

Original paper

Chemical composition of weathering products in neutral and acidic mine tailings from stibnite exploitation in Slovakia

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Here we describe the chemical composition of the weathering products at two abandoned stibnite deposits, Dúbrava and Poproč in Slovakia. The tailings at Dúbrava are circumneutral (pH 7–8), richer in Sb than As and rich in carbonates. The tailings at Poproč are acidic (pH 3–5), the Sb/As ratio is usually close to 1, carbonates are missing, and the tailings have elevated Pb contents. The most common sulphide at both sites was pyrite (FeS₂), less frequently stibnite (Sb₂S₃) and arsenopyrite (FeAsS); minor berthierite (FeSb₂S₄) was found only at Poproč. At both sites, sandy layers of the tailings contain the weathering products; the clayey portions are sterile. The most frequent secondary phases in the Dúbrava impoundments are oxidation rims on pyrite and arsenopyrite, with relics of the primary sulphides commonly preserved. At Poproč, the primary sulphides were completely oxidized and decomposed. A common feature of the oxidation rims on all primary sulphides is their enrichment with respect to elements rather rare in the primary phase, an effect which is most apparent in the outermost portions of the rims. Rims around arsenopyrite may be enriched in Sb, around pyrite in As and Sb, and around stibnite in Pb. Antimony is usually incorporated into Sb–Fe, Fe–Sb, Sb, or Sb–Ca oxides, with the Sb/(Sb + Fe) ratio varying from 0 to 1. Arsenic behaves differently in comparison with Sb in that the highest As/(As + Fe) ratio on a wt. % basis is 0.41, as observed in weathering rims on arsenopyrite, the only primary sulphide with a substantial As content. Our results show that the nature of the weathering products is controlled by the primary mineralogy and the ability of the aqueous solutions to transport As, Sb, Ca, Fe, and Pb. There is no indication that the final products would be chemically or mineralogically different if weathering reached the terminal stages at the two studied sites.

Keywords: weathering, tailings, antimony, arsenic, Slovakia

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1. Introduction

The oxidation of sulphide minerals in mine tailings usually leads to the release of many elements into aqueous media. The concentration of these elements often exceeds that acceptable for living organisms or permissible by law. The quantity and quality of the sulphide weathering products depends on the availability of oxidizing agents (dissolved O₂, Fe³⁺), the nature and composition of the sulphides and their reactive surface area, physical parameters of the tailings (porosity, particle size distribution), climate, water saturation level of the pores, water in- and outflow to and from the impoundment, and chemical and biochemical reactions in its interior (Nicholson 1994; Ritchie 1994; Seal and Hammarstrom 2003). Sulphide oxidation leads to the generation of sulphuric acid which can be neutralized by carbonate minerals such as calcite or dolomite. Aluminosilicate minerals such as plagioclase can also consume acid, even though they are not as reactive as carbonates (Plumlee 1999; Jambor et al. 2002).

The oxidation of pyrite (FeS₂), the most common cause of acid mine drainage, has been described by many authors (Lowson 1982; Davis and Ritchie 1986; Jambor 1994, 2003). Similarly, oxidation processes involving arsenopyrite (FeAsS) are relatively well known (Buckley and Walker 1988; Richardson and Vaughan 1989; Nesbitt et al. 1995; Nesbitt and Muir 1998; Corkhill and Vaughan 2009). The weathering products in tailings rich in pyrite or pyrrhotite (Fe_{1–x}S) have been described in detail (Jambor 1994; Blowes et al. 2003). In contrast, little is known about oxidation of antimony sulphides, especially stibnite (Sb₂S₃) and the distribution of antimony in the environment (Živković et al. 2002; Ashley et al. 2003; Flynn et al. 2003; Scheinost et al. 2006; Ackermann et al. 2009).

A detailed study of the chemistry of the weathering products is an important step toward the comprehension of the complex processes operating in the mine tailings environment. Identification of the carriers of the pollutants is a prerequisite for the assessment of the contamination risk and a remediation or immobilization strategy.

In this study, we compare sulphide oxidation processes and the resulting chemical compositions of the weathering products within several Fe-, Sb- and As-rich tailing ponds (impoundments) from two abandoned stibnite deposits in Slovakia. Differences between the two localities selected are the petrology of the host rocks, mineralogy of the primary hydrothermal ores, concentrations of the toxic elements, pH values of the tailings, technical characteristics of the tailing impoundments, age of the deposited sediments, and climatic conditions.

2. Description of the study sites

2.1. Dúbrava deposit

The first report of mining activities at the Dúbrava deposit dates back to the beginning of the 18th century. The period of the most intense mining began in 1944 when the oldest impoundment was established. Between 1944 and the end of the mining operation in 1991, the deposit produced 1 300 000 metric tons of ore and 22 000 metric tons of antimony, placing it among the biggest world Sb producers (Arvensis et al. 1994).

Hydrothermal veins and diagonal veinlets contain stibnite and pyrite as the major ore minerals; minor phases include arsenopyrite, zinkenite ($\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$), sphalerite (ZnS), and tetrahedrite ($\text{Cu}_{12}(\text{Sb,As})_4\text{S}_{13}$). The most frequent gangue minerals are quartz and dolomite (Chovan et al. 1994). Abundant illite, chlorite, and carbonates formed in the host rocks during hydrothermal alteration (Orvošová et al. 1998). Country rocks of the Dúbrava deposit are predominantly biotite granodiorites and tonalites with smaller elongated bodies of migmatites and gneisses which represent relics of the crystalline basement.

The ores were milled in two steps (dry and wet) in ball mills to a grain size under 0.071 mm and stibnite was extracted by flotation with a recovery factor for Sb of 85 % (Arvensis et al. 1994). The waste was deposited in four impoundments situated in the Križianka creek valley (Fig. 1). The tailing ponds at Dúbrava are conventional raised embankment tailings storage facilities but with no impermeable (e.g., clay) layer at their bases. The tailings lie directly on alluvial sediments. After mining operations ceased, the impoundments were covered by a mixture of soil and rocks to lessen the contact of the tailings with atmospheric oxygen and water. The old impoundment was covered by 2.5–3 m of industrial waste, the impoundment no. 2 by 20 cm of soil, and the impoundments 1 and 3 by up to 1 m of industrial waste.

Climate in this region is moderately warm and humid, with average temperature in January of 5–8 °C, average temperature in July of 14–16 °C and average annual precipitation 900 mm.

2.2. Poproč deposit

At Poproč, exploitation of Sb ores started in the 17th century and the mines were closed in 1965. The most intense mining took place between 1931 and 1965 when more than 10 000 metric tons of antimony and c. 80 kg of gold were recovered (Kaličiaková et al. 1996).

The main minerals of the hydrothermal veins are quartz and stibnite, with less common pyrite, arsenopyrite, berthierite (FeSb_2S_4), tetrahedrite, sphalerite, and the Pb–Sb sulphosalts zinkenite and fülöppite ($\text{Pb}_3\text{Sb}_8\text{S}_{15}$) (Klimko et al. 2009). The Poproč deposit is hosted by Early Paleozoic low-grade metapelites and acid metapyroclastics which were later intruded by Permian granites (Grecula et al. 1995).

Tailings from the Poproč deposit were more or less scattered in local geographic depressions or other suitable locations, sometimes even without dams to protect their flanks and a layer of clays or at least industrial waste to diminish the rate of oxidation. At several points, the tailings are in a direct contact with surface waters. In this study, we divided these scattered tailings storage pools into three impoundments situated in the valley under the mine (Fig. 1). The biggest one (tailing impoundment no. 3) carries about 18 000 m³ of sediments (Kaličiaková et al. 1996), tailing impoundments 1 and 2 are smaller.

Climate in this region is moderately warm and humid, with average annual temperatures of 5–8 °C and an average annual precipitation of 900 mm.

3. Materials and methods

3.1. Sample collection and preparation

Samples of the tailing material at Dúbrava were collected from two boreholes, one situated in the old impoundment (borehole DU–1, entire length 13.5 m), and the second one in the impoundment no. 2 (borehole DU–3, entire length 20 m) (Fig. 1). In both cases, the boreholes penetrated the tailings from the top layers into the eluvial sediments. Samples from the impoundment no. 3 were collected from a well (DUT–7) dug to a depth of approximately 2 m.

At the Poproč deposit, where tailing impoundments were not built at any prearranged sites, samples were collected from profiles on the exposed slopes of the impoundment no. 3 (POT–3) and from dug wells in the impoundments no. 1 (POT–1) and no. 3 (POT–2) (Fig. 1).

The samples were composites of 20–100 cm of the profile in the boreholes or the dug wells. These were homogenized and two thirds of each sample separated into light and heavy fraction by panning in water or in ethanol. Selected heavy-grain concentrates were prepared

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for further study in a form of standard thin and polished sections, to be inspected in transmitted and reflected polarized light, respectively. The remainder of each sample was used for geochemical study and pH measurements.

Chemical compositions of the samples were determined by X-ray fluorescence (XRF) analyses with a Philips PW 2400 instrument (Friedrich-Schiller University, Jena, Germany). The samples were finely ground, mixed with wax, and pressed into pellets. For all elements except As and Sb, the standard materials used for rock analysis were applied. For the two metalloids, we used home-made secondary standards made of finely-ground granite with admixed known amounts of As and Sb to derive calibration curves.

The pH values were measured in a suspension of tailings sediments with water (10:1) which was allowed to stand for 24 hours prior to measurement (Conklin 2005).

The electrode was calibrated with standard pH solutions (4.01 and 7.00).

The carbonate content in selected samples was measured from the volume of CO₂ released by 15% hydrochloric acid. The finely ground samples were weighed out and brought into the contact with acid in a tightly sealed glass flask. The CO₂ volume was read in a sealed and calibrated glass cylinder. The samples were allowed to outgas for 20–30 minutes, until the reaction stopped and the volume of gas did not increase anymore. No attempt was made to distinguish calcite, dolomite, and ankerite by this method. All data were recalculated on the basis of equivalent weight per cent of calcite, that is, the amount of calcite that would be responsible for an identical volume of CO₂ released during an experiment. A sensitivity analysis carried out on samples with known carbonate (calcite) concentration of 5–10 % has

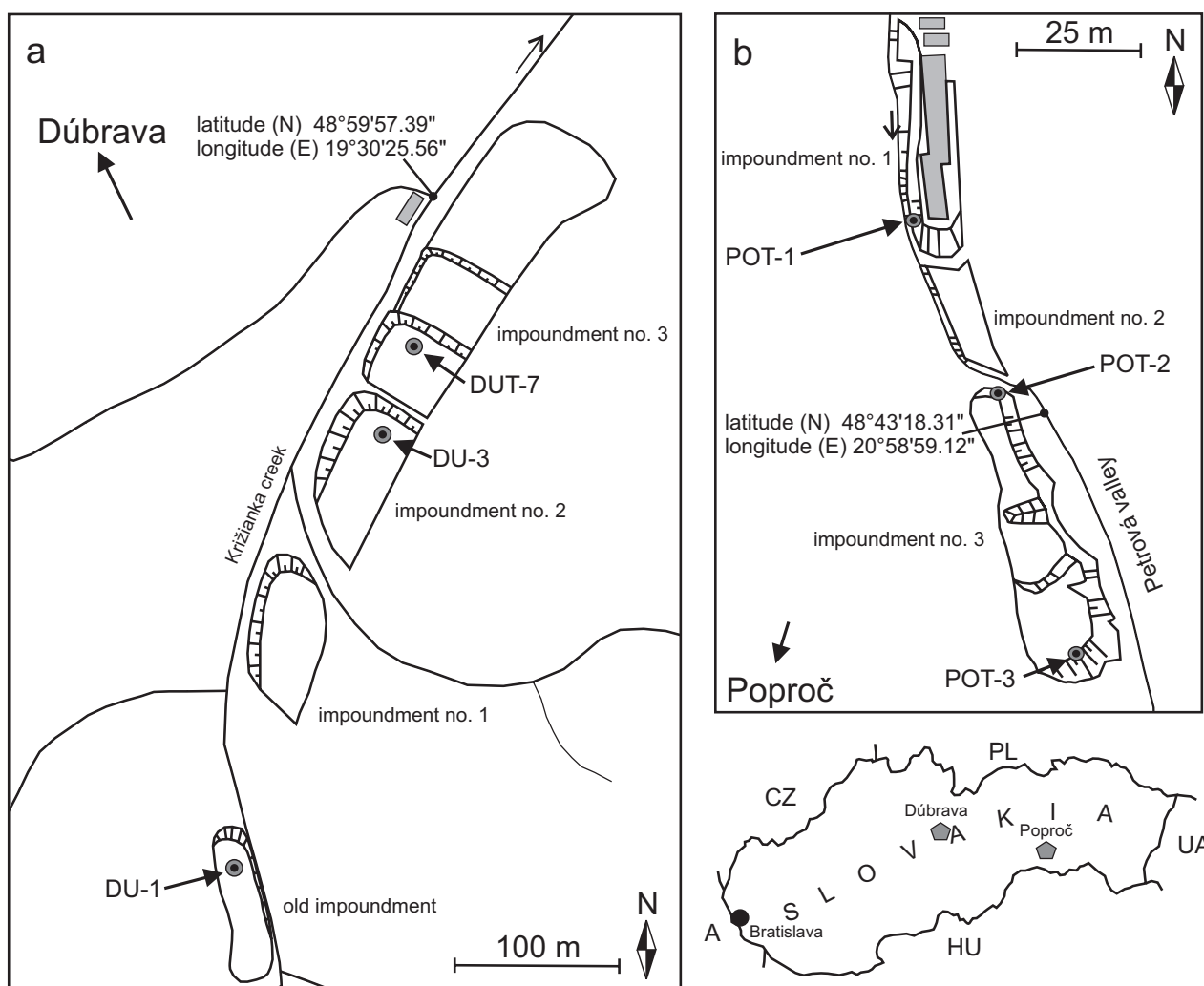


Fig. 1 Schematic maps of the study sites. The bottom right panel shows the location of both deposits in Slovakia. Each map depicts the location of tailings, the sampling sites discussed in the text and contains one point with precise geographic coordinates.

shown that the accuracy of the method is 0.3–0.5 %. Repeated measurements on the samples of the impoundment sediments have shown that the standard deviation of the measurements is 0.3–1.0 %, increasing with decreasing carbonate content in the samples.

Neutralization potentials of the tailing materials were determined using EPA (Environmental Protection Agency (U.S)) methodology (after Sobek et al. 1978). This method is based on a treatment of the sample with a known amount of standardized HCl. The calcium carbonate equivalent is calculated by titration of the HCl not consumed with standardized NaOH solution. The ability of the material to produce H_2SO_4 was tested by a static net acid generation test (Miller et al. 1997). In this method, the sulphides present in the sample are forced to oxidize by hot H_2O_2 . The amount of generated acid is then calculated by titration with a standardized NaOH solution.

Quantitative mineral compositions of heavy fractions were determined by counting a statistically significant number of grains in each sample under a reflected polarized light microscope and in a scanning electron microscope. The ore minerals and their weathering products were subsequently analyzed by a Cameca SX-100 electron microprobe (State Geological Institute of Dionýz Štúr, Bratislava) in wavelength-dispersive mode (WDS) under conditions of 20 kV, 20 nA, and beam size of 1–5 μm . The following lines, standards, and crystals were used for the analyzed elements: Mg (K_α , forsterite, TAP); Al (K_α , Al_2O_3 , TAP); Si (K_α , SiO_2 , TAP); S, Fe, Cu (K_α , CuFeS_2 , PET); P (K_α , GaP, PET); Ca (K_α , wollastonite, PET); Mn (K_α , metallic Mn, LIF); Co (K_α , metallic Co, LIF); Ni (K_α , metallic Ni, LIF); Zn (K_α , ZnS, LIF), Pb (M_α , PbS, PET); Sb (L_β , Sb_2S_3 , PET), As (L_β , FeAsS, TAP). The counting time on each peak was 20 s, on background 10 s (20 s for Sb). All electron microprobe analyses are available as an electronic supplement to this article.

4. Results

4.1. Primary, secondary, and tertiary minerals

Primary sulphides, i.e. those which formed by the action of hydrothermal fluids as a part of the ore mineralization, can be subsequently replaced by various weathering products. We distinguish here between weathering products which were produced only naturally ('secondary minerals') and weathering products which form owing to human activities in the dumps, waste piles, and impoundments ('tertiary minerals'). Recently formed minerals appear in the tailings as oxidation rims and films on the primary sulphides or precipitates in voids between tailings particles. We suspect that most of these recently formed

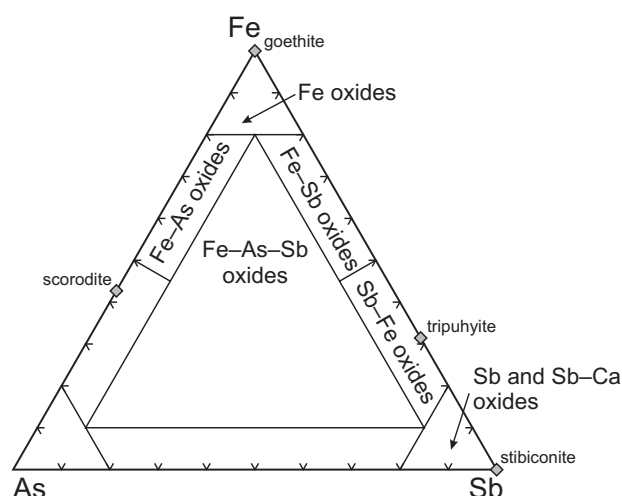


Fig. 2 A triangular diagram showing the division of the weathering products based on their chemical compositions as used in this work.

minerals are tertiary but the secondary origin of at least some of them is difficult to prove or disprove. Hence, if such distinction cannot be made, we will refer to all newly formed minerals in the studied impoundments as secondary. We should note, however, that the secondary and tertiary minerals at a single locality are not necessarily the same, even though they form from the same primary minerals. The pore waters in the impoundments are richer in many elements than the natural waters and the processes of dissolution, weathering, and precipitation run a different course.

The secondary and tertiary minerals will be collectively called here oxides, a term which includes oxides, hydroxides, and oxyhydroxides. For the discussion of the chemical composition of the weathering products, we divide them arbitrarily into several groups (see Fig. 2). The distinction is based on the projection of the chemical composition of a given material in a triangular Fe–Sb–As plot. Among the Sb-rich weathering products, we further distinguish between Sb oxides and Sb–Ca oxides. The latter are those which contain at least 5 wt. % Ca.

4.2. Dúbrava deposit

4.2.1. Geochemical characteristics of the tailings materials

Tailings materials at Dúbrava consist of alternating sandy and clayey sediment layers of mm to 5 meters thickness. Alternation of the layers is easily observable, especially in the top parts of the tailings where sand prevails. Clays become more abundant with depth and in some sections of the impoundments clay-rich layers may be up to 5 m

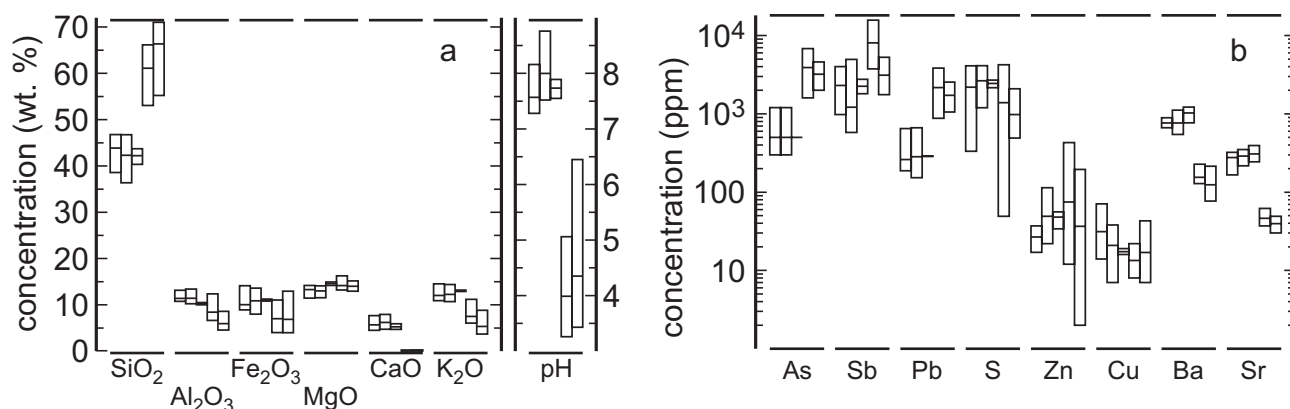


Fig. 3 Chemical composition of the tailings as determined by XRF and their pH: **a** – Major oxides and pH; **b** – Minor and trace elements. Note that the vertical scale in panel (b) is logarithmic. The boxes represent the minima and maxima of the variables plotted, and the bar inside each box is the mean. For each variable, the five boxes plotted represent the five sampling sites in the order DU-1, DU-3, DUT-7, POT-1, POT-2.

thick (borehole DU-3, depth 850–1350 cm). These clayey sediments do not contain sulphides or products of their oxidation. The concentrations of the major oxides (Fig. 3a) disagree with values expected for granodiorite or tonalite; the differences, especially lower SiO_2 , higher Al_2O_3 , K_2O , and CaO contents, are related to the pervasive illitization and carbonatization of the granitoid rocks (Orvošová et al. 1998).

Tailings at Dúbrava contain up to 5000 ppm Sb and the concentration of Sb usually exceeds that of As (Figs 3b, 4). The Pb, Zn, and Cu contents are relatively low, corresponding to the minor proportion of zinkenite, sphalerite, and tetrahedrite in the ores. The presence of barite in the veins is traceable by elevated Ba and Sr contents.

The average pH value of tailings materials is 7.57 in the case of the old impoundment (borehole DU-1), 8.00 for impoundment number 2 (borehole DU-3) and 7.73 at the youngest one (DUT-7). The pH values in the tailings are buffered by abundant carbonates. The carbonate content measured directly (as volume of gas released in reaction with HCl) varied usually between 3 and 4 wt. % calcite equiv., with maxima of 2.0 and 5.6 wt. %. The calculated neutralization potential of the tailings corresponds to 70–120 t CaCO_3 per 1000 t of tailings. The tailings at Dúbrava are not expected to produce acidity (H_2SO_4), both according to simple calculations from the measured sulphur and carbonate contents, and the static net acid generation tests.

4.2.2. Oxidation products of pyrite and arsenopyrite

The most frequent sulphide in the tailings is pyrite and its crystals are often intensively corroded and replaced by

secondary Fe oxides (Fig. 5). They form oxidation rims on the pyrite crystals or replace pyrite along cracks and contain 0.01 to 4.50 wt. % As and up to 7.75 wt. % Sb (Tab. 1). Both of the metalloids are bound predominantly in the outer parts of the rims (Fig. 6, Tab. 2). At least part of the As in these rims may have originated from the primary pyrite. Although pyrite is nominally FeS_2 , hydrothermal pyrite from Dúbrava is often zoned and the As concentrations in the outer parts of the crystals reach 5.17 wt. %; the Sb contents in the pyrite are below the detection limit (~ 0.05 wt. %) of the electron microprobe (Chovan 1990).

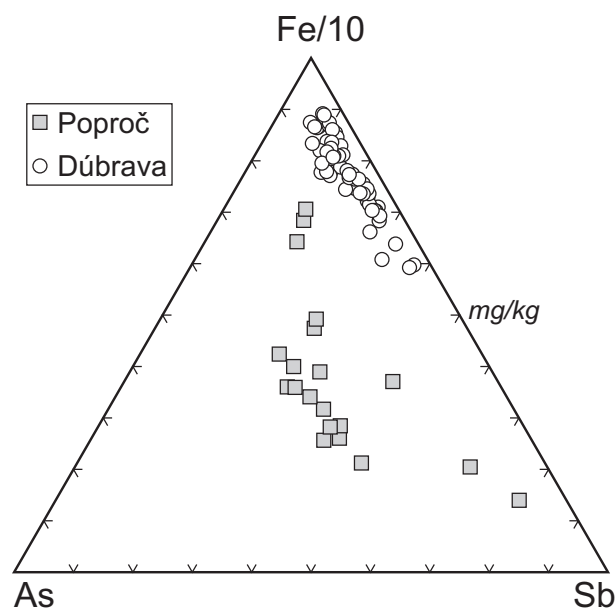


Fig. 4 A triangular plot of the chemical compositions of the tailings from Dúbrava (circles) and Poproč (squares). All data plotted are based on XRF analyses.

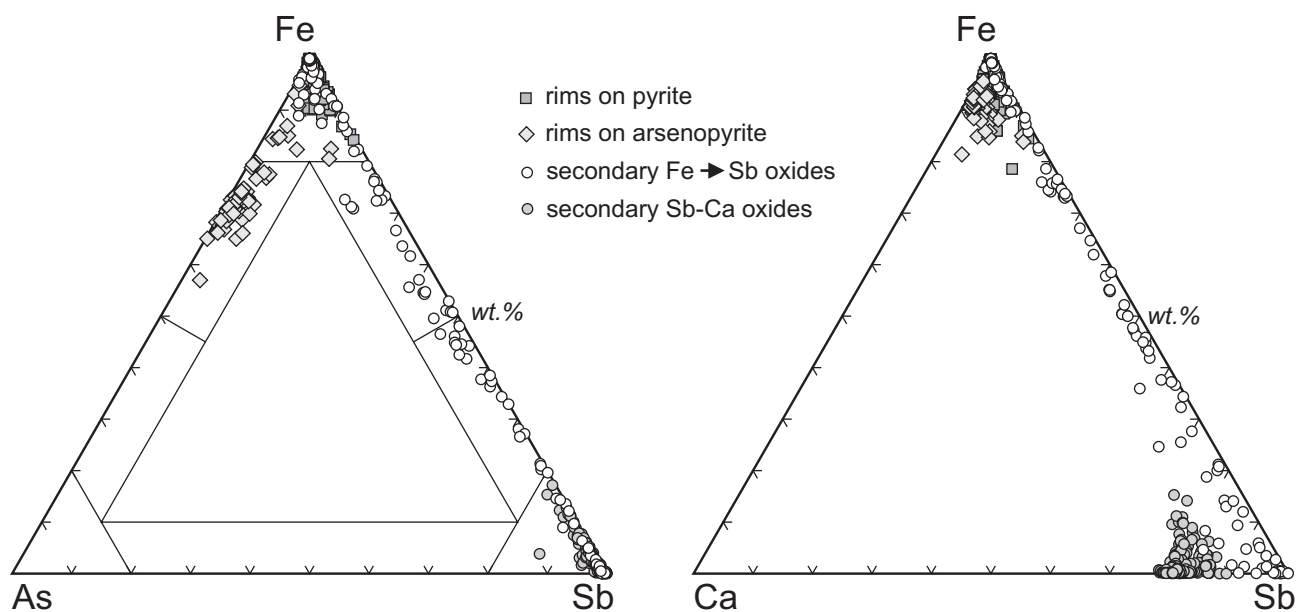


Fig. 5 Triangular plots of the chemical compositions of the rims on pyrite (squares), arsenopyrite (diamonds), and grains with no relics of primary sulphides (circles) from the tailings at Dúbrava. All data plotted are based on spot electron microprobe analyses. For the fields plotted in the left panel, see Fig. 2.

In few cases, the Fe oxides replaced the pyrite crystals completely, forming pseudomorphs with the original crystal shape, having 0–9.78 wt. % Sb and 0–2.33 wt. % As. Quantitative proportions of the Fe oxides are the same at all the impoundments studied. Outside of the oxidation zones, subhedral pyrite crystals show little or no visible corrosion.

In the oxidation zones of the tailings, arsenopyrite crystals are coated by oxidation rims which consist of

Fe–As or Fe oxides (Figs 5, 7a, Tab. 1). The As content in these rims (2.69–19.87 wt. %) is lower than in primary arsenopyrite, suggesting that, during oxidation and weathering, As was partially lost to the pore solutions. The Sb content is also relatively high, ranging from 0.12 to 7.01 wt. %. The Sb concentration in primary arsenopyrite does not exceed 1.89 wt. % (Sahan and Chovan 1991). Outside the oxidation zones, arsenopyrite crystals are not affected by weathering and oxidation.

Tab. 1 Electron microprobe analyses of the weathering products from Dúbrava (wt. %)

	rims on arsenopyrite	rims on pyrite	Fe oxides	Fe–Sb oxides	Sb–Fe oxides	Sb oxides	Sb–Ca oxides
element/ <i>n</i>	73	159	32	16	10	23	140
Mg	0.36(0.07)	0.25(0.14)	1.57(3.34)	0.16(0.05)	0.10(0.05)	0.06(0.03)	0.13(0.04)
Al	0.23(0.81)	0.34(1.86)	0.36(0.64)	0.20(0.25)	0.15(0.18)	0.04(0.05)	0.10(0.18)
Si	0.66(0.54)	1.74(2.31)	1.25(1.16)	0.93(0.70)	0.50(0.29)	0.44(0.25)	1.33(0.50)
S	0.43(0.70)	0.71(2.30)	0.18(0.75)	0.90(1.95)	0.14(0.23)	0.08(0.11)	0.05(0.12)
P	0.01(0.02)	0.07(0.15)	0.12(0.21)	0.12(0.08)	0.15(0.14)	0.02(0.04)	0.02(0.04)
Ca	2.91(0.64)	1.22(0.96)	0.41(0.24)	1.19(0.40)	1.01(0.75)	1.84(1.55)	8.63(1.27)
Mn	0.02(0.05)	0.03(0.10)	0.37(0.48)	0.12(0.11)	0.08(0.12)	0.03(0.04)	0.04(0.05)
Fe	40.90(6.43)	53.13(7.62)	51.81(9.87)	35.99(6.43)	18.06(6.11)	5.61(8.43)	0.96(1.39)
Co	0.08(0.02)	0.10(0.04)	0.07(0.02)	0.05(0.03)	0.03(0.02)	0.01(0.01)	0.01(0.01)
Ni	0.01(0.01)	0.01(0.02)	0.02(0.02)	0.01(0.01)	0.01(0.01)	0.01(0.01)	0.01(0.01)
As	13.21(4.01)	0.60(0.79)	0.48(0.66)	1.63(1.36)	0.52(0.35)	0.33(0.27)	0.32(0.25)
Sb	1.32(1.18)	1.30(1.28)	2.19(2.42)	19.19(6.62)	40.11(6.94)	45.30(8.86)	41.07(4.66)
Cu	0.03(0.02)	0.04(0.10)	0.07(0.11)	0.16(0.17)	0.08(0.19)	0.07(0.20)	0.03(0.09)
Zn	0.04(0.03)	0.03(0.05)	0.04(0.06)	0.05(0.04)	0.02(0.02)	0.03(0.09)	0.02(0.03)
Pb	0.15(0.31)	0.09(0.12)	0.13(0.25)	0.55(0.80)	1.92(2.11)	0.38(0.83)	0.24(0.88)

The values listed are averages with standard deviations in parentheses; *n* is the number of individual analyses averaged

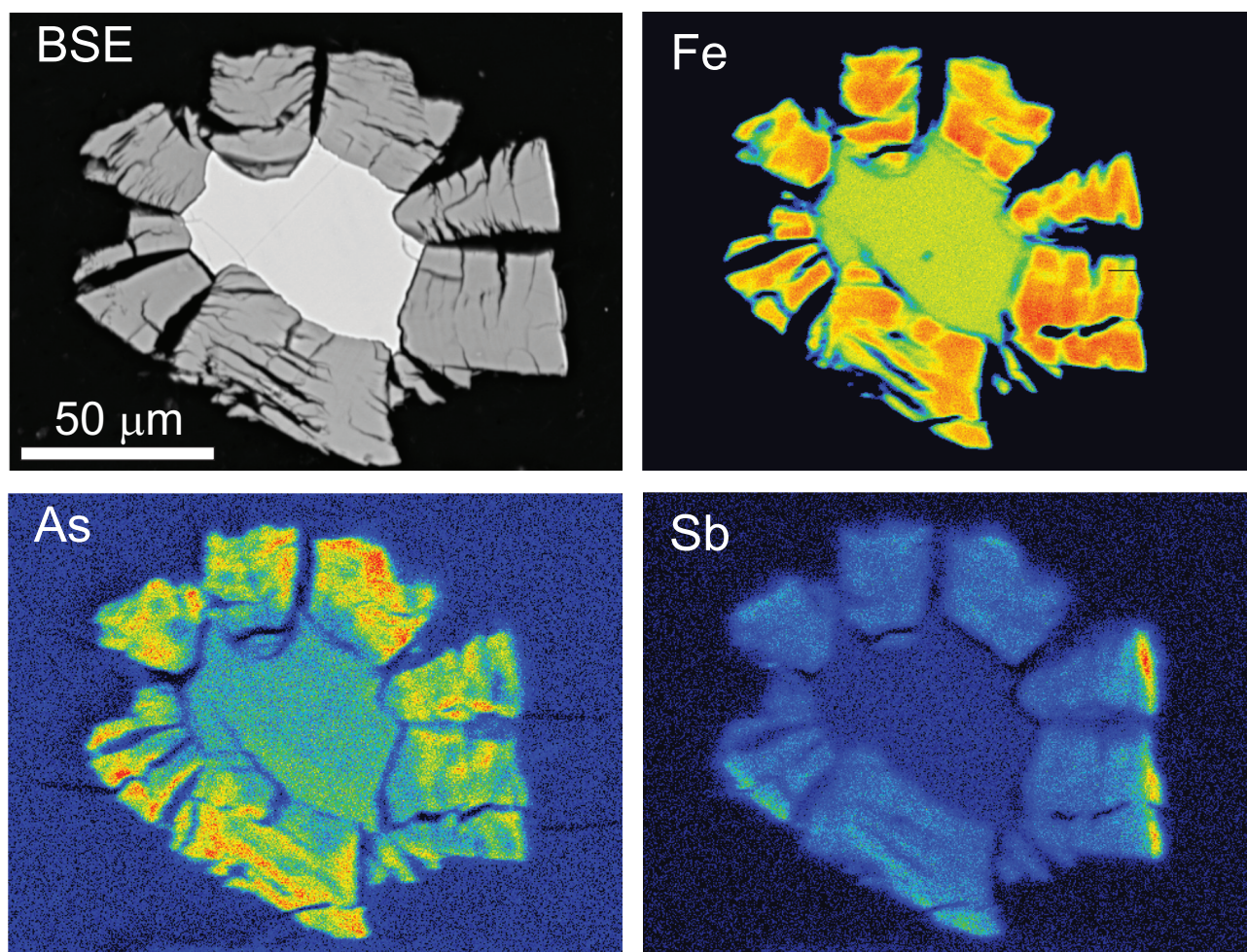


Fig. 6 A back-scattered electron (BSE) image of pyrite and its oxidation rim from the oxidation zone of the old impoundment at Dúbrava together with element distribution maps for Fe, As, and Sb. Note the enrichment of As and Sb towards the outer parts of the rims.

4.2.3. Secondary Sb minerals

Due to fast oxidation and dissolution of stibnite (Maruška et al. 2000), its presence in the oxidation zones of the tailings is minimal. At least some of the stibnite grains were transformed to secondary Sb oxides which occur frequently. Other grains may have been partially or completely dissolved in pore solutions. The dissolved antimony could be then adsorbed onto hydrous ferric oxides or precipitate to form Sb, Fe–Sb, or Sb–Fe oxides within the impoundment. A certain fraction of the dissolved Sb stays in solution and causes groundwater contamination (Ženišová et al. 2009).

At Dúbrava, the Fe–Sb and Sb–Fe oxides (Fig. 5, Tab. 1) are less common in the tailings than in the rims around pyrite and arsenopyrite crystals described above. The Fe–Sb and Sb–Fe oxides are approximately equally abundant in all samples of sandy, oxidized tailings; the clayey tailings within the oxidation zones do not contain these phases at all. Textural evidence such as distinct

Tab. 2 Composition of an oxidation rim on a pyrite crystal from the oxidation zone of the old impoundment at Dúbrava (wt. %)

	location of the analysis		
	near the primary pyrite	middle	outer part of the rim
Mg	0.22	0.21	0.21
Al	0	0	0.03
Si	2.14	2.04	2.22
S	0.23	0.11	0.09
P	0	0.01	0
Ca	2.39	2.4	2.51
Mn	0	0	0
Fe	52.09	51.13	52.47
Co	0.08	0.09	0.12
Ni	0	0	0.01
As	0.3	1.26	2.34
Sb	1.05	1.4	3.29
Cu	0	0.02	0.01
Zn	0.02	0	0
Pb	0.02	0.02	0.07

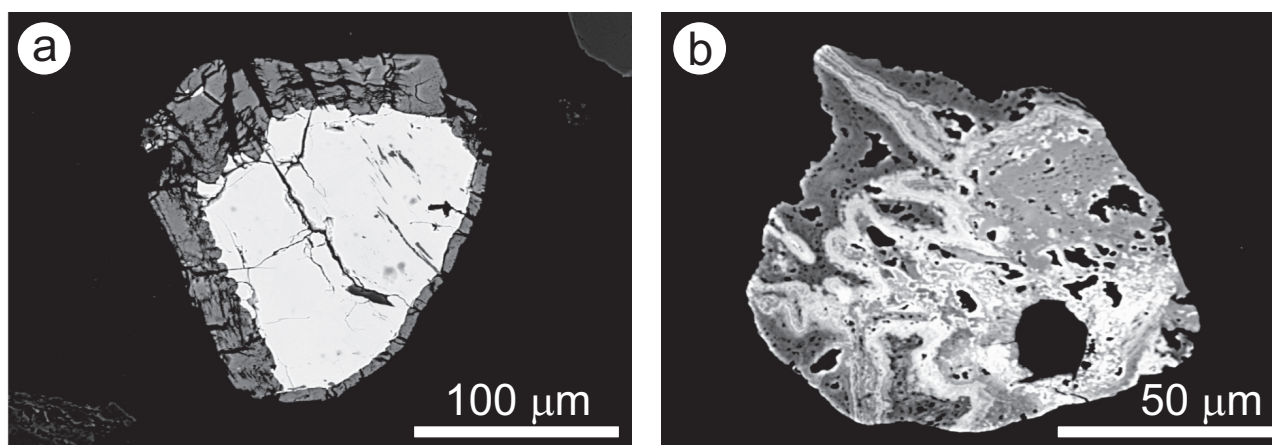


Fig. 7 Back-scattered electron images. **a** – Arsenopyrite and its oxidation rim from the oxidation zone of the old impoundment at Dúbrava; **b** – A Sb–Ca oxide from a depth of 7–9.6 m in the old impoundment in Dúbrava.

zoning suggests that the minerals crystallized from pore solutions in the tailing impoundments environment. Contents of As in the Fe–Sb oxides are 0.35–4.29 wt. %, while the Sb concentrations vary from 10.89 to 29.01 wt. % (Tab. 1).

The Sb and Sb–Fe oxides were identified in the material from the top oxidation zones (down to 2.5 m) of the impoundments nos. 2 and 3 and from deeper parts (7–12 m) of the old impoundment. Similar minerals were present in lower amounts in the oxidation zone of the old impoundment (3–5 m). Similar to the case of the Fe–Sb oxides, zoning of the grains causes their chemical heterogeneity.

Weathering products with much Sb and essentially no Fe were also observed and divided into two groups. The first group is characterized by high Sb as well as low Fe, As, and Ca contents. These Sb oxides are most likely a product of direct oxidation of stibnite, without any interactions with pore solutions; they are common especially in the oxidation zone of the old impoundment. The second group includes the more abundant Sb–Ca oxides (Fig. 7b) with a significant content of Ca (up to 10.71 wt. %, Tab. 1) and is most common in the younger impoundments.

4.3. Poproč deposit

4.3.1. Geochemical characteristics of the tailings materials

The largest impoundment (no. 3, Fig. 1) is formed by alternating layers of sandy and clayey sediments, each several mm to approximately 1 m thick. Sandy sediment is dominant in the top parts of the tailings, clayey material prevailing deeper. Sand-rich portions of the tailings are fully oxidised to a depth of 2 m. The smaller impound-

ments and piles of tailings scattered along the valley were not sampled in a detail comparable with impoundment no. 3. The content of the other impoundments and their oxidation zones, however, are probably very similar to those in the impoundment no. 3. Primary sulphides and especially products of their oxidation are concentrated in the sandy layers but were not found in the clayey sediment.

Chemically, the tailings are characterized by high SiO_2 concentrations, elevated MgO contents, moderate to low Al_2O_3 , Fe_2O_3 , and K_2O contents, and an especially striking lack of CaO (Fig. 3a). Concentration of both As and Sb are high, reaching maxima of 6 800 and 15 700 ppm, respectively (Fig. 3b). Except for a few outliers, the As/Sb ratio varies near 1 (Fig. 4). The concentration of Pb is also high, of the order of thousands of ppm, reflecting the relatively abundant Pb–Sb sulphosalts (Klimko et al. 2009). The contents of Zn and, to a lesser extent, Cu show significant scatter and can be explained by the rarity of sphalerite and tetrahedrite.

The pH values in the profiles POT–1 and POT–2 vary around averages of 4.00 and 4.35, respectively (Fig. 3a). The lowest measured pH value was 3.3 and the data show no discernible trend with sampling depth. The carbonate content of the tailings is essentially zero; an exceptional datum was 0.22 wt. % calcite eq. The calculated neutralization potential of the tailing is 16–18 t of CaCO_3 per 1 000 t. Static net acid generation tests indicated that the tailings in impoundment no. 1 could produce 0.78–2.65 kg H_2SO_4 /t, and tailings in the impoundment no. 3 some 2.35–2.74 kg H_2SO_4 /t.

4.3.2. Oxidation products of pyrite and arsenopyrite

Samples of tailing material collected at Poproč are characterised by an abundance of secondary oxides and

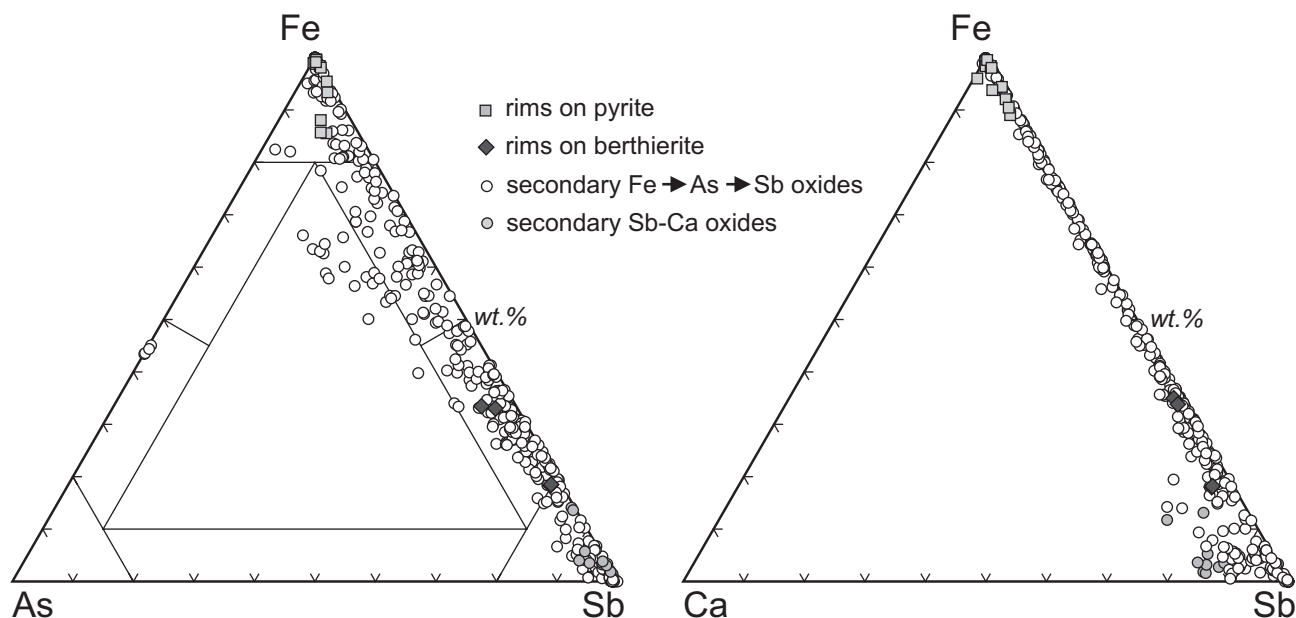


Fig. 8 Triangular plots of the chemical compositions of the rims on pyrite (squares), berthierite (diamonds), and grains with no relics of the primary sulphides (circles) from the tailings at Poproč. All data plotted are based on spot electron microprobe analyses. For the fields plotted in the left panel, see Fig. 2.

minimal contents of unweathered sulphides such as pyrite, arsenopyrite, stibnite and berthierite.

Pyrite was the most common sulphide and is, in most cases, replaced by pseudomorphs of secondary Fe oxides. Contents of Fe in these phases are 20.72–70.42 wt. %; of Sb 0–9.56 wt. % and As 0–9.87 wt. % (Fig. 8, Tab. 3). Rarely, some of the primary pyrite remained and

oxidation rims on such relics have contents of Fe from 38.65 to 60.19, As from 0 to 3.21 and Sb from 0.16 to 4.20 wt. %.

Arsenopyrite was a rare primary mineral in Poproč. Where it did occur, it was replaced in the tailings by scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) which was identified by WDS analyses (Fig. 8, Tab. 3).

Tab 3 Composition of the weathering products from Poproč (wt. %)

element/ <i>n</i>	Sb-Fe oxides 109	Sb oxides 86	Fe-Sb oxides 67	Fe oxides 57	Sb-Ca oxides 6	rims on pyrite 15	rims on berthierite 4	rims on stibnite 4	scorodite 4
Mg	0.10(0.09)	0.07(0.05)	0.12(0.16)	0.12(0.17)	0.09(0.04)	0.06(0.04)	0.13(0.06)	0.08(0.03)	0.04(0.03)
Al	0.75(0.99)	0.54(0.93)	0.80(0.90)	0.80(1.31)	0.28(0.13)	0.71(1.03)	0.09(0.07)	0.27(0.17)	0.07(0.08)
Si	1.05(1.57)	1.06(0.91)	2.20(2.35)	2.06(2.38)	1.71(0.73)	2.02(1.08)	0.27(0.05)	0.91(0.22)	0.08(0.11)
S	0.08(0.18)	0.06(0.15)	0.40(0.56)	0.51(1.32)	0.03(0.02)	1.03(0.87)	0.07(0.03)	5.03(4.46)	0.03(0.02)
P	0.10(0.10)	0.06(0.09)	0.21(0.16)	0.20(0.29)	0.04(0.03)	0.09(0.11)	0.05(0.05)	0.00(0.01)	0.01(0.02)
Ca	0.58(0.47)	1.76(1.75)	0.27(0.19)	0.14(0.14)	6.53(1.65)	0.26(0.19)	1.36(0.69)	2.19(2.09)	0.10(0.03)
Mn	0.03(0.06)	0.01(0.01)	0.03(0.08)	0.09(0.11)	0.05(0.04)	0.03(0.04)	0.07(0.07)	0.01(0.01)	0.00(0.00)
Fe	18.06(4.65)	2.79(2.83)	34.70(7.11)	50.64(10.59)	2.44(2.11)	54.43(6.26)	14.33(5.10)	0.77(0.38)	25.46(0.53)
Co	0.05(0.06)	0.02(0.03)	0.05(0.05)	0.09(0.05)	0.02(0.01)	0.26(0.13)	0.03(0.02)	0.01(0.01)	0.06(0.02)
Ni	0.02(0.03)	0.01(0.02)	0.03(0.17)	0.04(0.15)	0.01(0.02)	0.02(0.03)	0.01(0.01)	0.01(0.02)	0.04(0.05)
As	1.52(1.51)	0.89(0.71)	3.18(2.36)	1.68(2.33)	1.09(0.82)	0.67(1.10)	1.82(1.10)	1.19(0.16)	32.15(1.71)
Sb	40.92(8.26)	53.19(8.40)	17.29(4.67)	3.51(3.06)	44.69(9.29)	1.30(1.59)	38.95(4.64)	39.06(2.53)	0.15(0.09)
Cu	0.04(0.04)	0.04(0.04)	0.01(0.01)	0.04(0.05)	0.01(0.02)	0.47(0.98)	0.04(0.02)	0.04(0.04)	0.00(0.00)
Zn	0.26(0.30)	0.13(0.23)	0.09(0.11)	0.13(0.17)	0.05(0.05)	0.40(0.33)	0.28(0.31)	0.02(0.02)	0.05(0.03)
Pb	1.30(1.30)	4.23(7.22)	0.48(0.49)	0.39(1.25)	3.47(2.75)	0.15(0.17)	0.48(0.29)	9.14(6.27)	0.04(0.04)

The values listed are averages with standard deviations in parentheses; *n* is the number of individual analyses averaged

4.3.3. Secondary Sb minerals

Relics of stibnite are very rarely preserved in the tailings and if so, they are largely replaced by oxidation rims of variable composition. Contents of Sb in these rims range from 36.82 to 41.80 wt. %, contents of Fe are low (0.50–1.33 wt. %) and As varies between 1.04 and 1.38 wt. % (Tab. 3). Interesting is the high Pb content (up to 15.76 wt. %) in these oxidation rims, where it is probably adsorbed onto the secondary oxides from pore solutions. The source of Pb was likely the primary Pb–Sb sulphosalts zinkenite and füllöpite, which are known to occur in the ores (Klimko et al. 2009) but were not found in the tailings. Care was taken to identify the primary sulphides by EDS analyses because the optical properties of stibnite and Pb–Sb sulphosalts are rather similar. Therefore, we are sure that the Pb-rich rims grew on stibnite and not on Pb–Sb sulphosalts.

Berthierite was also identified in the samples and its crystals are occasionally replaced by oxidation rims (Fig. 9) with Sb contents of 34.64–43.59 wt. %, As 0.90–3.27 wt. %, and Fe 9.82–19.06 wt. % (Tab. 3). An example of the distribution of Sb, As, and Fe in the rims on a berthierite crystal is displayed in Fig. 9. The oxidation rims are enriched in Fe and As and depleted in Sb compared with primary berthierite. Contents of Sb in oxidation rims are similar to those in primary berthierite, sometimes even a little lower, and most likely caused by Sb dissolution.

Secondary oxides with no relics of primary sulphides are the most abundant Sb- and As-bearing phases in the heavy fraction of the tailings from Poproč. As shown in Fig. 8, these phases span a wide range of compositions and include Fe, Fe–Sb, Fe–As–Sb, Sb–Fe, Sb, and Sb–Ca oxides. Phases in which Sb dominates over Fe are more abundant than those where Fe > Sb (Fig. 8). Arsenic as-

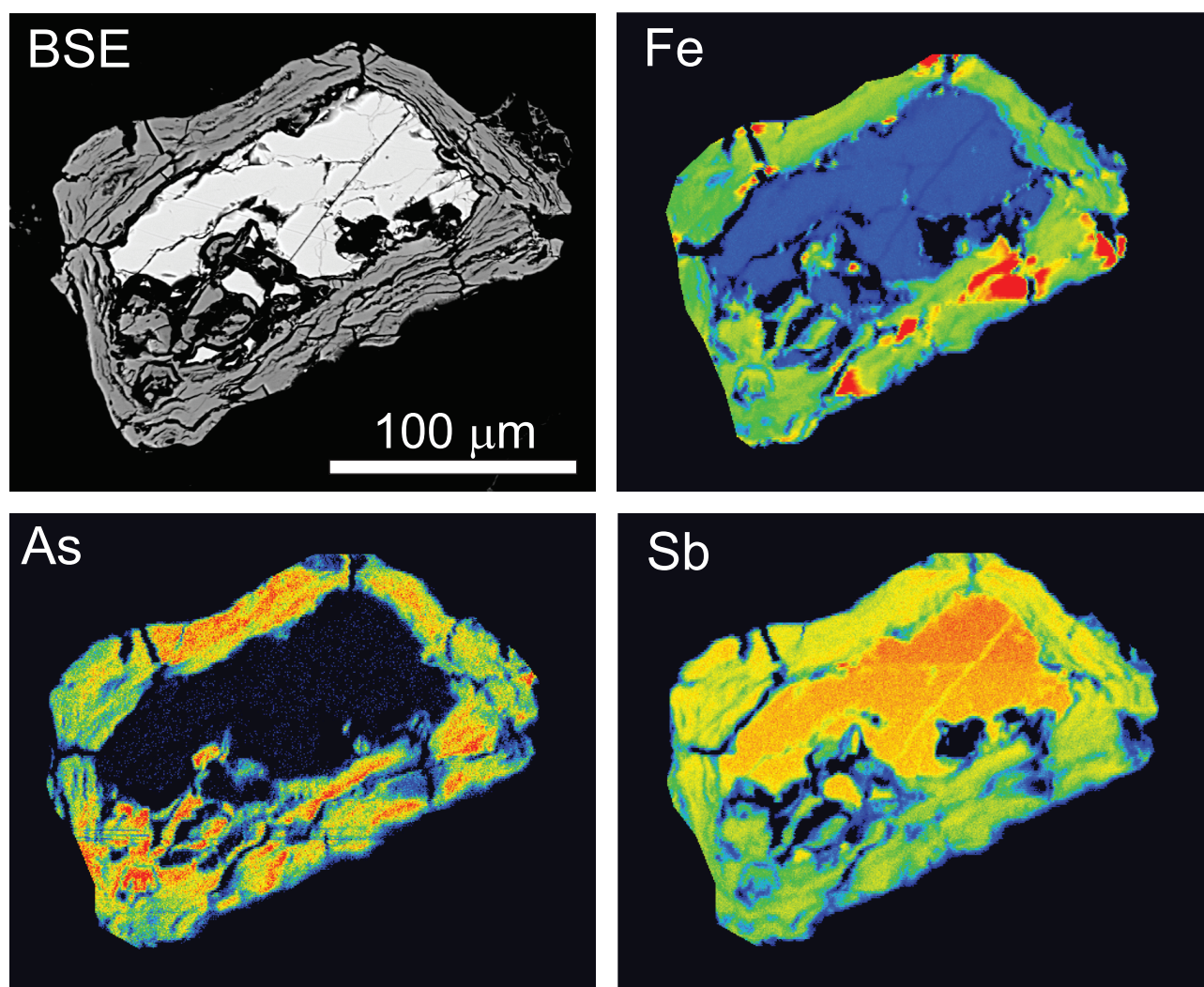


Fig. 9 A back-scattered electron image (BSE) of berthierite and its oxidation rim (impoundment no. 3 at Poproč) with element distribution maps for Fe, As, and Sb.

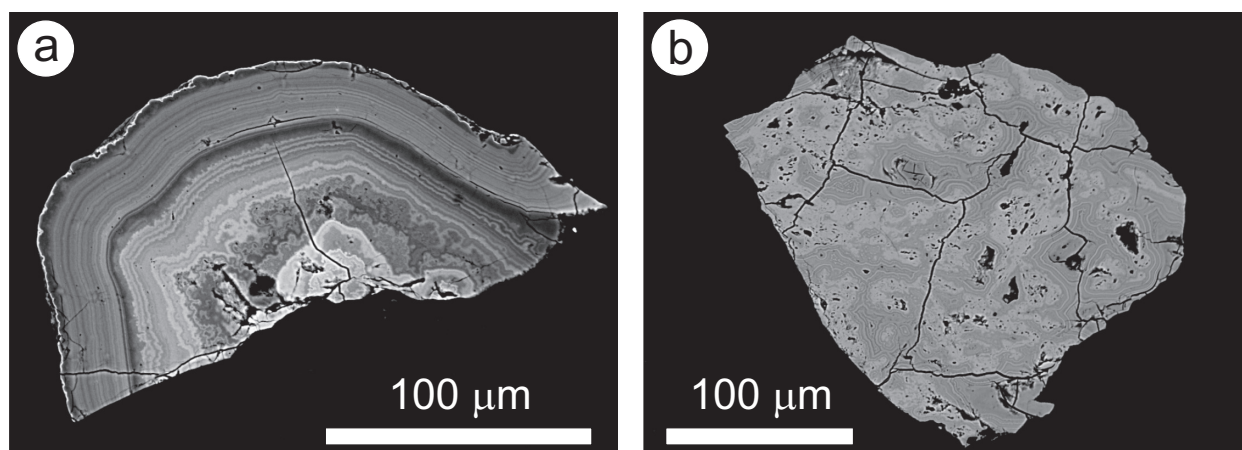


Fig. 10 Back-scattered electron images of two zoned grains from impoundment no. 3 at Poproč: Fe-Sb oxide (a) and Sb-Fe oxide (b).

sociates predominantly with the Fe-As-Sb and Fe-Sb oxides (up to 9.87 wt. %), less so with the Sb-Fe oxides (Tab. 3). Both Sb-Fe and Fe-Sb oxides form often zoned grains (Figs 10a-b), either compact or porous. The Sb-rich grains may contain elevated amounts of Pb (from 3.17 to 38.62 wt. %) and there is a significant negative correlation (-0.966) between Pb and Sb in grains with Pb contents over 5 wt. %.

5. Discussion

Results of this study document qualitative and quantitative differences between secondary oxides at the studied sites and point to the different mineralogical and geochemical behavior of As and Sb in the environments of the impoundments. There are several parameters, which differentiate the two sites and may affect the rate and nature of the oxidation processes. The Dúbrava deposit is situated at a higher altitude (930–1 300 m a.s.l.) than the Poproč deposit (356–630 m a.s.l.) and, therefore, the climate at Dúbrava is colder and oxidation processes are likely slower. Another difference is the mode of tailing deposition: at Dúbrava, the impoundments were properly built and later covered by layers of industrial waste from 20 cm to 250 cm thick. On the other hand, the tailings at Poproč were scattered along the valley and flotation waste lies in direct contact with air or surface waters. The oldest tailings in Dúbrava are 40–60, and those in Poproč 60–70 years old. All the mentioned conditions may have an influence on oxidation processes in the studied impoundments.

Iron contents in the tailings are higher at Dúbrava (average 11 wt. % Fe_2O_3) than at Poproč (7 wt. % Fe_2O_3), although chemical analysis alone says little about the nature of minerals that carry Fe (sulphides versus silicates). Antimony contents are much higher in tailings from

Poproč (average 5100 ppm) than from Dúbrava (1600 ppm) (Fig. 3). There are even greater differences in As contents, much higher at Poproč (average 3500 ppm) than at Dúbrava (500 ppm). Average Pb contents are 280 ppm in tailings from Dúbrava and 1900 ppm from Poproč. The last element of importance that influences not only the chemical composition of the secondary minerals, but also the pH of the impoundments, is Ca. Calcium is released from carbonates which are frequent in the tailings from Dúbrava but rare at Poproč. Consequently, Ca contents are high (6 wt. % CaO) and pH is approximately neutral in the Dúbrava tailings; Ca contents are low (0.1 wt. % CaO) and the pH acidic at Poproč.

The most common sulphide at both sites is pyrite, less frequent being stibnite and arsenopyrite; minor berthierite was found only at Poproč. Our results confirm the previously published conclusions that pyrite is the slowest mineral to oxidize, followed by arsenopyrite (Buckley and Walker 1988; Richardson and Vaughan 1989; Nes-

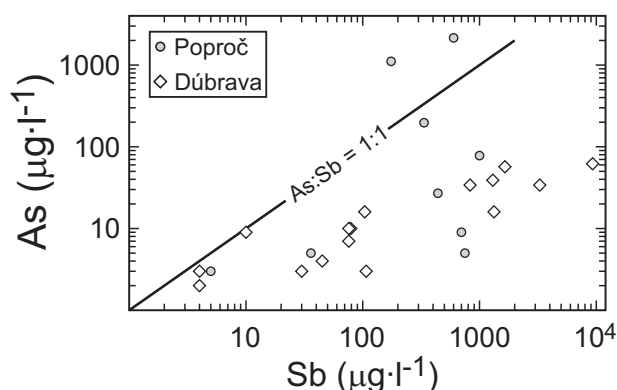


Fig. 11 Chemical composition of the aqueous solutions discharged from the old mines and impoundments at Dúbrava (diamonds) and Poproč (circles). All data are taken from Ženišová et al. (2009). Note the logarithmic scale on both axes.

bitt et al. 1995; Nesbitt a Muir 1998; Filippi 2004). As already observed (Vink 1996; Maruška et al. 2000; Ashley et al. 2003; Wilson et al. 2004), stibnite oxidizes and decomposes quickly and is only rarely observed in oxidation zones.

The most frequent secondary phases in the Dúbrava impoundments are oxidation rims around pyrite and arsenopyrite, with relics of the primary sulphides frequently preserved. The rims are common in the oxidation zones of the impoundments and represent effective scavengers of both As and Sb. Similar rims are largely missing in the acidic tailings at Poproč, mostly because the primary sulphides were completely oxidized and decomposed. The absence of sulphides at Poproč probably reflects the interplay of the acidic conditions within the impoundments (enhanced chemical weathering), the sandy nature of the tailings (enhanced water flow and better access of oxygen), and lower altitudes (higher average temperature).

A common feature of the oxidation rims around all primary minerals (pyrite, arsenopyrite, berthierite, stibnite) is an enrichment with respect to the elements not abundant in the primary phases; this effect is the most perceptible in the outermost portions of the rims. Rims on arsenopyrite may contain high amounts of Sb, rims on pyrite abundant As and Sb, and rims on stibnite elevated contents of Pb. The most likely explanation for these observations is the adsorption of As, Sb, or Pb from the aqueous solutions, circulating through the impoundments. Indeed, the waters sampled at the two deposits (discharges from mines and impoundments) do contain excessive amounts of Sb and As (Fig. 11). It is interesting that these waters usually contain more Sb than As and are able to transport these two elements (in the fraction $<0.45 \mu\text{m}$) even at circumneutral pH values.

Antimony is usually incorporated into Sb–Fe, Fe–Sb, Sb, or Sb–Ca oxides (Majzlan et al. 2007; Chovan et al. 2010; Lalinská et al. 2010). As we have observed, the Sb/(Sb + Fe) ratio may vary from 0 to 1 (Figs 5, 8). Pure Sb oxides are more common in the tailings from Poproč and are probably pseudomorphs after stibnite. These phases may correspond to the minerals stibiconite [$\text{Sb}^{3+}\text{Sb}_2^{5+}\text{O}_6(\text{OH})$], cervantite ($\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$), senarmontite (Sb_2O_3), or valentinite (Sb_2O_3), which are all known to be associated with weathering of Sb deposits (Chovan et al. 1981; Filella et al. 2002; Dill et al. 2008). The Sb–Fe oxide is the most likely tripuhyite (FeSbO_4), having presumably crystallized directly from pore solutions within the impoundments. The same phase was identified by micro-X-ray diffraction in the Sb-rich tailing impoundments from Pezinok (Slovakia) as a mineral controlling Sb distribution (Majzlan et al. 2011).

Behaviour of As is different from Sb in that the highest As/(As + Fe) (in wt. %) ratio observed was 0.41. The highest As concentration was detected in the Fe–As

oxides that form rims on arsenopyrite, the only primary sulphide with a substantial As content. Only the grains from Poproč plot in the field of the Fe–As–Sb oxides and these grains have in general higher As concentrations than those from Dúbrava. Enhanced adsorption of the arsenate anion to Fe-rich substrates can be easily understood as being the result of the acidic conditions at Poproč (Filella et al. 2002; Roddick-Lanzilotta et al. 2002; Smedley and Kinniburgh 2002). Scorodite, the most common stable product of arsenopyrite oxidation (Dove and Rimstidt 1985; Nordstrom and Parks 1987; Kraus and Ettel 1988; Alpers et al. 1994), was identified just in one sample from the Poproč deposit as the only As secondary mineral phase observed at both localities.

Calcium was found in low concentrations in nearly all identified phases, probably owing to electrostatic association with the small particles of the oxides (Voegelin et al. 2010). The highest concentrations of Ca were recorded in Sb–Ca oxides from the most recent tailings at Dúbrava. These phases are chemically close to romeite, $\text{Ca}_2\text{Sb}_2\text{O}_7$, described previously from oxidation zones of Sb deposits (Dill et al. 2008). It should be also noted that tailings with relatively low Ca contents, such as those at Poproč, contain Sb–Ca oxides with elevated concentrations of Ca.

Lead is bound most frequently to Sb–Fe, and less so to Fe–Sb oxides at both localities, suggesting that the pH of the tailings does not play a decisive role for this element. Some of these oxides could correspond to bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_7$), which could be a product of Pb–Sb sulphosalt oxidation (Bahfenne and Frost 2009).

6. Conclusions

The weathering products found at the two localities are chemically similar despite a number of physical and chemical differences between the two sites. The nature of these products is essentially controlled by primary mineralogy and the ability of the aqueous solutions to transport elements such as As, Sb, Fe, Ca, and Pb. Under the observed conditions of high redox potential and moderately acidic to circumneutral pH, aqueous solutions transport all these elements and enrich the weathering products in elements not available in the parental primary sulphides. A difference in the mineralogy of the weathering products could be perhaps expected under conditions which would mobilize some of these elements and separate them from the others, for example, at $\text{pH} < 2.5$ when Fe^{+3} is significantly soluble, or under reducing conditions, when more mobile As^{+3} dominates over As^{+5} .

Pyrite is the slowest mineral to oxidize, followed by arsenopyrite. Stibnite oxidizes and decomposes quickly and is only rarely observed in oxidation zones.

The differences in the mineralogy of the weathering products can be linked to the complete disappearance of the primary pyrite and arsenopyrite at Poproč; on the other hand, in Dúbrava their relics occur commonly. At both localities, stibnite weathers and decomposes rapidly. The Fe–Sb and Sb–Fe oxides are more abundant at Poproč, most likely as a consequence of the more abundant Fe supply into the pore solutions in the tailings from decomposing pyrite and arsenopyrite. Therefore, the differences appear to be the result of different rates of weathering and there is no indication that the final products would remain chemically or mineralogically distinct if weathering proceeded to the terminal stages. The only obvious difference is the enrichment of the weathering products in As at Poproč compared with Dúbrava. This fact can be explained easily by the higher As contents of Poproč tailings with the acidic conditions, under which the AsO_4^{3-} anion sorbs more strongly to Fe-rich weathering products.

These results are therefore applicable to other tailing ponds or mining dumps with high Sb concentrations. The data presented here could be used to predict which phases will appear in course of weathering of such tailings or dumps. We are currently studying more sites with high Sb, using a combination of chemical and crystallographic analysis to determine precisely the nature of the minerals present. These results will be presented later in a separate contribution.

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Electronic supplementary material. The GPS coordinates and a map of the two localities as well as original electron microprobe analyses are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.104>).

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