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GEOCHEMISTRY OF LEAD AT THE OLD MINE AREA OF BACCU LOCCI (SOUTH-EAST SARDINIA, ITALY)

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Abstract

About a century of exploitation of the galena-arsenopyrite deposit of Baccu Locci in Sardinia (Italy) has caused a severe, persistent arsenic contamination that extends downstream of the mine for several kilometres. Differently from As, the aqueous contamination of lead is only localised in the upper part of the mine despite very high Pb concentrations in geologic materials (waste rocks, tailings, stream sediments, soils) over the whole Baccu Locci stream catchment. The determination of aqueous and solid Pb speciation in various environmental media of the Baccu Locci system has pointed out that the peculiar geochemical behaviour of Pb is mainly due to (i) the short residence time of dissolved Pb in surface and ground water under near-neutral pH conditions and (ii) the low solubility of plumbojarosite that represents the main secondary Pb-bearing mineral in the Baccu Locci environment.

Introduction

Lead is one of the most dangerous inorganic contaminants owing to its high toxicity to living organisms. In some regions mining activity represents an important source of Pb to the environment. This is the case of Sardinia Island in Italy where an age-old mining tradition persisted until a few decades ago, above all with exploitation of huge galena-sphalerite deposits hosted in the Cambrian limestones and dolomites of the Iglesiente-Sulcis mining district (south-west Sardinia).

The sulphide deposit of Baccu Locci is located in the Sarrabus-Gerrei mining district, Quirra region, near the village of Villaputzu (south-east Sardinia). It represents a peculiarity in the metallogenesis of the island thanks to an unusual primary paragenesis made up of about equal proportions of galena and arsenopyrite. About a century (1873-1965) of exploitation for Pb and As has produced visible environmental impact, mainly due to the unwise practice of discharging tailings from the flotation plant, built in 1949, directly into the Baccu Locci stream (BLS) that drains the mined area. This has caused wide scattering of highly contaminated materials over the whole catchment as far as the coastal plain located about 10 km downstream of the mine. Arsenic is released to surface waters mainly by desorption from ferrihydrite contained in tailings/sediments along the course of the BLS. Arsenic heavily affects water quality with dissolved concentrations up to and over 1 mg/L (Frau and Ardau, 2003, 2004).

This study focuses on distribution and mobility of Pb in the BLS catchment, affected by past mining activity, and aims at understanding the geochemical behaviour of Pb by means of the determination of its aqueous and solid speciation.

Sampling and Analytical methods

1. Waters

Forty different water sampling points were monitored since 1999; they comprise the Baccu Locci stream (BL) and its tributaries (Tr), the artificial lake (Lk) and its influent and effluent (Tr), the Quirra river (RQ), some adits (Ad) and a spring (Sp). Data on waters presented in this paper refer to two different sampling campaigns corresponding to low-flow (LF) and high-flow (HF) conditions, respectively.

At the sampling site, water was filtered at 0.4 µm (Nuclepore® polycarbonate Ø 47 mm membrane) into pre-cleaned high-density polyethylene bottles, and acidified with suprapure HNO_3 for metal analyses by ICP-AES and/or ICP-MS. An unacidified aliquot for anion analysis by ion chromatography was also taken. Temperature, pH, Eh (redox potential), conductivity and alkalinity were measured in the field.

Speciation-solubility calculations were performed using the computer program PHREEQC (ver. 2.12.5.669; Parkhurst and Appelo, 1999) with the included thermodynamic database WATEQ4F that was appropriately implemented with solubility data of minerals of interest in order to calculate their saturation indices (SI).

2. Solids

Twenty five solid samples were chosen among waste-rock dumps (D), stream bed sediments (S) and flotation tailings (T). When tailings occurred interbedded and partially mixed with stream sediments to form multi-layer profiles, a sample for each layer was taken. Solid samples were air-dried, disaggregated, homogenised and sieved to 2 mm.

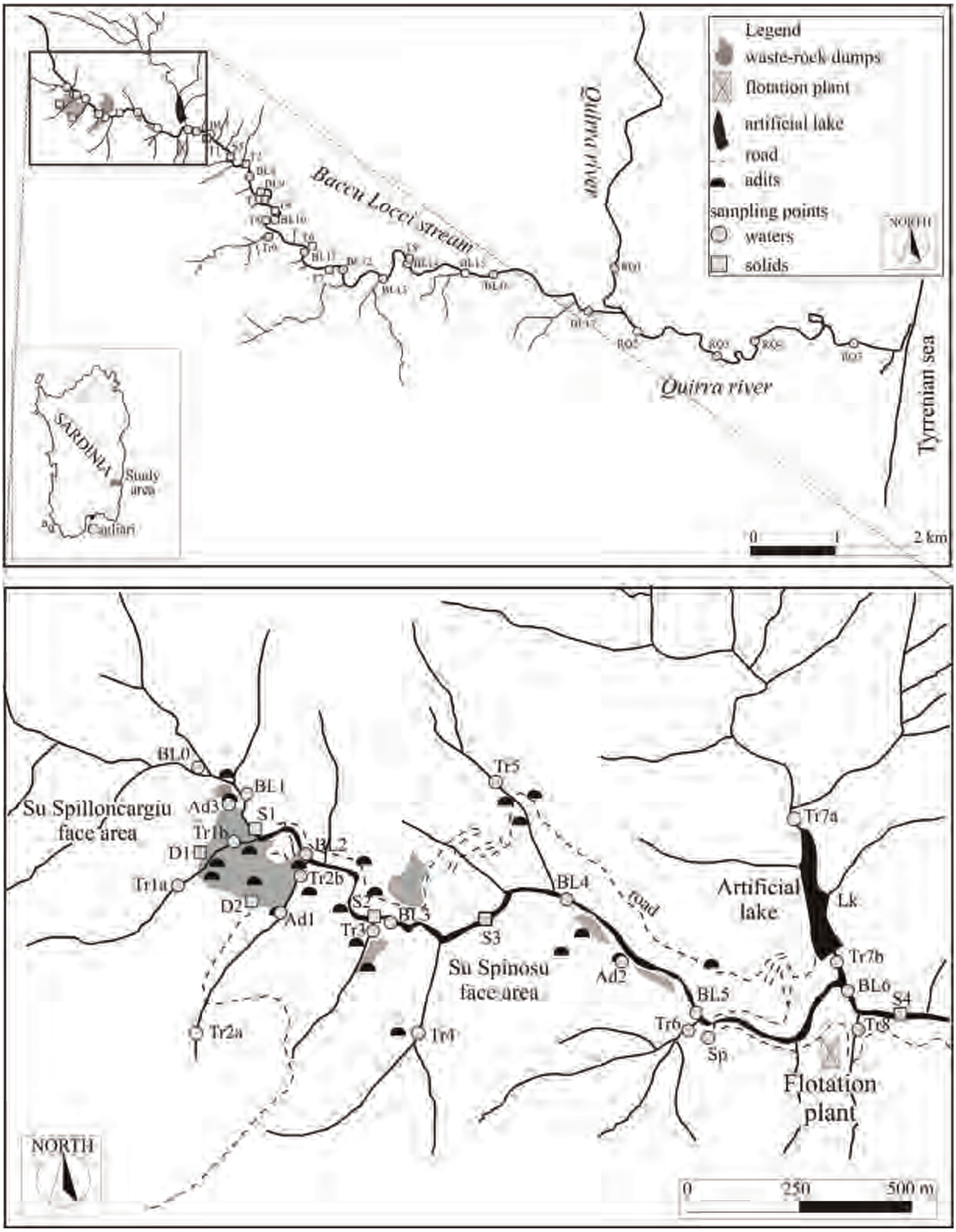

Figure 1. Schematic map of the study area with location of sampling points. Waters: BL = Baccu Locci stream, Tr = tributary, Lk = artificial lake, RQ = Quirra river, Ad = adit, Sp = spring. Solids: D = waste-rock dump, S = stream bed sediment, T = flotation tailing.

A 10 g portion of each sample was put through a sequential chemical extraction procedure (Frau and Ardau, 2004) consisting of six steps related to the following fractions (components extracted): 1) exchangeable (exchangeable ions and elements in soluble minerals); 2) carbonatic (elements bound to carbonate minerals); 3) easily reducible (elements bound to oxides/hydroxides of Mn); 4) moderately reducible (elements bound to amorphous or poorly-crystalline oxides/hydroxides of Fe); 5) sulfidic/organic (elements bound to sulphide

minerals and organic matter; 6) residual (elements bound to more resistant, non-silicate minerals).
A 30 g portion of each sample was leached with 100 ml of bidistilled water (pH 7, Eh 0.5 V) for 24 hours at 20 rpm stirring in order to estimate the water-leachable percentage of an element. Finally, a 3 g portion of each sample was left to react with ca. 30 ml of aqua regia for 16 hours at room temperature and for 2 hours at 155 °C in order to estimate the acid-leachable percentage of an element. Both extracted and leachate solutions were analysed by ICP-AES.
Chemical and mineralogical analyses of bulk solid samples were performed by using XRF and XRD, respectively. Micro-mineralogy and micro-chemistry of most interesting samples was determined by SEM-EDX and TEM-EDX.

Results and Discussion

1. Waters

With the exception of some acidic waters (pH 4.3-4.8) from adits, surface waters are neutral or slightly alkaline (pH 7-8), oxidizing (Eh 0.4-0.6 V) and with low TDS (Total Dissolved Solids 0.2-0.6 g/L). As soon as the BLS enters the mined area and interacts with mine wastes, its major hydrochemistry changes from a Ca-Mg-HCO_3 type to a Ca-Mg-SO_4 type; downstream the dominant anion becomes HCO_3^- again or remains SO_4^{2-} depending on if mixing with lake water occurs (Fig. 2, left plot) or not (not shown), respectively.

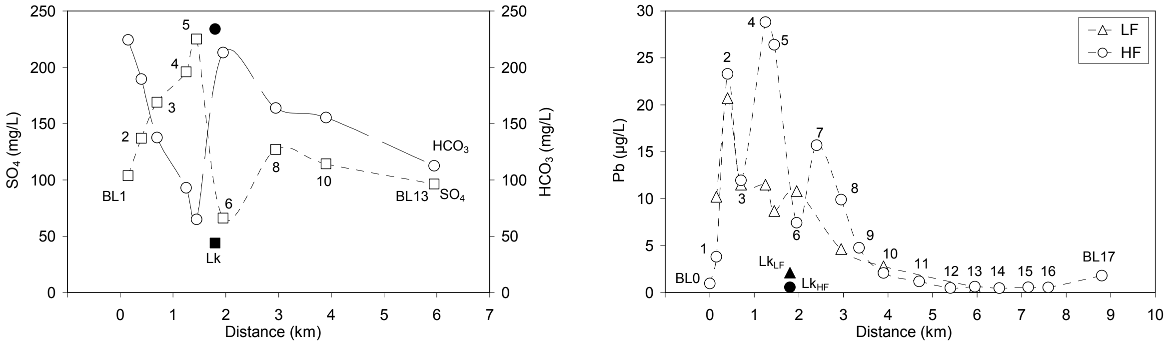

Figure 2. Left plot: Anionic composition of the BLS water (labelled BLn) vs. distance under low-flow conditions and mixing with lake water (Lk). Under high-flow conditions the trends result much less sharp due to dilution effect of heavy rains and no mixing with lake water (see Fig. 6 in Frau and Ardau, 2003). Right plot: Lead distribution along the BLS course under low-flow (LF) and high-flow (HF) conditions.

Lead initially increases together with sulphate, indicating a same source for both components (i.e. dissolution of metal sulphates formed by sulphide oxidation). However, under low-flow conditions Pb decreases about 1.5 km upstream of the confluence with lake water (2.12 µg/L Pb), suggesting that a removal process occurs (Fig. 2, right plot). A similar behaviour is also exhibited by other metals such as Cu, Zn and Cd. In particular, the removal sequence for divalent metal cations (Pb > Cu > Zn-Cd; Fig. 3, left plot) follows the sorption selectivity sequence on metal-oxide minerals, indicating sorption as a possible mechanism that accounts for dissolved Pb decrease. Another possible Pb removal mechanism might be represented by (co)precipitation with metal sulphates such as glaucocerinite [$(Zn,Cu)_5Al_3(SO_4)_{1.5}(OH)_{16}\cdot 9H_2O$], zincowoodwardite [$(Zn,Cu)_{5.5-4}Al_{2.5-4}(SO_4)_{1.5-2}(OH)_{16}\cdot 5\text{-}8H_2O$] and plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$] that has been observed along the tributaries Tr1 and Tr2 (Ardau et al., 2007).
Under high-flow conditions Pb distribution exhibits an accentuation of local variations in concentration (Fig. 2, right plot) partly due to spike effect from high-metal waters (e.g. Tr2b: 250 µg/L Pb, 650 µg/L Al, 750 µg/L Mn, 1.00 mg/L Cu, 47 mg/L Zn, 940 µg/L Cd) or to dilution effect from low-metal waters (e.g. Tr6: 1.4 µg/L Pb, 15 µg/L Al, 2.9 µg/L Mn, 2.1 µg/L Cu, 11 µg/L Zn, 0.14 µg/L Cd). It is interesting to note the good match between the Pb pattern and those of Fe and Al (Fig. 3, right plot). Considering that, contrary to TDS, the metal load is higher under high-flow conditions, and Fe and Al in river waters typically show high affinity for colloids, Pb distribution might be due to its association with suspended fine particles (<0.4 µm) whose abundance can significantly increase on occasion of heavy rains (Cidu and Frau, 2007).
In both low-flow and high-flow conditions Pb concentrations in the BLS tend to very low values (<1 µg/L; Fig. 2, right plot) that do not exceed the Italian guideline of 50 µg/L for drinking water and neither the limit of 10 µg/L established by the World Health Organization (WHO) in 2006. This indicates that, after Pb is removed, there is not longer release of Pb to surface waters from stream sediments/tailings although they contain very high Pb concentrations.

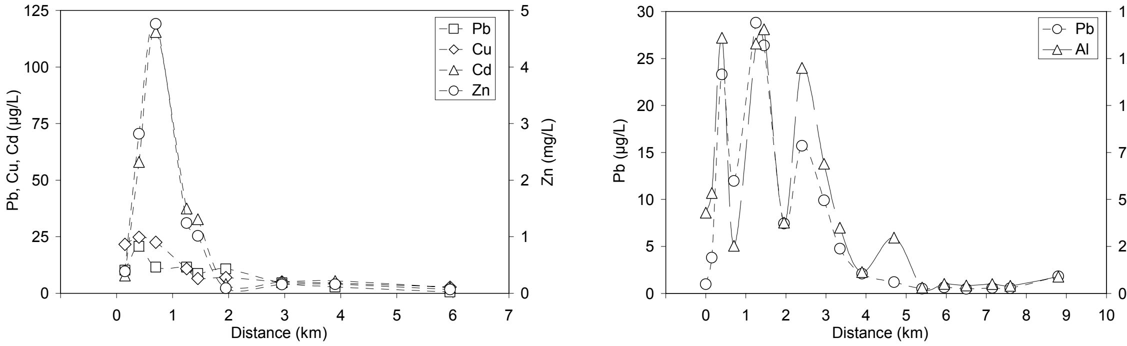

Figure 3. Left plot: Distribution of selected divalent metals along the BLS course under low-flow conditions. Right plot: Distribution of Pb and Al along the BLS course under high-flow conditions.

2. Solids

Lead concentrations in solid samples are very high: D = 19000-22000 ppm; S = 870-4900 ppm; T = 2100-8900 ppm. The amount of Pb solubilized by sequential chemical extraction is 82-100 % (average 92 %) for D samples, 63-83 % (av. 71 %) for S samples and 57-94 % (av. 78 %) for T samples.

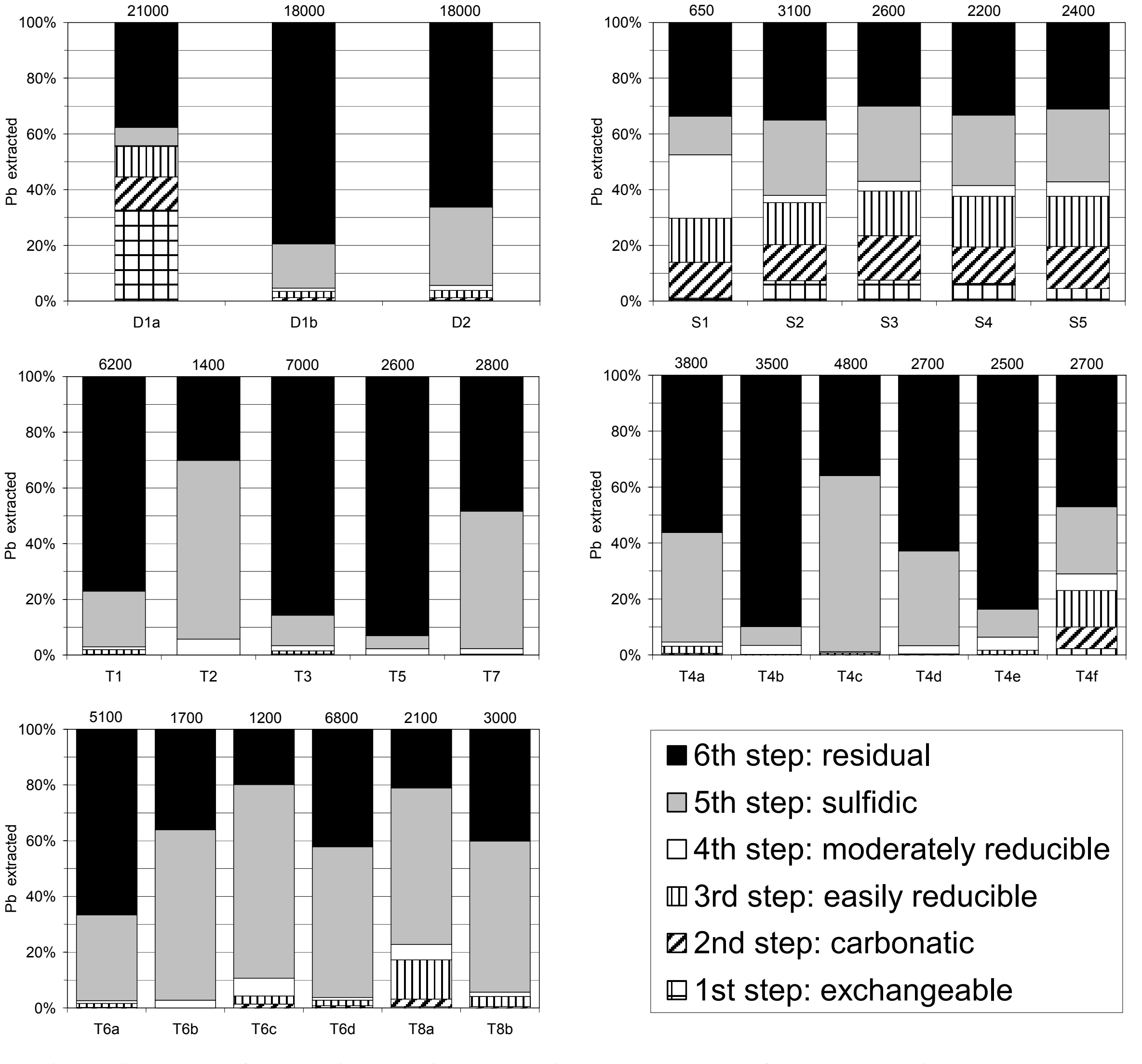

Figure 4. Results of sequential chemical extractions. Percentages of Pb extracted in each step are calculated on the total Pb amount solubilized that is reported (in ppm) above each single bar.

The D samples exhibit different Pb speciations (Fig. 4, upper left plot); in fact, Pb is mainly extracted from D1a in the 1st and 6th steps (33 % and 38 %, respectively) but also in the other steps (except the 4th), whereas the 5th and especially the 6th step dominate Pb speciation in D1b and D2. The abundant presence of anglesite [$PbSO_4$] as oxidation product of galena [PbS] (Fig. 5, upper left plot) accounts for Pb bound to the exchangeable/soluble fraction in D1a, whereas Pb bound to the carbonatic fraction (12 %) can be referred to the presence of cerussite [$PbCO_3$]. The residual fraction, as well as the non solubilized fraction, can be partly or entirely attributed to resistant minerals such as plumbojarosite that, together with residual galena, is the most abundant Pb-bearing phase in D1b (Fig. 5, upper right plot).

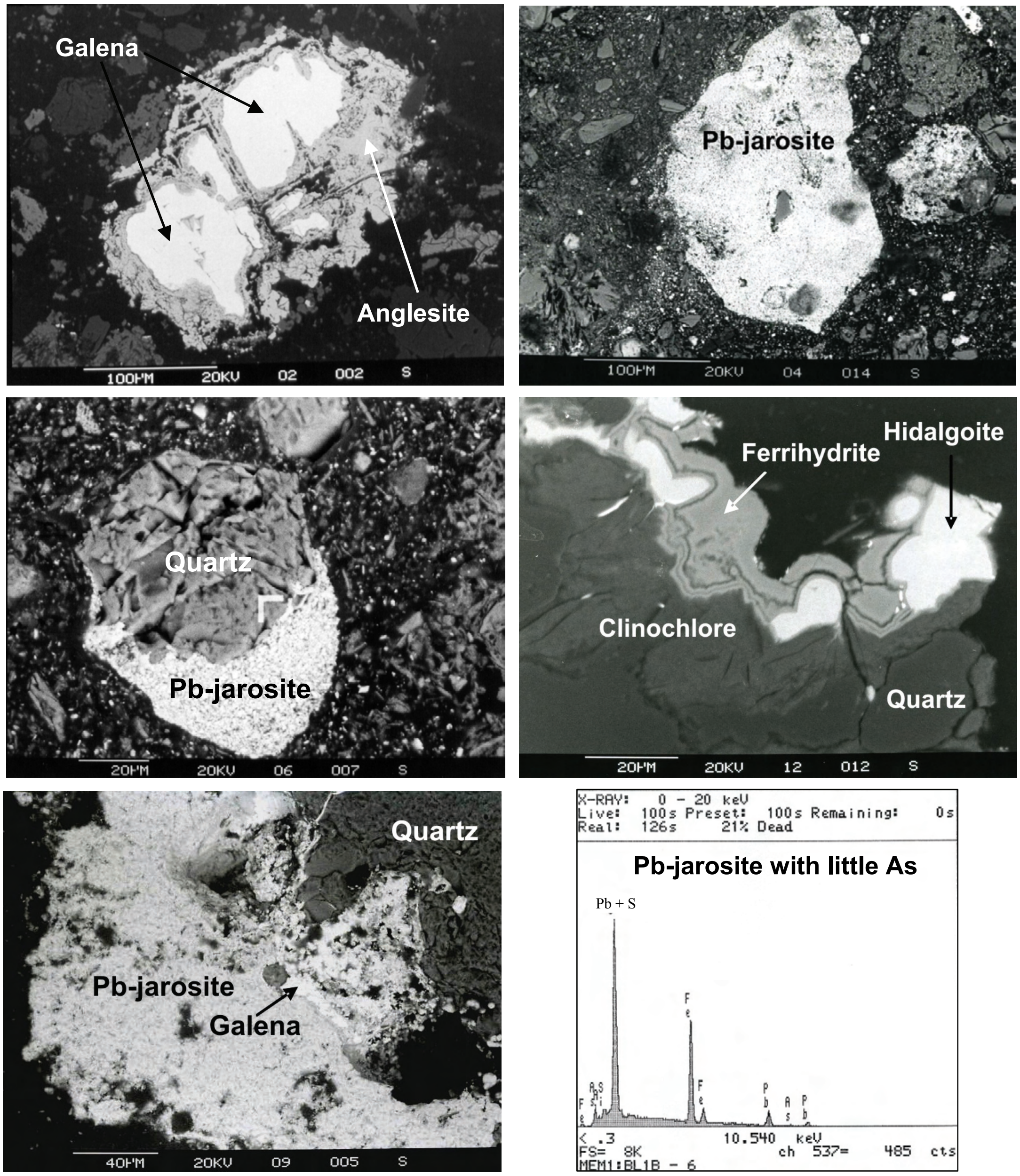

Figure 5. SEM images and EDX spectrum. Upper left plot: Residual galena crystal with an alteration rim of anglesite in the D1a sample (waste-rock dump) . Upper right plot: Granular aggregate of plumbojarosite in D1b. Middle left plot: Granular aggregate of plumbojarosite coating a quartz grain in the S3 sample (stream bed sediment). Middle right plot: Banded precipitate made up of probable hidalgoite and ferrihydrite coating an aggregate of quartz and clinochlore in S3. Hidalgoite appears to be precipitated before ferrihydrite; this has been also observed for plumbojarosite. Lower plots: Granular aggregate of plumbojarosite with residual galena (left plot) and EDX spectrum of plumbojarosite (right plot) in the T3 sample (flotation tailing).

The S samples exhibit a more homogeneous Pb distribution among the six fractions (Fig. 4, upper right plot), the less important being the 1st and the 4th (except for S1) and the most abundant being the 5th and the 6th (galena and plumbojarosite, respectively) as confirmed by SEM and TEM analyses (Fig. 5, middle left plot). Very rarely it has been observed a precipitate (Fig. 5, middle right plot) whose chemical composition suggests to be hidalgoite [$PbAl_3(AsO_4)(SO_4)(OH)_6$], a mineral belonging, like plumbojarosite, to the alunite-jarosite family. On the other hand, also plumbojarosite from Baccu Locci often contains significant amounts of As (Frau et al., 2005), so that it can be considered a term very close to beudantite [$PbFe_3(AsO_4)(SO_4)(OH)_6$].

Although with variable amounts, the sulfidic and residual fractions dominate Pb speciation in the T samples (Fig. 4, middle and lower plots), galena and plumbojarosite being the corresponding minerals (Fig. 5, lower plots).

Finally, contrary to As, Pb is generally not bound to oxides/hydroxides of Fe (4th step). This is confirmed by previous studies (Frau and Ardau, 2004; Frau et al., 2005) that showed as Pb is not present, or rather, is not detectable by SEM and TEM on the surface of ferrihydrite.

Water-leachable Pb is very low (0-10 ppm, corresponding to 0-0.2 % of total Pb in the solids), whereas acid-leachable Pb is generally very high (average 91% of total Pb in the solids). These results are in accordance with the low mobility of Pb observed along the BLS course (Fig. 2, right plot) and with the solid speciation of Pb that indicates galena and plumbojarosite to be the main Pb-bearing minerals in most samples (Figs. 4 and 5).

3. Speciation-solubility calculations

With the exception of acidic adit waters (Ad1, Ad2), the aqueous speciation of Pb is always dominated by $PbCO_3^{\circ}$, with other species (Pb^{2+}, $PbHCO_3^+$, $PbOH^+$, $PbSO_4^{\circ}$, $Pb(CO_3)_2^{2-}$) lower of one/two orders of magnitude. All waters are clearly undersaturated with respect to anglesite (SI: -6.6 to -1.1; except Ad1, SI: -0.2), cerussite (SI: -2.8 to -0.8; except Tr1 and Tr2, SI: -0.5 to 0.0), plumbojarosite (SI: -19.9 to -3.7; except Ad1 and Ad2, SI: 5.6 to 7.3; solubility product from Chapman et al., 1983) and hydronium-plumbojarosite (SI: -9.8 to -2.3; except Ad1 and Ad2, SI: 3.9 to 4.5; solubility product from Smith et al., 2006). Beudantite is above saturation in all waters (SI: 4.4 to 13.3; solubility product from Roussel et al., 2000). These results would indicate that Pb is removed by beudantite precipitation, but the poor or not proved reliability of the thermodynamic data of beudantite, as well as of plumbojarosite, suggests caution.

Conclusions

Lead release to BLS waters is initially due to dissolution of anglesite (and probably cerussite) formed by galena oxidation. Subsequently, Pb attenuation occurs as a consequence of (co)precipitation/sorption processes not fully identified. The stability of plumbojarosite (and/or beudantite) seems to prevent Pb from being released downstream, maintaining dissolved Pb concentrations below the Italian and WHO limits for drinking water.

Acknowledgements

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