Geochemistry of waters associated with the old mine workings at Fonte Santa (NE of Portugal)

M. E.P. Gomes[1], I.M.H.R. Antunes[2], P.B. Silva[3], A.M.R. Neiva[4], F.A.L. Pacheco[1]

[1]Department of Geology, University of Trás-os-Montes e Alto Douro (UTAD), Portugal
[2] Polytechnic Institute of Castelo Branco, Portugal
[3] National Laboratory of Energy and Geology (LNEG), Portugal
[4] Department of Earth Sciences, University of Coimbra, Portugal

Abstract: The quartz veins containing scheelite from Fonte Santa mine cut the Lower Ordovician quartzites. A muscovite-biotite granite (G1) and a muscovite granite (G2), both S-type, crop out close to the Fonte Santa mine and are related to the Moncorvo - Bemposta shear zone. The most altered samples of G2 show intense muscovitization and microclinization and contain chlorite, columbite-tantalite, wolframite, W-ixiolite and Fe-oxides. The tin-bearing granites contain 18 ppm (G1) and 73 ppm (G2) Sn. The most altered samples of G2 correspond to a tungsten granite. The quartz veins contain muscovite, chlorite, tourmaline, scheelite, pyrrhotite, pyrite, sphalerite, chalcopyrite, galena, arsenopyrite, iron oxides, Fe-sulfates, phosphates of Pb, Fe and Al. The Fonte Santa mine area was exploited for W between 1942 and 1982. At the end of November 2006, a flood event damaged the tailings dam of Fonte Santa mine, releasing contaminated material and increasing contaminant levels in water within the area of influence of the mine. The waters related to the Fonte Santa mine are poorly mineralized, with electrical conductivity < 965 µS / cm, and of a mixed type or HCO_3^- and SO_4^{2-} types. Most pH values (5.0 – 8.5) indicate that there is no significant acidic drainage in the region, as found in other areas. More acidic values (pH = 3.4) were found in the mine's lagoon. Waters associated with mineralized veins and old mine activities have Fe and Mn concentrations that forbid their use for human consumption and agriculture. Natural Na, Mg and K water contents are associated with the alteration of albite, chlorite and muscovite of country rock, while Ca with the W-bearing quartz veins. Weathering agents are carbonic and sulphuric acids and the latter has a strong influence in areas draining fine-grained mine tailings.

Key-words: mineralizations, scheelite, waters, contamination

1. Introduction

Mining activities have been and remain important contributors to the Portuguese economy. The Neves Corvo and Panasqueira mines are still active. Although about ninety abandoned mining areas are known to be contaminated in Portugal (Oliveira *et al.,* 2002), only a few of these have been subjected to environmental remediation. The abandoned mining sites are frequently located close to occupied rural areas and some of the waters and soils are used for agriculture or human consumption without any assessment of environmental and human health risks (Abreu *et al.,* 2008).

Sulfides are stable and very insoluble under reducing conditions, but oxidation takes place when these minerals are exposed to atmospheric conditions. The weathering of sulfide minerals promotes the formation of sulfuric acid, together with ferrous and ferric sulfates and ferric hydroxides, which lead to acidic conditions in the environment (Bell, 1998), with acid waters containing a high level of dissolved metals (e.g., Marszalek and Wasik, 2000; Cánovas *et al.,* 2008; Navarro *et al.,* 2008). The extent and degree of heavy metal contamination in waste rock and around mines vary depending upon geochemical characteristics and the content of sulfide minerals in the tailings (Johnson *et al*., 2000). Although metals released by sulfide oxidation are attenuated by precipitation, co-precipitation and sorption reactions (McGregor *et al.,* 1998; Berger *et al.,* 2000) in the mines and around them, the content of elements in the environment also depends on their mobility and solubility from rocks and stream sediments to waters. Effluents of abandoned mine workings typically consist of acid mine drainage, eroded material from mine tailings and waste rocks.

The Fonte Santa mine area was mined for W between 1942 and 1982 (Triede, 2002), and since then a significant development in the area has not occurred. The tailings and waste were deposited at the surface and have not been revegetated. As they are exposed to the air and water, they make an important contribution to the environmental geochemistry of the area. At the end of November 2006, after a major rain event, flooding at the Fonte Santa mine damaged the dam tailings, releasing fine eroded material into the Ribeiro da Ponte creek, which drains into the Sabor River.

The aim of this paper is to present a detailed study of the geochemistry of Fonte Santa granites and related scheelite quartz veins and of the associated waters from the area, and to understand the distribution and mobility of the chemical elements. Waters from inside and outside the Fonte Santa mine area are compared, using data collected over a one year period, to evaluate the geochemical impact of the W deposits and the respective old mine workings on the quality of surface waters. The mineralogy of granites and the chemistry of minerals from granites and W-bearing quartz veins were used to model water-rock interactions that affect the composition of surface waters within the studied area.

2. Geological setting

The Fonte Santa mine is located in the northeast of Trás-os-Montes region (Fig. 1a), along the southern border of the Mirandês Plateau in northern Portugal. Wolframite mining started in 1941, but scheelite was only discovered in 1942 and the maximum production in the mine was attained in 1953. Mining stopped in 1982. About 2784 tonnes of tungsten ore were produced along with 100 000 m^3 of tailings (Triede, 2002). The main quartz veins were exploited in open pits and underground.

The Fonte Santa area is located in the autochtonous Central Iberian Zone (ZCI), where Ordovician rocks crop out extensively. The mine country rocks consist mainly of Lower Ordovician chloritic phyllites with rare intercalations of Armorican quartzites and Cambrian metasediments. Magnesian marbles crop out close to the area (Silva, 2000).

Syn- to late-kinematic medium- to coarse-grained, porphyritic, muscovite-biotite granite (G1) and fine- to medium-grained muscovite granite (G2) intruded the host Ordovician metasedimentary rocks in the Fonte Santa mine area (Fig. 1b) and were emplaced along the major sinistral Bemposta-Moncorvo shear zone, which is 5 km wide and 90 km long and strikes ENE-WSW. The granites produced a narrow contact metamorphic aureole, which consists of hornfels with andalusite and biotite in direct contact with G1 and schist containing biotite and andalusite in contact with G2. Both granites are deformed, but the muscovite granite (G2) shows higher strain rates, with "S-

C" foliation arrangements striking N80ºW, as a result of its proximity to the northern branch of the shear zone. The muscovite-biotite granite (G1) occupies the inner part of the shear zone, and therefore is less deformed, showing only a very incipient lineation defined by the alignment of K-feldspar phenocrysts in a WNW-ESE direction (Silva and Pereira, 2001). The geometry of this granitic massif (G1) is consistent with its emplacement in the core of a major Variscan antiform, and obeys to a heterogeneous simple shear pattern, revealing weak flattening and deformation (Silva and Pereira, 2001).

The mine is associated with the Bemposta-Moncorvo shear zone, and is emplaced along tensional fractures (Parra *et al*., 2001). Two generations of veins are recognised in the mine. The oldest generation is an irregular to lenticular vein set, folded by the last kinematic Variscan deformation phase, and the youngest generation forms a *stockwork* with mining shafts oriented along the tension and shear cracks. Scheelite occurs mainly in quartz veins hosted by pelitic rocks, but is also found in skarns that have replaced magnesian marble in the apical area of Fonte Santa muscovite granite (G2). The mineralized area is 300 m wide and 1100 m long, elongated ENE-WSW, parallel to the regional structures; the maximum depth of mining is 200 m and the volume can be estimated at around 20 million cubic meters (Ribeiro and Rebelo, 1971). Alluvial scheelite occurs in the stream bed and in adjacent alluvium.

3. Climate, Soils and Land Use

The Fonte Santa area lies between 450 and 700 m altitude and is characterized by very hot summers (to 40.2 °C) and cold winters (to -12.6 ºC). For the period 1960–1980, the average annual precipitation was 566 mm and the average annual temperature was 15.9 ºC (http://snirh.pt). Data from 2006 show a maximum precipitation of 219.4 mm in October, but data were not recorded for November due to a flood event that damaged the register system (http://www.meteo.pt). The year of 2007 had atypical climatic conditions. It was characterized by a very dry climate, with seasons not well represented by the respective months, while December was a dry month. The annual precipitation varied from a minimum of 9.60 mm in July to a maximum of 120 mm in February.

Chloride concentrations in rain water are available for the northern Portugal (http://www.emep.int). For the period 2005–2007, they are 5.44 mg/l in Viana do Castelo, close to the Atlantic coast, and 0.88 mg/l in Bragança around 60 km to the North of Fonte Santa.

Soils in the area are of the lithosol type (http://scrif.igeo.pt). These soils are on average 30 cm deep and are consist of 62 % sand, 23 % loam, 15 % clay, and 3.9 % organic matter (Caetano and Pacheco, 2008). Based on these percentages of sand, clay and organic matter, the field capacity was estimated to be 90 mm, using an approach proposed by Macedo (1991). This field capacity was applied in the estimation of evapotranspiration (ET) by a water balance using the Thornthwaite & Mather (1955) method and ET is 431 mm/y. This is a high portion (76.2 %) of the annual precipitation, but is justified given the combination of low precipitations and high temperatures observed in the region. Land use and occupation in the area are dominated by shrubs (42 %), forests (29 %), dry farming (22 %), olive yards (6 %), and the Fonte Santa mine area (1 %) (http://snig.igeo.pt). Farmers still use farmyard manures as the main source for supplying nutrients to fields or pastures; dressings of commercial fertilizers for agricultural land remain low. Apart from the 70 % of water and 26 % of organic matter, average-matured cow manures are composed of 0.74 % potassium 0.06 % magnesium, 0.12 % calcium, 0.45 % sulfate, and 3.14 % nitrate (Pacheco *et al.*, 1999).

4. Analytical techniques

Detailed studies of samples collected from granites, W-bearing quartz veins and tailings included transmitted and reflected-light microscopy and electron-microprobe analyses. Major and trace elements (Rb, Sr, Y, Zr, Nb, Ba, Ta, Sn, W and Th) were determined by X-ray fluorescence according to the method of Tertian and Claisse (1982), using a Philips PW 2404 Spectrometer. Precision is better than 1 % for major elements and Rb and better than 4 % for the other trace elements. Copper, Cr, Ag, B, Zn, Sb, Pb, Ni, V, Be, Mo, As, Co and Cd were analyzed by multi-element emission spectrometry (DCP – Direct Current Plasma), using a SMI–III Spectrometrics Incorporated model, with a mean precision of 10 %. Duplicate blank (pure quartz) and laboratory standards were analysed routinely for quality control. FeO was determined by titration with a standardised potassium permanganate solution, and H_2O+ was determined using a Penfield tube, both with an precision of 5 %. Lithium was determined by flame atomic absorption spectrometry, and F was determined by direct potentiometry, with an precision of 2 % and better than 5 %, respectively. These determinations were carried out at the Department of Earth Sciences of Coimbra University (Portugal).

Minerals from the muscovite granite (G2) and associated quartz veins were analyzed using a Cameca Camebax electron microprobe and a Jeol JXA-8500F at the National Laboratory of Energy and Geology (LNEG) (Porto, Portugal). Analyses were conducted using an accelerating voltage of 15 kV; beam currents of 20 nA and 10 nA were used in the Cameca and the Jeol microprobes, respectively. Each element was counted for 20 seconds. Beam diameter was 5 µm for most analyses, except for mica where a beam of 10 µm was used. Standards used include albite (Na Kα); orthoclase (Al Kα, Si Kα; K Kα); cassiterite (Sn Lα); $MnTiO_3$ (Mn Kα, Ti Kα); Fe_2O_3 (Fe Kα); sphalerite (Zn Kα, S Kα); pyrite (S Kα, Fe Kα); galena (Pb Mα); wollastonite (Ca Kα, Si Kα); AsGa (As Lα); MgO (Mg Kα); Au (Mα); Mo (Lα); Ni (Kα); Cu (Kα); As (Lα); Ag (Lα); Co (Kα); Cd (Lα); Sb (Lα); Bi (Mα); Ta (Mα); Nb (Lα); Mo (Lα) and W (Lα, Mβ). Mineral standards were analysed routinely by electron microprobe for quality control.

The location of the Fonte Santa mine area and of 10 sites selected for water sampling are shown in Figure 1. Four water samples were collected from each site in the months of January, April, August and December of 2007, with the exception of site FS1 that dried out in August and December. January and April represent the wet season whereas August and December represent the dry season.

Temperature, pH, Eh, electrical conductivity and alkalinity were determined *in situ*. The waters were filtered through a 0.45 µm Fioroni Cellulose Nitrate Membrane model filter and divided into two aliquots, one acidified to pH<2 using nitric acid and both kept at 4 ºC. Anions were determined in the non-acidified aliquot by ion chromatography with a Dionex ICS 3000 Model and cations were determined in the acidified aliquot by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy) using a Horiba Jovin Hyvon JY 2000-2 Model. Arsenic was determined by flame atomic absorption spectrometry. The detection limit was 0.02 mg/L for most elements, except for As and K (0.01 mg/L). The precision for most analyses was better than 5 %, but better than 15 % for Na and Al. Duplicate blanks and a laboratory water standard were analysed for quality control. The laboratory analyses were performed at the Department of Earth Sciences, University of Coimbra (Portugal).

The charge balance is better than 5 %, with the exception of samples FS2, FS3, FS4, FS5 and FS7. In these cases, the deviations are attributed to an anion excess caused by a flood event that brought suspended contaminated load from neighbour agricultural zones to the study area. However, all charge balances are below 10 %, the maximum deviation accepted for further consideration.

5. Geochemistry of granites

Following the classification of Le Maitre (2003), G1 is a granite and G2 is an alkali feldspar granite. Both have a subhedral granular texture and contain quartz, microcline, plagioclase, muscovite, chlorite, tourmaline, sillimanite, zircon, apatite, rutile and ilmenite. G1 also has biotite. Plagioclase composition is albite-oligoclase (An_3-An_{25}) in G1 and pure albite (<An_1) in G2. The most altered samples of G2 show intense muscovitization and microclinization, and contain wolframite, columbite-tantalite and W-ixiolite.

Representative chemical analyses of major, trace and rare earth elements in granite samples are given in Table 1. Both granites are peraluminous with a molecular A/(CNK) = $Al_2O_3/(CaO+Na_2O+K_2O)$ ratio of 1.2; they are interpreted as S-type granites. As the Sn content of representative samples of granites G1 and G2 are 18 ppm and 73 ppm, respectively, they are Sn-bearing granites (Lehmann, 1990). Tungsten is always below the limit of detection in granite G1 but the most altered samples of G2 contain up to 158 ppm of W. The most intensely muscovite-microcline-altered samples of G2 are specialized for W (Tischendorf, 1977).

Granite G2 is highly differentiated (Rb-Ba-Sr diagram) and has low ratios of K/Rb, Mg/Li and Ba/Rb and a high Rb/Sr ratio (Table 1), typical for tungsten granites (Srivastava and Sinha, 1997). A Geochemical Characterization Index (GCI = $\log_{10}$ (Rb^3 x Li x 10^4/Mg x K x Ba x Sr)) was proposed to characterize tungsten granites and barren granites (Srivastava and Sinha, 1997). Positive GCI values for any granite suggest a W potential. Both G1 and G2 granites have positive GCI but the values are quite different, varying in the interval 0.3-1.0 in the unaltered samples of granite G1 and between 3.0 and 4.9 in the altered samples of granite G2, respectively (Table 1), which suggests that the mineralization may be related to G2. The geochemical data suggest that late magmatic fluids, which were responsible for the hydrothermal alteration of granite G2, transported W and reacted with carbonates from country rocks producing scheelite (Silva and Pereira, 2001). G2 is the closest granite to the mine (Fig. 1).

6. W-bearing quartz veins

The W-bearing veins contain quartz, scheelite, sphalerite, galena, pyrite, pyrrhotite, chalcopyrite, arsenopyrite and rare siderite. The representative chemical compositions of granites, W-bearing minerals and sulfides from quartz veins are given in Tables 1, 2 and 3, respectively. Quartz is partly recrystallized, locally brecciated and impregnated by sulfides that fill joints, fractures and microfissures.

Scheelite ($Ca_{1.02}W_{0.99}O_4$) is anhedral, light coloured, with typical blue fluorescence. Either stolzite ($(Pb_{0.93}Mg_{0.04}Ca_{0.03})W_{0.99}O_4$) (Fig. 2a) and ferritungstite ($K_{0.08}Ca_{0.11}W_{1.55}Fe^{3+}_{0.64}O_6(H_2O)$) (Fig. 2b) fill the fractures in scheelite (Table 2). Wolframite was not found in quartz veins, but is a common accessory mineral in the hydrothermally altered granite G2.

Monoclinic pyrrhotite ($Fe_{0.88}$ $S_{1.00}$) is associated with chalcopyrite and included in sphalerite (Fig. 2c, Table 3). Some pyrrhotite crystals are replaced by pyrite.

Sphalerite is one of the most abundant sulfide minerals and shows “chalcopyrite disease” (Fig. 2d). Many grains of chalcopyrite with pyrrhotite associated and galena were probably introduced along the microfractures (Fig. 2d). Sphalerite contains Fe, Cu, Mn and Cd that can replace Zn, but their abundances are in total below 12 wt.%. The mean sphalerite composition is $(Zn_{0.86}Fe_{0.18}Mn_{0.01})\ S_{1.00}$ (Table 3). In general, each sphalerite grain has a homogeneous composition. The total variation in FeS found in sphalerite grains is 16.1 to 18.5 mole %, which may reflect constistency in the sulfur fugacity of the fluid during precipitation. Chalcopyrite was found solely as blebs in sphalerite and is homogeneous $(Cu_{0.87}Zn_{0.05})Fe_{1.07}S_{2.00}$, although has some silver up to 0.19 wt. % (Table 3).

Pyrite crystals are euhedral or subhedral and fractured. They have inclusions of galena and electrum. Pyrite locally fills fractures in quartz. Average pyrite composition is $Fe_{1.01}S_{2.00}$ (Table 3). Arsenopyrite is rare and has a near ideal composition.

Galena is abundant and occurs in three generations: 1. subhedral crystals that locally are replaced by Pb sulfate veins (Fig. 2f); 2. anhedral grains filling fractures in sphalerite; 3. anhedral grains replacing pyrite (Fig. 2e). Galena $((Pb_{0.94}Bi_{0.03}Ag_{0.02})S_{1.00})$ has Ag and Bi contents up to 1.6 % and 3.3 %, respectively, and 0.3 wt. % of Zn (Table 3).

Magnetite occurs in subhedral crystals (Fig. 2f) and also associated with ilmenite and chlorite. Supergene Al, Fe and Pb hydrated phosphates and Fe sulfates (Fig. 2g, h) occur in brecciated fragments of quartz veins surrounded by quartz.

7. Geochemistry of waters

The results of chemical analyses of waters from the Fonte Santa mine area are presented in Table 4. Samples from a spring (FS1) and from a stream (FS2) were collected upstream of the mine area, away from its influence, to be used as references of the background water chemistries. Although stream (FS5, FS6, FS9, FS10) and mine lagoon waters (FS3, FS4, FS7, FS8) were located inside the impact area of the mine and reflect the influence of abandoned mining activities and mineralized veins, only the stream waters were affected by the flood event (Fig. 1). Sites FS3 and FS4 collect waters from coarse-grained tailings, while sites FS7 and FS8 receive waters from fine-grained tailings and waste rock.

The relation between rock types and water cation-anion compositions are commonly displayed in Piper diagrams (Appelo and Postma, 2005). Most waters from Fonte Santa area do not contain a dominant cation composition and plot in the mixed water type. However, some of them are Na and Mg water types (Fig. 3). Relatively to the anions, HCO_3^- and SO_4^{2-} water types dominate. From January to April 2007, during the wet period, the waters had similar composition with local variations in Na and HCO_3^- contents, particularly for water collected inside the area influenced by mining (Fig. 3a, b). The waters from the dry period (August and December 2007) present an higher variability than the waters from wet months, particularly on the SO_4^{2-} content of waters located inside the mine influence (Fig. 3c, d).

The waters from Fonte Santa plot mainly in the field of near-neutral/low metal waters (Fig. 4), according to the classification of Ficklin *et al*. (1992). This classification considers that Zn, Cu, Cd, Ni, Co and Pb are the major heavy metals found in mine drainage waters (Fig. 4). Most waters from the Fonte Santa mine area are poorly mineralized, but waters inside the mine influence are richer in Zn+Cu+Cd+Ni+Co+Pb than those from outside that influence (Fig. 4), showing the effect of abandoned old mining activities on water quality. The mine lagoon water samples FS8 and, particularly, FS7 are acidic and have high metal concentrations (Fig. 4) and also tend to have the highest Eh values, electrical conductivity, SO_4^{2-}, K, Ca, Mg, Mn, Al, Sr, Li and the highest metal contents (Table 4). Low pH values promote the dissolution of metallic minerals and high metal concentration in waters (Bell, 1998). However, if the sulfide minerals are non-reactive or if the rocks contain materials to neutralize the acidity, the pH will be near neutral (Bell, 1998). In Fonte Santa, there is no significant acid mine drainage because the area contains a small amount of sulfides and scheelite, and quartz veins cut the regional schist and quartzite, with rare marble intercalations, which can contribute to the neutralization of the waters and promote the decrease of trace element contents, as observed in other old mining areas (e.g., Antunes *et al.,* 2002; Frau *et al.,* 2008).

Iron-tungstite, stolzite, Fe-sulfates and Fe, Pb and Al phosphates found in the scheelite quartz veins retain some metallic elements and consequently these metals are not present in significant concentrations on the waters. Secondary Fe- and Al-phases in a gold-arsenic mine with scheelite from Salanfe (Switzerland) adsorbed the elements and decreased the contamination (Pfeifer *et al.*, 2007). Secondary sulfate minerals play an important role in acid drainage and metal sequestration in surface environments (Hammarstrom *et al*., 2005). The phosphate minerals also retain the PO_4^{3-}, which was not detected in most water analyses (Table 4).

The waters with the highest SO_4^{2-} and metal concentrations and the lowest pH (FS7 and FS8) are associated with mine lagoons that receive water from fine tailings and rejected mining materials (Fig. 1; Table 4). This correlation can be associated with oxidation and dissolution of Fonte Santa sulfide minerals, such as pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and pyrrhotite. Most element contents from water mine lagoons (FS3 and FS4) are similar or lower than the ones found on stream waters (Table 4), because these points receive water from coarse-grained tailings. SO_4^{2-} has positive correlations with electrical conductivity, Ca, Sr and metals (Cu+Zn+Pb+Ni+Co+Cr) (Fig. 5), because the dissolution of SO_4^{2-} will promote an increase in dissolved elements and electrical conductivity. Waters from the abandoned Ervedosa tin mine area also show positive correlations between SO_4^{2-} and electrical conductivity and metal contents but a negative correlation between SO_4^{2-} and pH (Gomes and Favas, 2006). Correlations between trace elements are poor and do not show a significant trend, as found in other areas (e.g., Antunes *et al*., 2002; Gomes and Favas, 2006).

The water samples containing Fe above detection limit were plotted in the Eh-pH diagram for iron species (Deutsch, 1997). The waters from Fonte Santa plot mainly in the $Fe(OH)_3$ field (Fig. 6). Therefore, precipitation of $Fe(OH)_3$ may control the Fe concentration. Pyrite is not stable at Eh and pH values of the water samples. The pyrite oxidation decreases the water pH of the mine lagoons and the dissolved iron occurs as Fe^{2+} (Fig. 6).

Arsenic has an irregular distribution in Fonte Santa waters and in some water samples is below the detection limit (Table 4) which can be attributed to the rare occurrence of arsenopyrite or the possible precipitation or adsorption of this element on stream sediments and soils (e.g., Fe-oxyhydroxide, suspended organic matter). In other Portuguese abandoned W-Sn mines the soils have significant As concentrations but As has not been detected in waters (Cama *et al.,* 2008). Metals such as Fe, Mn form oxyhydroxide compounds which are able to complex with As compounds and precipitate As out of the solution (Serfor-Armah *et al.,* 2006, Cama *et al*., 2008).

The seasonal variation of waters from Fonte Santa is not regular (Table 4). However, most water samples contain the highest electrical conductivity, SO_4^{2-}, Na, Mn, Sr, Li values during the dry months (August and December 2007; Table 4). This is observed particularly in water from mine lagoons (FS7 and FS8), which is the most acid and characterized by an increase in metal content with decrease in rain (e.g., Fe, Mn, Sr, Cd; Table 4).

Iron and Al concentrations in water from the FS5, FS6, FS9 and FS10 sample sites were highest in January 2007 (Table 4), after the flood event. In the streams, Fe and Al are transported in fine suspended solid particles, which increase with flow and turbidity. The key role of flood events in the hydrochemical variations and contaminated load were highlighted during the monitoring of three flood events in the Rio Tinto, SW Spain (Cánovas *et al.,* 2008). Other elements such as Mn, Zn and Ni tend to increase in the streams during August and December 2007 (Table 4) due to ion concentration effect, associated with the less quantity of water in the streams (e.g., Antunes *et al.,* 2002; Gomes and Favas, 2006).

Although most major and trace element content of metals in waters from Fonte Santa are low (Table 4), some of them exceed the accepted values for human consumption and/or agricultural use (Portuguese Law, 2001; 2007). The water from mine lagoon, FS7, is the most contaminated of the area and must not be used for human consumption, according to the Portuguese Law (2001; 2007), due to its electrical conductivity (> 450 μS/cm), SO_4^{2-} (> 250 mg/L), Mg (> 30 mg/L), Fe (> 0.05 mg/L), Mn (> 0.05 mg/L), Zn (> 0.5 mg/L), Al (> 0.2 mg/L), Ni (> 0.05 mg/L) and Co (> 0.05 mg/L) (Fig. 7 and Table 4). Iron, Mn and Ni water contents in FS5 to FS10 sites, at least once during the year of observation, are higher than parametric values defined for human consumption (Fig. 7). Some of these waters may not be used for agriculture due to their Fe and Mn contents (Fig. 7). Most waters from the Fonte Santa area have NO_2^- (0.1

mg/L) contents above those recommended for human potable water. In the most mineralized waters (FS7 and FS8), NO_2^- is below the recommended values probably due to low pH (Table 4). The environmental impact of this abandoned mine is not very high and the contamination problems are essentially related with the flood event that carried contaminant load by stream along 2 km from the tailings and with mine lagoons draining fine-grained tailings and waste rock.

8. Weathering and Hydrochemistry

The following paragraphs discuss how atmospheric, anthropogenic and natural contributions of major inorganic compounds to the composition of groundwater were assessed by mass balance calculations. The contributions were first calculated for each sample, excluding the samples collected at site FS7 because the bicarbonate contents were not analyzed in these cases (Table 4), and then were averaged for each contribution and compound. The average values are depicted in Table 5.

The samples have relatively homogeneous chloride concentrations (4.87 ± 0.99 mg/L). The estimated evapotranspiration (ET) by a simple chloride balance (ET = (1 – $[Cl^-]_r/[Cl^-]_g$)×P, where $[Cl^-]_r$ and $[Cl^-]_g$ are the chloride concentrations in rainwater and groundwater, respectively, and P is the average annual precipitation) is 464 mm/yr. This value is comparable to the 431 mm/y estimated above by a conventional water balance method (Thornthwaite & Mather, 1955), suggesting that chloride concentrations in groundwater mainly result from simple concentration of rain water by evapotranspiration. For this reason, all $[Cl^-]$ in groundwater is assumed sourced from sea salt/seaspray. It is further assumed that atmospheric deposition will account for variable amounts of the other major cations and anions (X) to keep with the $[Cl^-]/[X]$ ratios in seawater (Appelo and Postma, 2005), which means that any effect of fractionation affecting these contributions in the path of rainwater from the Atlantic coast to the study area is neglected. The contributions of sea salt deposition to the water chemistry are depicted in the first row of Table 5.

Around the Fonte Santa mine area, 22 % of the area is occupied by farmyards where manures are applied annually as main sources of nutrients, releasing variable amounts of nitrate, potassium, magnesium, calcium and sulfate to groundwater. In this study, all [NO_3^-] in groundwater is assumed sourced by these manures. It is also assumed that manures release K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} (X) to the solution in the same proportions as they appear in the fertilizer, meaning that their concentrations can be equated to [X] = (mole ratio X/NO_3^- in manure) × [NO_3^-]. The mole ratios were deduced from the published composition of average-matured cow manure presented above. The calculated [X] values are listed in the second row of Table 5. The nitrate concentrations are on average relatively low (1.86□ mg/L), but show a high standard deviation (3.29 mg/L) meaning that the sources of [NO_3^-] are irregularly distributed within the study area, contaminating some samples to some extent (e.g. sample FS1 with an average [NO_3^-] = 8.93 mg/L) and leaving others practically undisturbed (e.g. sample FS8 with an average [NO_3^-] = 0.31 mg/L). The average concentrations in mg/L of K^+(0.88), Mg^{2+}(0.14), Ca^{2+}(0.07) and SO_4^{2-}(0.27) derived from leachates of manures are even lower.

The overall contribution of rock weathering to the water composition can be deduced from the difference between the total concentrations (heading *Major Dissolved Compounds*) and the contributions by the other sources (Table 5). It is assumed that the dominant weathering agent is carbonic acid derived from CO_2 dissolved in soil water. However, because the sulfate concentrations remain very high, even after correction of the total concentrations for the atmospheric plus anthropogenic inputs (average: [SO_4^{2-}] = 31.57 mg/L), it is also assumed that a weak sulfuric acid derived from sulfide oxidation can also act as a weathering agent.

The corrected sulfate concentrations are also very heterogeneous (standard deviation: [SO_4^{2-}] = 46.8 mg/L), suggesting that the action of sulfuric acid will be significant only in some places. This is consistent with the location of the sampling sites: from FS6 to FS10 are located close or downstream the area, where fine-grained tailings were deposited and sulfide residues have accumulated. In these sites, it is expected that sulfuric acid is the main weathering agent. Mineral/water interactions in tailings of a tungsten mine at Mount Pleasant (New Brunswick, Canada), particularly the sulfide oxidation, contributed to the geochemical processes and water composition in the area (Petrunic and Al, 2005). In contrast, sites FS1 to FS5 are located upstream the area of fine-grained taillings. For these sites, it is expected that sulfuric acid plays a role in the weathering reactions if the flow paths of groundwater cross sectors of the rock massif where mineralized veins or disseminated sulfide minerals are still in situ.

Natural contributions to the water composition are derived from weathering of minerals in contact with water travelling along flow paths from the recharge areas to the discharge sites across a soil/saprolite cover succeeded by a network of fractures, fissures and joints. In some cases (sites FS6–FS10), the flow paths may also cross fine-grained tailings deposited around the Fonte Santa Mine, or be affected by drainage derived from them. The geologic environments are characterized by metasediments and muscovite granite (G2) with albite (An_0) which are cut by quartz veins containing sulfides and scheelite. In these rocks, the most weatherable minerals are usually albite and chlorite (Van der Weijden and Pacheco, 2006). The alterations of these minerals are assumed the sources of natural sodium and magnesium present in water. The metasediments may contain some carbonate layers, but in the presence of metal ores the weathering of scheelite should also account for some of the natural calcium. For that reason, natural Ca is assumed sourced by the dissolution of both minerals. Finally, it is assumed that the source of natural potassium is the weathering of muscovite. The fine-grained tailings are composed of crushed metasediment and granite and residues of sulfide minerals, produced by the mine workings. Within these tailings, weathering of minerals will be enhanced by the presence of sulfuric acid resulting from the oxidation of sulfides.

The release of cations during weathering of rock-forming minerals and ores is accompanied by precipitation of secondary phases such as clay minerals (halloysite, smectite, vermiculite), metal oxides (ferritungstite) and Fe sulfates. Regardless the specific reaction involved, equivalent proportions of bicarbonate and/or sulfate must be released with the cations, depending on whether carbonic acid or/and sulfuric acid is/are the weathering agent(s), to comply with the charge-balance condition (electric neutrality of water). It is assumed that carbonic acid plays the dominant role in weathering because this acid is added to the system right from the beginning of the flow path, when soil water dissolves atmospheric CO_2. Conversely, sulfuric acid enters the system only if the flow path crosses mineralized sectors of the rock or fine-grained tailings, or is affected by their leachates.

The contributions of weathering reactions to groundwater chemistry were assessed by the stepwise subtraction of the different contributions, following the approach used by Garrels and Mackeinzie (1967), and starting with the water composition corrected for the atmospheric plus anthropogenic inputs. Subtractions followed the sequence: albite → carbonates + scheelite → chlorite → muscovite. The results are not inherently dependent on the sequence adopted because in this study each contribution is assumed to link to a single cation (e.g. weathering of albite links to Na; of chlorite to Mg; etc.), but the proportions of cations and anions ascribed to each weathering agent depend on whether carbonic acid is assumed to act first and sulfuric acid later, or vice versa. For the present case study, it was already assumed and defended that minerals will react first with carbonic acid producing HCO_3^- and later with sulfuric acid producing SO_4^{2-}.The concentration of cations, bicarbonate and sulfate derived from weathering of albite, carbonates+scheelite, chlorite and muscovite are listed in Table 5.

In most samples, bicarbonate was in excess of sodium and for that reason all sodium in these samples was attributed to weathering of albite by action of carbonic acid. But in samples collected during the dry season of 2007 (August and December), in the vicinity of the fine-grained tailings, sodium was in excess of bicarbonate. For these samples, an amount of sodium equivalent to the bicarbonate concentration was attributed to weathering of albite by action of carbonic acid and the rest to weathering of albite but by action of sulfuric acid. On average (considering the samples from all sites), dissolution of albite released 3.06 mg/L of Na when H_2CO_3 was the weathering agent and 0.74 mg/L when the agent was H_2SO_4 (Table 5). The results obtained for this cation are striking as they confirm a distinguishable role of fine-grained tailings in the promotion of sulfuric weathering. The fact that sulfuric acid is required to explain the Na concentrations only during the dry season suggests that sulfide minerals may be concentrated at the bottom of the tailings.

The rationale used to assign sodium to weathering of albite by carbonic and sulfuric acid was repeated for the other cations. The results for Ca resemble the Na results because weathering of carbonates+scheelite by sulfuric acid is significant for 12 (out of 16) samples collected close to the fine-grained tailings but only for 3 (out of 18) samples collected away from them. On average, dissolution of carbonates+scheelite released 1.96 mg/L of Ca when H_2CO_3 was the weathering agent and 4.62 mg/L when the agent was H_2SO_4 (Table 5).

In contrast to albite and carbonates+scheelite, sulfuric acid seems to weather chlorite in the vicinity of the fine-grained tailings, but also away from them. However, the proportions ascribed to carbonic and sulfuric acid weathering differ if F6–FS10 samples or to the FS1–FS5 samples are taken into account. In the first case, carbonic weathering releases 0.1 mg/L of Mg to solution and sulfuric weathering 6.7 mg/L, whereas in the second case the values are 0.7 and 0.8 mg/L, respectively. On average, this gives a release of 0.4 mg/L of Mg when H_2CO_3 is the weathering agent and 3.8 mg/L when the agent is H_2SO_4 for dissolution of chlorite (Table 5). These results stress that mine tailing drainage is a key factor controlling sulfuric weathering, although the passage of groundwater through mineralized sectors of the rock massif may also play a role in this process.

When weathering of muscovite was accounted for, most of the carbonic acid has already been consumed by the other reactions. For that reason, only 3 samples of the FS1–FS5 sites and 1 sample from the F6–FS10 sites could be linked to carbonic weathering of muscovite, contributing negligibly to the average water composition. It could be questioned that this result is a consequence of the order in which weathering contributions were subtracted from the initial water composition, but it should be recognised that muscovite is also the least soluble of the minerals included in the mass balance calculations. Consistently with the results obtained for the other cations, sulfuric weathering is more important when calculations are made for the F6–FS10 samples (average K release of 1.8 mg/L) than when they are made for the FS1–FS5 samples (average K release of 0.7 mg/L), emphasizing the dominance of this process in areas affected by drainage of sulfide mine wastes. When considering the samples altogether, sulfuric dissolution releases 1.18 mg/L of K to groundwater (Table 5).

The average results depicted in Table 5 show that weathering of minerals promoted by the attack of carbonic acid to the crystal lattices represents 45.5 % of the total weathering and is materialized by a production of 278 μmol/L of bicarbonate. The remaining 54.5 % are attributed to weathering by attack of weak sulfuric acid and are manifested in 329 μmol/L of sulfate released during the reactions. Presented as is, this fact seems to question the role of carbonic acid as weathering agent, but it should be noted that the average values of natural sulfate are biased by huge concentrations present in a few samples, particularly in sample FS8 (average: $[SO_4^{2-}]$ = 1395 μmol/L). Calculating the average HCO_3^- and SO_4^{2-} concentrations, but neglecting sample FS8, gives HCO_3^- = 290 μmol/L and SO_4^{2-}= 186 μmol/L, which ascribe 61 % of total weathering to bicarbonate, i.e. a dominant role.

The consistency of the cation and anion distributions by the atmospheric, anthropogenic and natural sources is deduced from the residual concentrations (Table 5). The differences found for the K^+, Mg^{2+}, HCO_3^- and SO_4^{2-} water contents can be associated to the analytical procedures.

9. Conclusions

1. The muscovite-biotite granite (G1) and muscovite granite (G2) from the Fonte Santa mine area are tin-bearing S-type granites. However, the most altered sample of granite G2 is W specialized. The late magmatic fluids that hydrothermally altered G2 carried W, which probably reacted with calcium carbonates from country rocks and deposited scheelite in quartz veins.

2. Scheelite from W-bearing quartz veins has a homogeneous composition, but its fractures are filled by stolzite and ferritungstite. Mineral paragenesis of W-bearing quartz veins consists of pyrite, pyrrhotite, sphalerite, chalcopyrite, arsenopyrite, galena, iron oxides, Al, Fe and Pb hydrated phosphates and Fe sulfates.

3. Waters from the Fonte Santa area are poorly mineralized. However, there is an increase in most parameters and element contents from outside to inside the mine

influence, showing the effect of abandoned old mining activities on water quality. Most of the waters from Fonte Santa do not contain a dominant cation-anion composition and are of mixed water type. Some of them are Na and Mg water types and HCO_3^- and SO_4^{2-} waters.

4. The environmental impact is essentially related with the flooding event that carried a suspended contaminated load, increasing immediately Fe and Al contents in natural stream waters inside the mine influence.

5. There is no significant acid drainage associated with old mine workings, which can mainly be attributed to the presence of calcium carbonates in country rocks and scheelite in quartz veins, that probably neutralized the waters and decreased metal concentrations.

6. Waters with the highest SO_4^{2-} are associated with mine lagoons FS7 and FS8, which received waters from fine-grained tailings and waste rock and contain the highest metal concentrations and the lowest pH values.

7. Most waters associated with the mineralized veins and old mine activities at Fonte Santa have Fe and Mn concentrations that forbid their use for human consumption and agriculture. Some waters present concentrations above parametric Portuguese values for other contaminants (such as SO_4^{2-}, NO_2^-, Mg, Zn, Al, Ni and Co) and should not be used for human consumption.

8. The alteration of albite, chlorite and muscovite of country rock are responsible for the natural sodium, magnesium and potassium present in water and the weathering of carbonates and scheelite are the most reasonable sources for natural calcium. The weathering of rock-forming minerals and mineralizations will also result in precipitation of secondary phases such as clay minerals (halloysite, smectite, vermiculite) metal oxides (ferritungstite) and Fe sulfates.

9. Finally one of the important conclusions of the study is the relative importance of sulfuric versus carbonic acid for weathering.

Acknowledgments

We are grateful to Prof. M.R. Machado Leite, Dr. J.M. Farinha Ramos and Eng. Fernanda Guimarães for the use of the electron-microprobe at LNEG (Oporto, Portugal), to EDM for the information on environmental impact of Fonte Santa mining area, to Prof. João Serra Pratas for the As water contents. This research work was carried out in the programme of the Geosciences Centre, Coimbra University, Portugal.

References

Abreu, M.M., Matias, M.J., Magalhães, M.C.F., Basto, M.J., 2008. Impacts on water, soil and plants from the abandoned Miguel Vacas copper mine, Portugal. Journal of Geochemical Exploration 96, 161-170.

Antunes, I.M.H.R., Neiva, A.M.R., Silva, M.M.V.G., 2002. The mineralized veins and the impact of old mine workings on the environment at Segura Central Portugal. Chemical Geology 190 (1/4), 417-431.

Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam, 649 pp.

Bell, F.G., 1998. Environmental Geology – Principles and practice. Blackwell Science, Oxford, 415-458.

Berger, A.M., Bethke, C.M., Krumhansl, L.K., 2000. A process model of natural attenuation in drainage from a historic mining district. Applied Geochemistry 15, 655-666.

Caetano, C.A.R., & Pacheco, F.A.L., 2008. Modelação de escoamentos fluviais na região de Trás-os-Montes e Alto Douro utilizando o modelo SWAT. In: V Seminário Recursos Geológicos, Ambiente e Ordenamento do Território, UTAD, Vila Real, 16-18 October, p. 44-53.

Cama, J., Rovira, M., Ávila, P., Pereira, M.R., Asta, M.P., Grandia, F., Martínez-Lladó, X., Álvarez-Ayuso, E., 2008. Distribución de arsénico en la región Ibérica. In: Bundschuh, J., Carrera, A.P., Litter, M.I. (Eds.), Iberoarsen - Distribución del arsénico en las regiones Ibérica e Iberoamericana, 95-136.

Cánovas, C.R., Hubbard, C.G., Olías, M., Nieto, J.M., Black, S., Coleman, M.L., 2008. Hydrochemical variations and contaminant load in the Rio Tinto (Spain) during flood events. Journal of Hydrology 350, 25-40.

Deutsch, W.J., 1997. Groundwater geochemistry, fundamentals and applications top contamination. Lewis Publishers, Boca Raton.

Ficklin, W.H., Plumlee, G.S., Smith, K.S., McHugh, J.B., 1992. Geochemical classification of mine drainages and natural drainages in mineralized areas. In: Kharaka Y.K., Maest A.S. (Eds.), Water-Rock Interaction. Balkema, Roterdam vol. **7,** 81-84.

Frau, F., Ardau, C., Fanfani, L., 2008. Environmental geochemistry and mineralogy of lead at the old mine area of Baccu Locci (south-east Sardinia, Italy). Journal of Geochemical Exploration, doi:10.1016/j.gexplo.2008.01.005.

Garrels, R.M., Mackenzie, F.T., 1967. Origin of the chemical compositions of some springs and lakes. In: Stumm, W. (Ed.), Equilibrium concepts in natural water systems. Am. Chem. Soc., pp. 222–242.

Gomes, M.E.P., Favas, P.J.C., 2006. Mineralogical controls on mine drainage of the abandoned Ervedosa tin mine in north-eastern Portugal. Applied Geochemistry 21, 1322-1334.

Hammarstrom, J.M., Seal, R.R., Meier, A.L., Komfeld, J.M., 2005. Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in superficial environments. Chemical Geology 215, 407-431.

http://snirh.pt. National Water Institute . Accessed on March 2010 http://www.meteo.pt. National Meteorological Institute. Accessed on March 2010

http://www.emep.int. European Monitoring and Evaluation Programme. Accessed on March 2010

http://scrif.igeo.pt. Information Network for Emergency Situations. Accessed on March 2010

http://snig.igeo.pt. Portuguese Centre for Geographic Information. Accessed on March 2010

Johnson, R.H., Blowes, D.W., Robertson, W.D., Jambor, J.L., 2000. The hydrogeochemistry of the nickel rim mine tailings impoundment, Sudbury, Ontario. Journal Contamination Hydrology 41, 49-80.

Lehmann, B., 1990. Metallogeny of tin. Lecture notes in earth sciences 32. Springer-Verlag, Berlin, 211pp.

Le Maitre, R.W., 2003. The Chemical variability of some common igneous rocks. South African Journal of Geology 106 (4), 343-360.

Macedo, J.R., 1991. Determinação de retenção hídrica por correlação múltipla e de variabilidade espacial em solos podzólicos de Seropédica, RJ. MSc Thesis, Federal University of Rio de Janeiro, Brazil, 174p.

Marszalek, H., Wasik, M., 2000. Influence of arsenic- bearing gold deposits on water quality in Zloty Stock mining area (SW Poland). Environmental Geology 39 (8), 888-892.

McGregor, R.G., Blowes, D.W., Jambor, J.L., Robertson, W.D., 1998. Mobilization and attenuation of heavy metals within a nickel mine tailings impoundment near Sudbury, Ontario, Canada. Environmental Geology 36, 305-319.

Navarro, M.C., Pérez-Sirvent, C., Martínez-Sánchez, M.J., Vidal, J., Tovar, P.J., Bech, J., 2008. Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. Journal of Geochemical Exploration 96, 183-193.

Oliveira, J.M.S., Farinha, J., Matos, J.X., Ávila, P., Rosa, C., Canto Machado, M.J., Daniela, F.S., Martins, L., Machado, Leite, M.R., 2002. Diagnóstico ambiental das principais áreas mineiras degradadas do Pais. Boletim de Minas. Lisboa 39(2), 67-85.

Pacheco, F.A.L., Sousa Oliveira, A., Van der Weijden, A.J., Van der Weijden, C.H. 1999. Weathering, biomass production and groundwater chemistry in an area of dominant anthropogenic influence, the Chaves-Vila Pouca de Aguiar region, north of Portugal. Water, Air and Soil Pollution 115, 481–512.

Parra, A., Quesado, P., Dias, M., 2001. SIORMINP - Sistema de Informação de Ocorrências e Recursos Minerais Portugueses. http://e-geo.ineti.pt/bds/ocorrencias/

Petrunic, B.M. and Al, T.A., 2005. Mineral-Water Interactions in Tungsten Mine Tailings: Mount Pleasant, New Brunswick . Geochimica Cosmochimica Acta. 69:(10), 2469-2483

Pfeifer, H-., Häussermann, A., Lavanchy, J-C., Halter, W., 2007. Distribution and behavior of arsenic in soils and waters in the vicinity of the former gold-arsenic mine of Salanfe, Western Switzerland. Journal of Geochemical Exploration 93, 121-134.

Portuguese Law. 2001. Decree Nº 243/2001. Portuguese Legislation on water quality. I-A: 5754-5766.

Portuguese Law. 2007. Decree Nº 306/2007. Portuguese Legislation on water quality. I-A: 5747-5765.

Ribeiro, A., Rebelo, J.A., 1971. Estudo geológico preliminar do jazigo de scheelite de Fonte Santa (Lagoaça). Serviço de Fomento Mineiro, 11pp. (Unpubished Repport).

Serfor-Armah, Y., Nyarko, B.Y.B., Adotey, D.K., Dampare, S.B., Adomako, D., 2006. Levels of arsenic and antimony in water and sediments from Prestea, a gold mining town in Ghana and its environs. Water, air and soil pollution 175, 181-192.

Silva, P.B., 2000. Estudo petrográfico, mineralógico e geoquímico dos maciços graníticos de Bruçó e Fonte Santa (NE de Portugal). University of Porto, Portugal, 199 pp. (Unpublished MSc thesis).

Silva, P.B., Pereira, E., 2001. Evolução geoquímica dos maciços graníticos de Bruçó e Fonte Santa (Mogadouro- NE de Portugal). Resumos do VI Congresso Geoquímica Países Língua Portuguesa. Faro, 173-177.

Srivastava, P.K., Sinha, A.K., 1997. Geochemical characterization of tungsten-bearing granites from Rajasthan, India. Journal of Geochemical Exploration 60, 173-184.

Tertian, R., Claisse, F., 1982. Principles of Quantitative X-ray Fluorescence Analysis. Heyden, London.

Thornthwaite, C.W., Mather, J.R., 1955. The water balance. Drexel Institute of Technology - Laboratory of Climatology, Publications in Climatology, vol. VIII, n.1, 104p.

Tischendorf, G., 1977. Geochemical and petrographic characteristics of silicic magmatic rocks associated with rare-element mineralization. In Stemprok, M., Burnol, L., Tischendorf, G. (Ed), Metallization associated with acid magmatism. Geological Survey, Prague, Czechoslovakia 2, 41-96.

Triede, 2002. Recuperação da área mineira de Fonte Santa. EDM. Internal Reports (Unpublished Repport).

Van der Weijden, C.H., Pacheco, F.A.L., 2006. Hydrogeochemistry in the Vouga River basin (central Portugal): pollution and chemical weathering. Applied Geochemistry 21, 580-613.