamination is due to the release of mine waste.

Table 4 summarizes the eigenvalues and the corresponding explained variance of the first four principal components, which account for 87.82% of the total variance in the original geochemical dataset.

Table 4 Results of principal component analysis on stream sediment data ($n = 41$)

Variables	PC1	PC2	PC3	PC4
Ag	0.9473	0.2719	−0.0643	0.0921
As	0.8950	0.2877	−0.0853	0.1239
B	0.9333	0.0942	−0.0835	0.0208
Ba	−0.5825	0.1474	−0.3782	0.2731
Cd	0.9319	0.2304	−0.0788	0.1325
Co	0.2333	−0.9112	0.1165	0.1664
Cu	0.9689	−0.0249	0.0131	0.1318
Fe	0.9008	−0.0603	−0.3033	−0.1844
Mn	0.3546	−0.8014	0.2628	0.2580
Ni	0.5285	−0.7733	−0.1072	−0.1476
P	0.1593	−0.0274	0.8604	−0.1160
Pb	0.8198	−0.0299	−0.2431	0.0682
Sb	0.8546	0.2496	0.0502	−0.0277
V	0.0671	−0.4413	−0.7153	−0.4654
Y	0.9657	−0.0249	0.0139	0.1323
Zn	0.8942	−0.1550	0.0831	0.1660
Sn	0.4797	0.0536	0.3392	−0.7359
W	0.9192	0.2549	0.0892	−0.1104
Eigenvalues	10.2263	2.6664	1.7975	1.1181
Total variance (%)	56.81	14.81	9.99	6.21
Cumulative variance (%)	56.81	71.63	81.61	87.82

Figure 3 shows the projections of the 18 variables in the 3 factorial planes (a, PC1/PC2; b, PC1/PC3, c, PC1/PC4) where 6 element associations can be spotted. One of these associations is concordant with the mine paragenesis, and is therefore most important in terms of environment pollution and public health, while the others are manly related to the local geology.

From analysis of Fig. 3a, three groups of variables can be identified, two of them with strong associations with PC1 and the third correlated with PC2. These associations
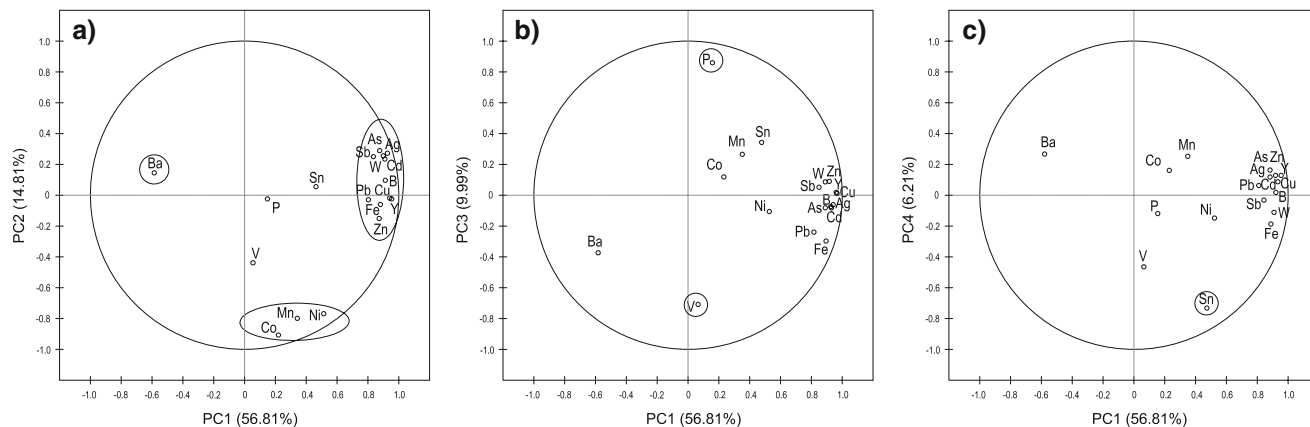

Fig. 3 Graphic representation of factorial planes for: **a** PC1/PC2; **b** PC1/PC3, and **c** PC1/PC4

with PC1 (Ag–As–B–Cd–Cu–Fe–Pb–Sb–Zn–W–Y and Ba in opposition) indicates that the elements representative of the original paragenesis maintain a close relationship in the secondary environment. The group related by PC2 (Co–Ni–Mn) are natural sediment components, associated with the presence of basic metasedimentary rocks in the area. The presence of Mn could be related to secondary Mn oxides and hydroxides, which are commonly present in the stream sediments.

The second factorial plane (PC1/PC3), Fig. 3b, is dominated by the *P* variable, with the *V* variable in opposition. This association is probably linked to apatite, related to the mineralization in the stream sediments. Apatite is a host mineral for *V* (Reimann and Caritat 1998), so probably *P* was substituted in the Panasqueira apatite structure by *V*.

The third factorial plane (PC1/PC4), Fig. 3c, is characterized by tin (separated from the other metalliferous elements, including W). Rolled crystals of cassiterite were observed in the Panasqueira stream sediments (but not rolled crystals of wolframite). The mobility of Sn in the natural environment is low (Rose et al. 1979) and highly pH dependent. In stream sediment, most detrital Sn is held in resistant oxide phases, such as cassiterite. This phase is highly resistant to both chemical and physical weathering and can be transported long distances from the source areas and concentrated in stream sediments. Weathering provokes the transport of natural and anthropogenic Sn under acidic and reducing conditions, although SnS_2 is insoluble under reducing conditions (Brookins 1988).

The mobility of tungsten is intermediate to low in neutral pH water (Rose et al. 1979). The principal ore mineral, wolframite, is similar to cassiterite in resistance to chemical weathering but is somewhat less resistant than cassiterite to physical weathering. Tungsten minerals are brittle and readily break down into fine particles that disperse in fine-grained sediment.

Figure 4 shows the spatial distribution of PC1 and indicates that the positive scores occur predominantly in Casinhas Stream, downstream of the Barroca Grande tailings, and also in the main Zêzere River immediately downstream of the Rio tailings. These high positive values are related to anomalous contents of Ag, As, Cd, Cu, Zn, Sn, and W. From the figure, it is also clear that the Barroca Grande tailings site appears to be the main source of chemical contamination of the area.

The mechanical dispersion of sediment downstream and down-gradient from Barroca Grande and Rio and the metalliferous acidic waters draining these sites contaminate the stream sediments and surface waters with As and sulphide-related heavy metals (Cu, Pb, Zn, and Cd). In Fig. 4, the positive anomalous patterns (related to the anomalous contents of Ag, As, Cd, Cu, Zn, Sn, and W) persist for
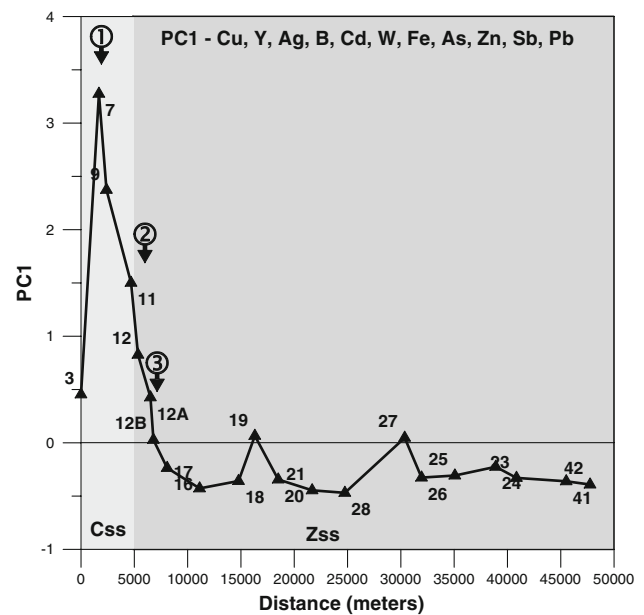

Fig. 4 Spatial distribution of PC1 scores along the Casinhas Stream and Zêzere River: ① input from Barroca Grande; ② confluence with Zêzere River; ③ input from Rio tailings

7 km downstream. The irregular decay of these patterns on the main river suggests the interference of local hydrological and physiographical factors (expressed by periods of severe and wet winters affecting the geomorphologically rugged region), which promote mechanisms of fast erosion, transport, and accumulation of solid materials, most of which are transported in suspension by surface waters.

The concentrations appear to decrease downstream in the Zêzere River, suggesting some attenuation, presumably the result of dilution by uncontaminated sediment. This interpretation is supported by chemical analyses of alluvium (samples A1, A2, A3, and A4; Fig. 2; Table 5) collected downstream of the Rio tailings. Results suggest that mechanical dispersion have more influence on redistribution of elements in the secondary geochemical environment. The solid material transport, due to the torrential dynamic river surface waters, favors primary mineral mobilization, which carries metals that will be incorporated in stream sediments, namely, As, Cd, Cu, Zn, Sn, and W (Table 5).

Table 5 Concentrations of selected chemical elements in alluvium samples, expressed in mg kg^{-1} except for Fe (%)

Sample	As	Cd	Cu	Fe	Mn	P	Pb	Sn	W	Zn
A1	533	4.0	282	3.40	852	1,152	32	83	208	310
A2	431	2.0	197	2.80	799	1,439	41	96	220	394
A3	185	2.0	438	3.00	675	1,285	39	102	210	448
A4	1,090	11.0	384	3.30	1,149	1,209	297	65	254	11,000

The values achieved for EI in the alluvium samples varies from 2.3 to 13, mainly due to the presence of significant levels of As, Pb, and Cu. These high values are probably related to mechanical dispersion of tailings as a result of erosion.

However, it must be stressed that other mechanisms also contribute to the secondary dispersion of these metals, such as: (a) precipitation of hydroxide, oxyhydroxide, or hydroxysulphate phases from aqueous species as pH increases; and (b) adsorption of metals onto neoformed mineral surfaces (carbonates or iron and manganese coatings, for example), according to Nordstrom ([1982]) and Chapman et al. ([1983]).

Iron coatings (precipitate) observed in the Zêzere River were sampled. Comparing the coating sample (As = 37,000 mg kg^{-1}; Cd = 423 mg kg^{-1}; Cu = 1,626 mg kg^{-1}; Fe = 25.1%; Mn = 712 mg kg^{-1}; Pb = 139 mg kg^{-1}; Zn = 1288 mg kg^{-1}) with the water sample SW6 collected nearby, it seems that the decrease in As, Cu, and Cd is associated with co-precipitation.

The ferruginous crust collected at the base of the Rio tailings dam also had high levels of Fe, Cu, Zn, Cd, and As (As = 40 000 mg kg^{-1}; Cd = 453 mg kg^{-1}; Cu = 3,305 mg kg^{-1}; Fe = 12%; Mn = 572 mg kg^{-1}; Pb = 319 mg kg^{-1}; Zn = 663 mg kg^{-1}) and confirms the transfer of these elements from the tailings and mud impoundment.

These neoformation mechanisms limit the downstream effects of the acid drainage since the crusts and clays efficiently fixate some of the contaminant elements, especially the iron oxides (Valente and Leal Gomes [1998]).

Chemical Characterization of Surface Waters

Stream water reflects the interplay between geosphere/hydrosphere and pollution, and can provide some clues that will allow the assessment of the influence of AMD (chemical dispersion) and tailings (mechanical dispersion) in the Casinhas Stream and Zêzere River (Table [6]; Fig. [2]a).

A local background reference unaffected by AMD was obtained by the collection of two samples (SW4 and SW4A) upstream of the mine sites (Table [6]). These samples had lower SO$_4^{2-}$ and Cl$^-$ concentrations, circumneutral pH, low conductivity values, and very low metal concentrations, though Fe, Al, and Zn were present in significant concentrations. The concentrations of other elements such as As, Ba, Cd, Co, Cu, Ni, Pb, and U were lower, close to or below the detection limit of the analytical technique. All of the detected cations were below drinking water standards (2 µg L^{-1} for Cu; 3 mg L^{-1} for Zn; 5 µg L^{-1} for Cd; 10 µg L^{-1} for As, 25 µg L^{-1} for Pb; 10 µg L^{-1} for Mn and Cr; 0.2 mg L^{-1} for Fe) based on Decree-Law 243/2001

([2001]), which dictates the quality required of surface water intended for drinking water in Portugal. According to the Ficklin diagram, these samples are near-neutral and low in metals.

The coexistence of wolframite, cassiterite, sulphides, carbonates, and silicates is responsible for the peculiar behavior in the tailings surface environment. Weathering of sulphide-rich materials results in AMD at the Panasqueira mine. During runoff events, rain water infiltrates the tailings and dissolves secondary minerals, producing strongly acidic water. The low pH keeps the trace elements dissolved and increases remobilization and spatial distribution. The chemical composition of these acid effluents is reported in Table [6]. Samples SW10, SW11, SW12 (see page waters of Rio), and SW13 (Barroca Grande mine adit) have pH values typical of AMD.

The chemical composition of these waters include extremely high concentrations of dissolved sulphate, Al, As, Cd, Co, Cu, Fe, Mn, Ni, and Zn. All of these concentrations exceed the reference limits for water quality. According to the Ficklin diagram (Plumlee et al. [1994]) these waters plot in the "acid, high metal" and "highly acid/extreme metal" zone (Fig. [5]). The observed metal concentrations are similar to other AMD case studies (Boult et al. [1994]; Brake et al. [2001]; Sainz et al. [2003]; Sracek et al. [2004]).

The highest SO$_4^{2-}$ and metal concentrations were found in the acidic leachate from the huge waste piles of Rio and are indicative of the oxidation and dissolution of pyrite and the accompanying sulphides (chalcopyrite, sphalerite, and arsenopyrite). An excellent correlation has been found between the electrical conductivity of these waters and the dissolved SO$_4^{2-}$ ($r = 0.99$, $p < 0.05$), which confirms that conductivity is a good indicator of stream waters that may be affected by AMD.

During dry seasons, these acidic waters evaporate, progressively depositing sulphate efflorescences characteristic of an extremely acidic environment. These are rarely found as mono-mineral phases; most consist of mixtures of Fe–Al hydrated sulphates such as melanterite and minor amounts of rozenite and szomolnokite. These Fe(II)-rich salts dominate the discharge points of the more acidic Fe(II)-rich waters and were observed at the base of the Rio tailings. This new mineralogy is mainly controlled, according to Frau ([2000]) and Valente and Leal Gomes ([1998]), by the wet–dry cycles related to seasonal variations in rainfall. The accumulation of these salts at the mine sites plays an important role in the transient storage of metals and acidity, since they can be easily redissolved during rainfall episodes.

The mine water flows seasonally, with minimal base flow conditions during the dry season and high flow during the rainy season. Discharge from the drainage tunnel is reported to range from ≈ 250 m^3/h during the summer to

Table 6 The pH, electrical conductivity, major ions (Cl$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg^{2+} and Ca^{2+}) (mg L^{-1}) and trace elements (µg L^{-1}) in surface waters collected in the Panasqueira area ($n = 11$)

	Casinhas stream			Zêzere river				Seepage waters			
	SW1	SW2	SW3	SW4	SW4A	SW5	SW6	SW10	SW11	SW12	SW13
pH	4.3	5.7	5.7	6.8	7.1	6.9	6.8	3.0	2.9	3.2	3.9
Cond	350	1,088	851	59	37	70	76	3,630	4,400	2,020	1,260
Si	18	16	16	10	12	10	11	103	108	99	30
Cl	5	7	6	5	4	5	7	5	6	4	5
SO$_4$	152	605	441	4	4	9	12	2,991	3,717	1,398	727
Na	5	12	10.4	6	4	7	7	17.8	19.3	11.8	12.7
K	1	5	4	1	0.3	1	1	6	0.1	1	2
Mg	23	73	56	1	1	2	3	274	357	103	95
Ca	22	120	87	3	1	3	4	287	401	175	107
Al	1,500	800	600	13	7	134	266	149,000	161,000	99,000	6,100
As	5[a]	13[a]	13[a]	2	4	3	4	2,138	544	146	48
Ba	20	17	39	4	1	4	4	36	29	25	32
Cd	15	58	40	0.2	0.2	0.9	1.6	464	393	226	88
Co	6	84	60	0.3	0.2	3.1	9.6	2,621	3,330	1,144	125
Cu	190	600	510	6.3	3	42.9	120.8	42,700	54,300	20,100	2,100
Fe	100	100	290	40	<30	<30	130	82,500	91,000	9,400	1,700
Li	32	140	101	<4	<4	<4	4	1,173	1,010	751	192
Mn	1,100	7,000	4,100	19	4	85	256	88,700	92,600	22,300	10,200
Ni	110	273	200	<1	1	4	9	2,153	2,827	1,137	397
Pb	<22	<22	<22	<0.3	<0.3	<0.3	<0.3	<22	<22	<22	<22
Rb	<18	36	28	2.5	0.6	2.5	2.5	76	37	31	28
Sr	75	338	256	18	9	20	21	658	507	380	396
U	<9	<9	<9	<1	<1	<2	<1	16	13	10	<9
Y	6	19	19	0.2	<0.1	0.7	1.3	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Zn	2,000	6,300	4,800	18	21	105	181	49,200	44,500	21,900	12,400

Samples SW1, SW2, and SW3, Casinhas Stream downstream of the Barroca Grande tailings; samples SW4 and SW4A, Zêzere river upstream of the Rio tailings; samples SW5 and SW6, Zêzere river; samples SW10, SW11, and SW12, seepage waters collected in Rio tailings; sample SW13, mine entrance in Barroca Grande

[a] These three values are lower than the quantification limit of the ICP-MS method but higher than the detection limit of the samples

≈600 m^3/h during the winter. The highly acidic water from the tailing piles flows into nearby streams. At Barroca Grande, the water is collected, pumped, and neutralized with lime [Ca(OH)$_2$] at a water treatment plant. The plant capacity is reported to be ≈300 m^3/h (Cavey and Gunning 2006).

The discharges are reported to coincide with high flows in the local streams and rivers. As a result, untreated AMD is diluted by surface water. The water samples collected in the Casinhas Stream (SW1, SW2, SW3) had very low concentrations of chloride but high levels of sulphate and metals. The results reveal that the Na–Cl regional hydrogeochemical facies modify to a CaSO$_4$ facies near the mines.

The lime used in the treatment plant increases the pH and efficiently removes the iron and also the As, through co-precipitation with Fe (see Table 6, samples SW1, SW2, SW3). The results also indicate that leaching at the Rio tailings site is affecting the Zêzere River hydrochemistry downstream (samples SW5 and SW6), increasing the Al, Cd, Cu, Mn, and Zn concentrations compared to the background values. However, these samples do not reveal high As concentrations, mainly due to the coprecipitation with Fe(III) oxyhydroxides at or near the Rio site. The contaminant concentrations in the Zêzere waters decrease with distance from the source of the pollution. Compare the analysis of SW10 and SW11 with that of SW6, collected in the Zêzere River near the source of the AMD. The pH and Eh (oxidizing environment) of the river, as well, as microbiological mechanisms, causes Fe and Mn precipitation, and coprecipitation of Mn and other contaminants.
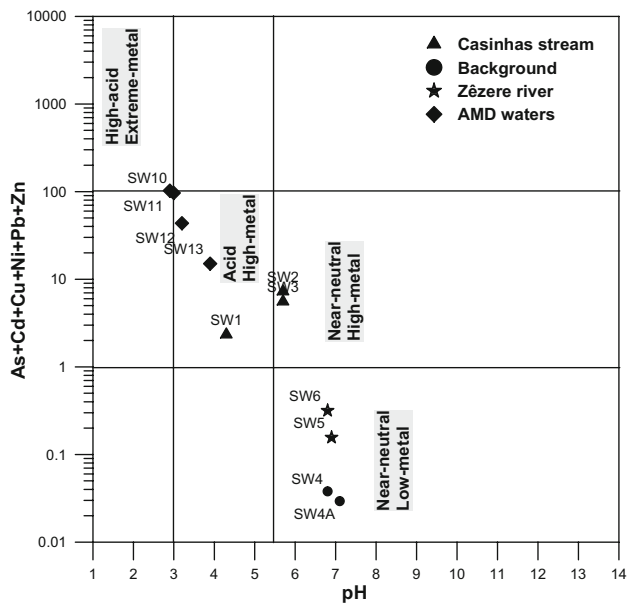
Fig. 5 Surface water samples classification according to Ficklin diagram (Plumlee et al. 1994)

Conclusions

The mining and beneficiation processes at Panasqueira mine produces arsenic-rich mine wastes that are largely responsible for the high levels of metals at the Barroca Grande and Rio tailings. It is clear that oxidation of sulphides tailings and flow from open impoundments are the main source of pollution in the surrounding area and is responsible for the mobilization and migration of metals from the mine wastes into the environment. Comparison to the Ontario aquatic sediment quality guidelines indicates that the majority of the streams located near Barroca Grande exceed the severe effect level for As, Cu, Cd, and Zn and are "grossly polluted".

The mineral assemblage identified in the stream sediment samples (wolframite, ilmenite, cassiterite, mica, chlorite, quartz, feldspar, kaolinite, chlorite-vermiculite, and hematite) confirms that mechanical dispersion occurs downstream and down-gradient from Barroca Grande and Rio. The data also demonstrate other chemical reactions around the mine site, involving leaching, transport, and precipitation of metals. The acidic waters draining these sites contaminate the stream sediments with As and sulphide-related heavy metals (Cu, Pb, Zn, and Cd). Together these mechanisms are responsible for anomalous patterns (related to the anomalous contents of Ag, As, Cd, Cu, Zn, Sn, and W) for 7 km downstream. The irregular decay of the patterns on the main river suggests the interference of local hydrological and physiographical factors, which promote fast erosion, transport, and accumulation of solid materials, most of which are transported in suspension by surface waters.

Secondary minerals also play an important role in the natural retention of oxyanions (e.g., H_2AsO_4) due to sorption and coprecipitation. Clays and iron oxyhydroxide precipitation contributes to arsenic adsorption on stream sediments.

References

Ali K, Cheng Q, Li W, Chen Y (2006) Multi-element association analysis of stream sediment geochemistry data for predicting gold deposits in south-central Yunnan Province, China. Geochem Explor Environ Anal 6(4):341–348

Alloway BJ (1993) Heavy metals in soils. Wiley & Sons Inc, New York, pp 339

Anazawa K, Kaida Y, Shinomura Y, Tomiyasu T, Sakamoto H (2004) Heavy-metal distribution in river waters and sediments around a "Firefly Village", Shikoku, Japan: application of multivariate analysis. Anal Sci 20:79–84

ASTM (American Society for Testing Materials) (1984) Annual book of ASTM standards, water environmental technology, V 11.01

Birke M, Rauch U (1993) Environmental aspects of the regional geochemical survey in the southern part of East Germany. J Geochem Explor 49:35–61

Bloot C, de Wolf LCM (1953) Geological features of the Panasqueira tin-tungsten ore occurrence (Portugal). Bol Soc Geol Port 11(1):1–58

Boult S, Collins ND, White KN, Curtis CD (1994) Metal transport in a stream polluted by acid mine drainage—the Afon Goch, Anglesey, UK. Environ Pollut 84:279–284

Boyle RW, Jonasson IR (1973) The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J Geochem Explor 2:251–296

Brake SS, Connors KA, Romberger SB (2001) A river runs through it: impact of acid mine drainage on the geochemistry of West Little Sugar Creek pre- and post- reclamation at the Green Valley coal mine, Indiana, USA. Environ Geol 40:1471–1481

Breiter K (2001) Report about laboratory investigations of rock samples from the Panasqueira mine and recommendations for future exploration, Nov 2001

Brookins DG (1988) E_h–pH diagrams for Geochemistry. Springer-Verlag, Berlin

Cavey G, Gunning D (2006) Updated technical report on the Panasqueira mine, Distrito de Castelo Branco, Portugal. ORE-QUEST, pp 67

Chapman BM, Jones DR, Jung RF (1983) Processes controlling metal ion attenuation in acid mine drainage streams. Geochim Cosmochim Acta 47:1957–1973

Chon HT, Cho CH, Kim KW, Moon HS (1995) The occurrence and dispersion of potentially toxic elements in areas covered with black shales and slates in Korea. Appl Geochem 11:69–76

Conde LN, Pereira V, Ribeiro A, Tadeu D (1971) Jazigos hipogénicos de estanho e volfrâmio. Livro-guia da Excursão #7, I Congresso

Hispano-Luso-Americano de Geologia Económica, Lisboa, Madrid, Spain, pp 81

Correa A, Naique RA (1998) Minas Panasqueira, 100 years of mining history paper presented at the 1998 International Tungsten Industry Association (ITIA) conference

Corrêa de Sá A, Naique RA, Nobre E (1999) Minas da Panasqueira—100 anos de História. Bol Minas 36(1):3–22

D'Orey FC (1967) Tin-tungsten mineralization and paragenesis in the Panasqueira and Vale de Ermida mining districts, Portugal. Comunicações Serviços Geológicos de Portugal, tomo LII, pp 117–167

de Carlo EH, Tomlinson MS, Anthony SS (2005) Trace elements in streambed sediments of small subtropical streams on O'ahu, Hawai'i: results from the USGS NAWQA program. Appl Geochem 20(12):2157–2188

Decree-Law 243/2001 (2001) Portuguese Republic Diary, Ministry for Environment, Spatial Planning and Regional Development. I SÉRIE-A #206, 5 Sept 2001

Dinis da Gama C (2002) Geotechnical and laboratory study of the tailings in the River Zêzere waste heap. Beralt tin and wolfram report, Lisbon, Portugal, pp 9

Dold B, Fontboté L (2001) Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy and mineral processing. Special issue: geochemical studies of mining and the environment. J Geochem Explor 74(1–3):3–55

Dove PM, Rimstidt JD (1985) The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. Am Mineral 70:838–844

e-EcoRiskDoW (2001) Regional enterprise network decision-support system for environmental risk and disaster management of large-scale industrial spills. EU project coordinated by C Banninger, pp 70

e-Ecorisk (2007) A regional enterprise network decision-support system for environmental risk and disaster management of large-scale industrial spills. WP3-case study characterisation. Deliverable 3.1, pp 20

Farinha JA (2005) Packing and sealing of the sulphides existent on Rio tailing, environmental concerns. Internal technical note, April 2005, pp 5 + appendices

Ferreira da Silva E, Matos J, Patinha C, Reis P, Cardoso Fonseca E (2005) The effect of unconfined mine tailings on the geochemistry of soils, sediments and surface waters of the Lousal area (Iberian Pyrite Belt, Southern Portugal). Land degradation and development, Wiley Europe, pp 213–228

Forstner U, Wittmann GTW (1983) Metal pollution in the aquatic environment. 2nd rev, 24th edn., Springer-Verlag, Berlin, pp 486

Frau F (2000) The formation-dissolution-precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: environmental implications. Mineral Mag 64:995–1006

Gieré R, Sidenko NV, Lazareva EV (2003) The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). Appl Geochem 18(9):1347–1359

Julivert F, Fontboté J, Ribeiro A, Conde L (1974) Mapa Tectonico de la Península Ibérica y Baleares, escala 1:1,000,000. Inst Geol Minero España, Madrid, Spain, pp 113

Kelly WC, Rye RO (1979) Geologic, fluid inclusion and stable isotope studies of the tin-tungsten deposits of Panasqueira, Portugal. Econ Geol 74:1721–1822

Kim KW, Lee HK, Yoo BC (1998) The environmental impact of gold mines in the Yugu-Kwangcheon Au–Ag metallogenic province, Republic of Korea. Environ Technol 19:291–298

Lee JS, Chon HT, Kim JS, Kim KW, Moon HS (1998) Enrichment of potentially toxic elements in areas underlain by black shales and slates in Korea. Environ Geochem Health 20:135–147

Lotze F (1945) Observation respect a la division de los variscides de la Meseta Ibérica. Publ Estrag Geol Espanã 5:149–166

Nimick DA, Moore JM (1991) Prediction of water-soluble metal concentrations in fluvially deposited tailings sediments, Upper Clark Fork Valley, Montana. USA Appl Geochem 6:635–646

Nishida H, Miyai M, Tada F, Suzuki S (1982) Computation of the index of pollution caused by heavy metals in river sediments. Environ Pollut (B) 4:241–248

Nordstrom DK (1982) The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3–SO_3–H_2O at 298 K. Geochim Cosmochim Acta 46:681–692

Nordstrom DK, Alpers CN (1999) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc Natl Acad Sci USA 96:3455–3462

Noronha F, Doria A, Dubessy J, Charoy B (1992) Characterization and timing of the different types of fluids present in the barren and ore veins of the W-Sn deposit of Panasqueira, Central Portugal. Miner Depos 27:72–79

Persaud D, Jaagumagi R, Hayton A (1993) Guidelines for the protection and management of aquatic sediment quality in Ontario. Ontario Ministry of the Environment and Energy, Queen's Printer for Ontario, Canada, pp 2

Plumlee GS, Smith S, Ficklin WH (1994) Geoenvironmental models of minerals deposits and geology-based- mineral–environmental assessments of public lands. USGS open-file report, pp 94–203

Ramsey MH, Thompson M, Banerjee EK (1987) Realistic assessment of analytical data quality from inductively coupled plasma atomic emission spectrometry. Anal Proc 24:260–265

Reimann C, Caritat P (1998) Chemical elements in the environment. Springer-Verlag, London, pp 398

Reis AC (1971) As Minas da Panasqueira. Bol Minas 8(1):3–34

Robins RG (1987) The solubility and stability of scorodite, $FeAsO_4 2H_2O$ (discussion). Am Mineral 72:842–844

Rodrigues Abrantes J, Gonzalez V (1973) O tratamento mecânico do minério nas Minas da Panasqueira. Bol Minas 19(4):239–247

Rose AW, Hawkes HE, Webb JS (1979) Geochemistry in mineral exploration. 2nd edn., Academic Press, London, pp 657

Sainz A, Grande JA, de la Torre ML (2003) Odiel River, acid mine drainage and current characterisation by means of univariate analysis. Environ Int 29:51–59

Smith M (2006) Panasqueira the tungsten giant at 100+. Operation focus. Int Mining, April, pp 10–14

Sracek O, Choquette M, Gélinas P, Lefebvre R, Nicholson RV (2004) Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada. J Contam Hydrol 69:45–71

Valente T, Leal Gomes C (1998) Tipologia e evolução dos materiais de neoformação supergénica detectados na escombreira da Mina de Valdarcas (Vila Nova de Cerveira–N Portugal)—Implicações ambientais. Cadernos Lab. Xeológico de Laxe 23:43–58

Wu Y, Hou X, Cheng X, Yao S, Xia W, Wang S (2007) Combining geochemical and statistical methods to distinguish anthropogenic source of metals in lacustrine sediment: a case study in Dongjiu Lake, Taihu Lake catchment, China. Environ Geol 52:1467–1474