A mineralogical, geochemical, and microbiogical assessment of the antimony- and arsenic-rich neutral mine drainage tailings near Pezinok, Slovakia

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ABSTRACT

The mineralogical composition of mining wastes deposited in voluminous tailing impoundments around the world is the key factor that controls retention and release of pollutants. Here we report a detailed mineralogical, geochemical, and microbiological investigation of two tailing impoundments near the town of Pezinok, Slovakia. The primary objective of this study was the mineralogy that formed in the impoundment after the deposition of the tailings (so-called tertiary minerals). Tertiary minerals include oxyhydroxides of Fe, Sb, As, Ca and are present as grains and as rims on primary ore minerals. X-ray microdiffraction data show that the iron oxyhydroxides with abundant As are X-ray amorphous. The limiting (lowest) Fe/As (wt/wt%) ratio in this material is 1.5; beyond this ratio, the hydrous ferric oxide does not retain arsenic. The grains with less As and little to moderate amounts of Sb are goethite; the grains where Sb dominates over Fe are poorly crystalline tripuhyite (FeSbO₄). Even the most heavily contaminated samples (up to 29 wt% As₂O₅) are populated with diverse communities of microorganisms including typical arsenic-resistant heterotrophic species as well as iron reducers and sulfur oxidizers. Several recovered clones cluster within phylogenetic groups that are solely based on environmental sequences and do not contain a single cultivated species, thus calling for more work on such extreme environments.

Keywords: Antimony, iron oxides, weathering products, electron microprobe, X-ray microdiffraction, microbial diversity

INTRODUCTION

The mineralogical composition of mining wastes deposited in voluminous tailing impoundments around the world is the key factor that controls retention and release of pollutants. Waste with small amounts of pollutant stored in labile species is of more concern than a waste reservoir with higher amounts of inert pollutants. Assessments of waste behavior by bulk chemical analysis (Filippi et al. 2004), sequential extraction (Goh and Lim 2005), or spectroscopy (Paktunc et al. 2003; Cances et al. 2005) address this point but are not specific enough to define the phase(s) that control pollutant mobility. Detailed studies of the mineralogical composition of mine waste (e.g., Walker et al. 2005) document the mineralogical richness of these materials and may not only help in designing better remediation strategies, but also in explaining the results of bulk studies. Although minerals are mostly considered as the products of inorganic processes, the role of microorganisms in the destruction and creation of minerals in weathering processes is now widely recognized (Kornhauser 2007). The competition, interplay, and consonance of the inorganic and biological pathways of mineral

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transformations should be examined and tested to determine which process is dominant.

Antimony is mined mostly from hydrothermal ores where the mineral stibnite (Sb_2S_3) usually dominates (Fowler and Goering 1991). Other primary Sb sulfides, such as berthierite (FeSb₂S₄), gudmundite (FeSbS), or sulfosalts may be present in smaller amounts. In hydrothermal ores, antimony may be present in appreciable amounts even if it is not targeted as the element of interest (e.g., in tetrahedrite) and, therefore, will be included in ore processing and disposal of waste. If exposed to the ambient atmosphere, the primary Sb sulfides give way to a limited number of Sb-bearing secondary minerals stibiconite [Sb³⁺Sb⁵⁺O₆(OH)], kermesite (Sb₂S₂O), valentinite and senarmontite (Sb₂O₃), and cervantite (Sb³⁺Sb⁵⁺O₄). In tailing impoundments, the primary or secondary minerals can be converted to tertiary minerals typical for these settings.

Secondary Sb oxidic minerals are known from several localities (Aral 1989; Meden et al. 1993; Szakall et al. 2000; Wilson et al. 2004; Filella et al. 2009b). These secondary minerals are usually identified by the means of optical microscopy, X-ray diffraction (XRD), or electron microprobe analyses (EMPA). Environmental mobility of Sb at these sites has been evaluated using various sequential leaching protocols or dissolution studies

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(Lintschinger et al. 1998; Ashley et al. 2003; Flynn et al. 2003). These authors concluded that the oxidation of stibnite, the most important Sb sulfide, is rapid. The products of this oxidation are the Sb oxide minerals senarmontite, valentinite, stibiconite, or rarely cervantite. The dissolution rates of these minerals are variable; with sufficient water flow, they may slowly release Sb into the environment. However, at many sites, secondary Fe oxides form a formidable barrier to Sb mobility (Ashley et al. 2003; Majzlan et al. 2007). Therefore, as long as these Fe oxides are not disturbed. Sb may be not bioavailable (Flynn et al. 2003). The occurrence of secondary Sb-bearing minerals can be rationalized with Eh-pH diagrams (Vink 1996) although some of the calculated assemblages contradict the observations from nature (Filella et al. 2009a). This discrepancy could be simply due to the fact that equilibrium has not been established during the Sb oxide formation and it underscores the need for careful and detailed observations in the field and laboratory.

In this work, we have investigated Sb- and As-bearing tertiary minerals (those newly formed in tailing impoundments) at the abandoned Sb-Au deposit Pezinok in Slovakia. Our primary goal was to identify the Sb sinks in the waste impoundments. The waste material also contains appreciable amounts of As, which cannot be overlooked. In a previous work (Majzlan et al. 2007) and here, we investigated the affinity of As to iron oxides and Sb-poor and Sb-richer tertiary minerals, respectively. We established the total budget of the metals and metalloids (Fe, As, Sb) in waste form and the fractionation of these elements within the waste. Heavy minerals were concentrated and hundreds of the grains were closely examined by electron microprobe analysis; a smaller number of selected grains were further investigated by a series of micro-techniques, including micro-X-ray diffraction, micro-X-ray absorption spectroscopy, and transmission electron microscopy. This work, therefore, spans a range of scales, from macro- to micro- and nanoscale. We have also identified the microbial inhabitants of the waste material and can speculate about their role in mineral transformations.

GEOLOGIC SETTING AND HISTORY OF THE DEPOSIT

The Pezinok deposit is located in the Malé Karpaty Mountains, the westernmost mountain range of the Western Carpathians (Slovakia). The ore deposits in the area are hosted by Variscan granodiorites and regionally metamorphosed rocks formed from a Devonian volcanic and sedimentary complex (Korikovskij et al. 1984) that consists today of metapelites with zones of black shales and metabasic rocks (Cambel and Khun 1983). The zones contain commonly stratiform pyrite-pyrrhotite (FeS2-Fe1-xS) mineralization (Chovan et al. 1994) and later hydrothermal ores. The earlier stages of mineralization produced gold-bearing pyrite and arsenopyrite (FeAsS), and subsequently Sb ores, which comprise stibnite, but also relatively abundant berthierite, gudmundite, native antimony and primary kermesite and valentinite. The Sb mineralization occurs as quartz-carbonate (mostly Fe-dolomite) lenses, veinlets, nests, and impregnations in the host rocks. The ore grade is variable, and the chemical compositions of the ores are in the range of 1.2-2.5 wt% Sb, 0.8-1.3 wt% As, and 1.8-2.0 wt% S (Koděra et al. 1990).

The natural oxidation zone of the deposit was poorly developed and secondary minerals (i.e., minerals that were formed by natural oxidation of the ores) are relatively rare. Andráš and Chovanec (1985) identified stibiconite, cervantite, valentinite, and kermesite as secondary minerals. Polák (1983) described a rare occurrence of chapmanite $[Fe_2Sb(SiO_4)_2(OH)]$ in the oxidation zone.

Exploitation of the pyrite-pyrrhotite mineralization dates back to the late 18th century and flourished between 1850 and 1896. The hydrothermal Sb mineralization was mined at the Pezinok deposit between 1790 and 1992, with its most intensive period in 1940. A flotation processing plant operated since 1906. The ore was ground to a particle size of 40–90 μ m and Sb sulfides were partially extracted in the flotation process. A significant fraction of the Sb sulfides and most of the Sb oxides were lost to the waste (Grexová 1991). The flotation reagents used were lead nitrate, potassium ethyl xantogenate, 2-ethyl hexanol, petroleum, sodium carbonate, and sodium cyanide. The pH of the flotation pulp ranged from 6.5–8.0. The generated waste was deposited in two tailing impoundments whose geographical coordinates are given in Table 1.

The impoundments are located at the mouth of the Hrubá dolina valley, ~ 250 m above the sea level. The average annual temperature is 9 °C and the average annual precipitation is 800–1150 mm per year (150–200 mm in winter, 200–250 mm in spring, 250–400 mm in summer, and 200–300 mm in fall). The maximum snow depth is 25–50 cm and the snow-cover period lasts for 50–80 days.

MATERIALS AND METHODS

The sandy-silty material from the tailing impoundments and the underlying alluvial sediments were sampled in three boreholes PK-6, PK-7, and PK-8 and in outcrops in the steep side slopes (PE-2, PE-3, and PE-6) of the impoundments (Fig. 1). The material was recovered, sealed in plastic bags, transported to the laboratory (~1 h drive) and stored in a refrigerator. The particle density (i.e., density of the solid fraction) of the samples was measured by an air-comparison pycnometer. The overall density of the samples was estimated by simple pressing of the powdery samples into cylinders of known volume and mass followed by weighing the cylinders. The difference between the two density values is related to the power volume of the material.

For bulk chemical analyses, an aliquot of each sample was dried overnight at 105 °C, ground in an agate mortar to grain size of <50 μ m, weighed, and digested in a microwave in an aqua regia solution. The solutions were separated from the residua by filtering and were analyzed, after appropriate dilution, for Fe, As, and Sb by flame atomic absorption spectrometry (AAS), using an AAS vario 6 (Analytik Jena). The residua consisted of quartz with a minor amount of graphite, as shown by X-ray diffraction analyses.

The X-ray diffraction (XRD) experiments were carried out with a Bruker D8 Advance diffractometer, employing $CuK\alpha$ radiation, graphite secondary-radiation monochromator, and a scintillation detector.

The heavy fractions of the samples were concentrated by panning in water or ethanol. Selected heavy-grain concentrates were prepared for further study in the form of standard thin and polished grain mounts, for inspection in transmitted and reflected polarized light, respectively. Samples of interest were later prepared for micro-X-ray diffraction experiments as special thin grain mounts using epoxy that could be detached easily from the supporting glass.

Chemical compositions of the individual grains were determined with a Cameca

 TABLE 1.
 The geographic coordinates and the As, Sb, and Fe budget of the two impoundments in Pezinok

	Upper impoundment	Lower impoundment
Latitude (N)	48.320904	48.318678
Longitude (E)	17.235489	17.237549
Total As (tonnes)	910	4830
Total Sb (tonnes)	780	5580
Total Fe (tonnes)	9725	40 380



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FIGURE 1. An aerial photograph of the studied area shows the two studied impoundments, the former ore-processing plant, and the sampling locations for this study.

SX100 electron microprobe (Freiburg, Prague, Bratislava) in wavelength-dispersive mode under the operating conditions of 15 kV, 20 nA, and a beam diameter of 5 μ m. The following lines, standards, and detector crystals were used for the analyzed elements: As (*La*, GaAs, TAP), Sb (*La*, Sb, PET), Ca (*Ka*, wollastonite, PET), S (*Ka*, SrSO₄, PET), Al (*Ka*, corundum, TAP), Mn (*Ka*, Mn, LIF), Fe (*Ka*, hematite, LIF), Si (*Ka*, wollastonite, PET). The counting time on each peak was 20 s, on background 10 s (20 s for Sb).

The micro-X-ray diffraction (μ -XRD) and micro-X-ray absorption spectroscopy (μ -XAS) data were collected at the beamline of the Synchrotron Radiation Laboratory for Environmental Studies (SUL-X, Angströmquelle Karlsruhe, Germany) in the synchrotron radiation source ANKA. A silicon (111) crystal pair with a fixed beam exit was used as a monochromator. The X-ray beam was aligned to an intermediate focus, and then collimated by slits located at a distance of the intermediate focus to about 100 × 100 μ m and subsequently focused with a Kirkpatrick-Baez mirror pair to about 50 × 50 μ m at the sample position.

The μ -XRD data were acquired in transmission mode with a Photonic Science CCD detector XDI VHR-2 150. The samples were thin grain mounts in epoxy detached from the supporting glass. For the experiments, the beamline was operated at a constant energy of 14 keV ($\lambda = 0.886$ Å). Powdered Si was used as the calibrant to verify the wavelength and to refine the sample-to-detector distance. The images were integrated with the program Fit2D (Hammersley et al. 1996) and the 1D XRD patterns were further used for Rietveld refinement with the program GSAS (Larson and von Dreele 1994) after a background subtraction.

The μ -XAS spectra at the As *K* edge were measured in fluorescence mode in energy steps of 5 eV in the region from -150 to -50 eV relative to the absorption edge, of 2 eV in the region from -50 to -20 eV, of 0.5 eV from -20 to +20 eV, and with a *k* step of 0.05 from +20 to +400 eV (about *k* = 10). The intensity of the primary beam was measured by an ionization chamber. Fluorescence intensities were collected with a 7 element Si(Li) solid state detector with the energy window set to the AsK α line. Data were dead time-corrected, summed up for all seven channels and divided by the input intensity, which was measured in an ionization chamber prior to the sample analysis. The collected data were processed by ATHENA (Ravel and Newville 2005). Selected grains were extracted from the thin grain mounts, mounted on molybdenum grids, and thinned to electron transparency by argon-ion bombardment of 4.5 kV acceleration voltage using a Gatan DuoMill machine. Transmission electron microscopy (TEM) studies were performed on a LEO 922 Omega microscope using a LaB₆ cathode and 200 kV accelerating voltage. The microscope is equipped with a high-resolution objective lens and a ThermoNoran EDX-detector.

DNA was extracted from selected samples with the UltraClean Soil DNA Kit from MoBio Laboratories (Carlsbad, U.S.A.) according to the manufacturer's instructions. 16S rRNA gene sequences were amplified from the extracted DNA via PCR using primers specific for bacterial (27F and 1525R, Rainey et al. 1992) or archaeal [21F and 958R; Bano et al. (2004)] sequences. The following thermal cycling program was applied: 95 °C for 30 s, followed by 30 cycles of 95 °C for 30 s, 44 °C for 30 s, 72 °C for 1.30 min and a final extension step at 72 °C for 5 min. Amplified DNA was loaded on an agarose gel for amplicon size verification and thereafter cloned using the Zero Blunt TOPO PCR Cloning Kit from Invitrogen (Karlsruhe, Germany) according to the manufacturer's instructions. From each sample, 48 clones were selected. For restriction fragment length polymorphism (RFLP) analysis, the insert of the vector was amplified via polymerase chain reaction (PCR) with primers specific for the vector. The PCR product was then digested with the restriction enzyme BfuCI at 37 °C for 2 h. The digested products were loaded on a 1.5% agarose gel. Cloned 16S rRNA gene inserts were sequenced at GATC (Konstanz, Germany). Identification of 16S rRNA gene sequences and similarity comparisons were performed using the Ribosomal Database Project (RDP) (http://rdp.cme.msu.edu) and the blast program of the National Center for Biotechnology Information (NCBI) (http://www.ncbi.nlm.nih.gov).

RESULTS

Sediments of the impoundments

Since 1992, the two tailings impoundments in Pezinok were gradually covered by 1.5-4.5 m of overburden of industrial waste (soil mixed with blocks of concrete). The profile of the tailings consists of an oxidation zone located directly below the industrial waste, an inactive zone with tailings with little or no signs of oxidation, and an oxidation zone located at the bottom of the impoundments. Although each successive layer of the tailings was exposed to the atmosphere for a certain time, the oxidation processes were too slow to alter them during the short exposure. Therefore, we assume that the top 60-80 cm thick oxidation zone has most likely developed over the last 18 years since the mine operation ceased. Occasional very thin reddish layers within the inactive zone may represent intermittent breaks in the mine operation when the uppermost tailing layer was exposed to the atmosphere for a longer time. The ~100 cm thick oxidation zone at the bottom of the impoundments is driven by water that flows along the base of the impoundments. The tailings lie directly on alluvial sediments. The pH of the aqueous solutions sampled in the boreholes or those discharged from the impoundments is 7.0 ± 0.6 (Majzlan et al. 2007) despite the oxidation and decomposition of the sulfides. The acidity generated by the decomposing sulfides is neutralized by abundant carbonates (calcite and dolomite) within the ores. The impoundment material contains, on average, 3.9 wt% carbonates. The impoundments in Pezinok are therefore specific because they hold neutral mine drainage (NMD). The occurrence of NMD is less common than acid mine drainage (AMD) but not unique to Pezinok (cf. Heikkinen et al. 2009; Lindsay et al. 2009).

In the downstream direction, the impoundments discharge voluminous masses of hydrous ferric oxides (HFO), locally with extremely high As_2O_5 and Sb_2O_5 concentrations of 28.3 and 2.7 wt%, respectively (Fig. 2). The As-rich HFO was investigated previously by Majzlan et al. (2007).

On average, the tailings contain $47.7 \pm 8.0 (1\sigma)$ g Fe/kg, $6.6 \pm$

3.0 g Sb/kg, and 6.0 ± 2.1 g As/kg (average of 118 analyses). In an extensive estimate of the element budget of the impoundments after the mine shut down, Pomorský et al. (2002) determined that the tailings contain 5.8 g Sb/kg, 5.9 g As/kg, and 1.12 g Au/t. Iron dominates in all tailings samples (Fig. 2). The Sb/As ratios concentrate in the interval between 0.5 and 2.0 (Fig. 3). Upon transition from the tailings material into the underlying alluvial sediments, the As and Sb concentration decreases sharply but Fe concentration diminishes only slightly. There are occasional thin layers within the tailings with little or no As and Sb; they may represent attempts to cover the tailing impoundments with soil during intermittent breaks in the mine operation. We have integrated our analytical results to estimate the total load of the metalloids in the two impoundments. The area of the impound-



FIGURE 2. A triangular plot of the chemical compositions of the tailings (circles) and the ochres (HFO, diamonds) discharged from the impoundments (bulk measurements by atomic absorption spectrometry).



FIGURE 3. The distribution of the Sb/As ratios in the tailings (bulk measurements by atomic absorption spectrometry).

ments was estimated from air photographs and the calculated volume for each layer was converted to mass using the measured bulk density (Table 1). The average bulk density is $1.56 \pm 0.16 (1\sigma)$ g/cm³, while the average particle density is $2.90 \pm 0.20 (1\sigma)$ g/cm³. The porosity of the tailings is $45 \pm 4 (1\sigma)$ %, as calculated from the bulk and particle density. The total As, Sb, and Fe contents of the impoundments are listed in Table 1. The errors in these values are dominated by the analytical error in the AAS and the lateral heterogeneity of the tailing sediments. A conservative estimate of the uncertainty of the total As, Sb, and Fe values (Table 1) is 10%.

Mineralogy and chemistry of the tailings

The primary minerals identified in the tailings are well known from previous mineralogical studies (Chovan et al. 1992). Our X-ray diffraction patterns showed that the tailings are dominated by quartz, plagioclase, actinolite, illite, calcite, dolomite, and pyrite. Among the primary ore minerals in the tailings, pyrite and arsenopyrite prevailed directly after flotation (Fig. 4) and do so until now. Stibnite was the major ore mineral and was targeted by the flotation separation but, owing to the fine-grained nature of the ores, a significant fraction of stibnite escaped into the tailings (Fig. 4; Grexová 1991). Stibnite is essentially absent in the tailings today, most likely because of its rapid weathering. Berthierite and gudmundite, albeit less common than stibnite in the ores, are found sporadically in the tailings. Primary Sb oxides and sulfoxides (valentinite and kermesite) were rare in the ores and we did not find them in the tailings. EMP analyses of these phases (Bukovina 2007) show that they are devoid of Fe and Ca and this criterion can be used to distinguish them, if necessary, from the weathering products in the impoundments.



FIGURE 4. Mineral compositions of the flotation feed (gray circles), concentrate (white squares), and tailings (white diamonds) in August 1990. Abbreviations: py = pyrite, asp = arsenopyrite, sbt = stibnite, berth = berthierite. Stibnite and berthierite were not distinguished because their optical properties are very similar. Data from Grexová (1991).

The secondary minerals were uncommon and we assume that they are present in the tailings in trace amounts. Of greatest interest in this study were the tertiary minerals, that is, minerals which formed by the oxidation of the material directly in the tailing impoundments.

Electron microprobe analyses. The tertiary minerals are found in the form of rims on the primary ore minerals (Figs. 5–6) and as individual loose grains with no relics of the primary ores (Fig. 7). These two modes of occurrence will be hereafter referred to as rims and grains.

The chemistry of the rims is strongly influenced by the primary ore mineral. The rims on arsenopyrite (red in Fig. 8) are, in general, the richest in As (see rims PK7-A, PK7-M, PK8-C in Table 2). In our samples, the lower limit of the Fe/As (wt/wt%) ratio is 1.5 (Fig. 8). Most of the analyzed rims on arsenopyrite show the Fe/As (wt/wt%) ratio varying between 1.5 and 2.5. Interestingly, the As-richest HFO that is discharged from the impoundment has an Fe/As ratio (wt/wt%) of 1.9, in the cluster of the analyses of the arsenopyrite rims. The Fe/As value of 1.5 seems to be a saturation level beyond which the HFO cannot accept any additional As. It is also interesting to note that the Fe/As ratio in arsenopyrite is ~0.75. This means that even the As-richest rims on arsenopyrite are significantly depleted in As with respect to the primary ore mineral. Some portions of the rims, especially the external rims, on arsenopyrite may be extremely Sb-rich (see Figs. 5-8). In this case, Sb is most likely incorporated into the rims from aqueous solutions and the rims may also serve as nucleation substrate for iron oxides with elevated As and Sb contents.

The rims on pyrite usually have less As and Sb than those on arsenopyrite (see rims PK7-H, PK8-B, PK8-C in Table 2) but the maximum concentrations of As_2O_5 and Sb_2O_5 can reach 16.0 and 13.2 wt%, respectively, corresponding to the lowest Fe/As (wt/wt%) ratio of 2.9. Therefore, the rims on pyrite may be enriched to a large extent with As and Sb (Fig. 6) although these elements are found in this primary ore mineral only in trace amounts. The rims on gudmundite (e.g., PK8-D, Table 2) and berthierite are rich in Sb as well as As. The small number of analyses of these rims reflects the fact that gudmundite and berthierite are rare minerals.

The grains may be a product of a complete replacement of the ores or they may have precipitated from the solutions that circulated through the impoundments. An example of the former are probably the porous Sb oxides (Fig. 7c). We suspect that they are the replacement products of stibnite grains although unambiguous textural evidence is missing. On the other hand, the compact grains with zonal textures (Fig. 7) probably precipitated directly from aqueous solutions. In many cases, they contain an appreciable amount of As, although never as much as the rims on arsenopyrite. The limiting Fe/As ratio for the grains (Fig. 8) lies between 3.0 and 3.5. Their chemical compositions span the entire range from almost pure iron oxide to almost pure antimony oxide and the EMP analyses alone indicate that Fe and Sb can be mixed in any ratio in the grains. To elucidate this capability, we investigated a small number of grains by advanced micro-techniques.

An interesting correlation in the EMP analyses is the distribution of calcium and magnesium in the weathering products. Calcium concentrations are highest in the porous, almost pure Sb oxides (Fig. 8). Furthermore, calcium is found especially in those products which are rich in As (Fig. 8). Apart from the Sb oxides, the high Ca concentrations were measured in the rims on arsenopyrite and in the As-rich iron oxide grains. A similar trend can be seen in Mg that correlates relatively strongly with calcium (Fig. 9), but is less abundant by a factor of ~10. Enhanced co-adsorption of Ca and Mg in the presence of phosphate on goethite was described by Rietra et al. (2001) and Stachowicz et al. (2008). Because of the chemical similarity of phosphate and arsenate, they predicted that a similar effect should be observed for arsenate. This prediction was confirmed by Wilkie and Hering (1996) who observed that the adsorption of As(V) was significantly enhanced by Ca²⁺ and slightly suppressed by sulfate. Voegelin et al. (2010) suggested that Ca also influences the local coordination of As in Fe-oxide precipitates, either directly or indirectly. They explained the enhancement of PO_4^{3-} or AsO₄³⁻ adsorption in the presence of Ca or Mg by an electrostatic effect, where the divalent ion bridges the negatively charged Feoxide particles with adsorbed phosphate or arsenate. Our data further corroborate the enhanced co-adsorption of Ca and Mg in the presence of arsenate in a natural system.

X-ray absorption spectroscopy at the As K edge. The oxidation state of As in the rims and grains was probed by μ -XAS experiments on the As K-edge. All X-ray absorption near-edge structure (XANES) spectra from the grains, irrespective of their chemical composition, compare well with the standards with As⁵⁺. The rims are usually only a few micrometers thick. The spectra, collected with a beam of ~50 µm size, are contaminated by the signal from the primary ore sulfide, either pyrite or arsenopyrite. In both of these minerals, As is reduced (that is, As⁻), as expected and as seen in their spectra. The spectra from rims represent a mixture of reduced and pentavalent As. No evidence of As³⁺ was found, either in the rims or the grains.

Another insight into the speciation and element association is provided by micro-extended X-ray absorption fine-structure (μ -EXAFS) spectra. The spectra were collected at the As K edge in Sb-poor or Sb-rich grains. The investigated grains, in contrast to the rims, are larger than 100 μ m, and therefore the spatial beam resolution of 50 µm was no problem for the measurements. Irrespective of the Sb concentration, the spectra are essentially identical (Fig. 10). In addition, the μ -EXAFS spectra are very similar to the bulk EXAFS spectra from the As-rich HFO (Majzlan et al. 2007). The similarity of the µ-EXAFS spectra and their resemblance to the bulk EXAFS spectra suggests that As retains its affinity for Fe even in grains that are rich in Sb and depleted in Fe. This tendency of As to associate preferentially with Fe may be a reason why the Sb-rich grains contain at least some As (Fig. 8) and why there is a negative correlation between Sb and As in the rims (Fig. 6).

X-ray microdiffraction. The μ -XRD analyses were carried out only on the grains (~100 grains analyzed). The rims, usually a few micrometers thick, were not investigated because the beam size was larger, ~50 µm, and most of the signal originated from the primary ore mineral. To evaluate the μ -XRD data sets, the 2D Debye-Scherrer rings were integrated and the resulting 1D patterns were analyzed by a full-profile Rietveld refinement. In this procedure, it was difficult to subtract the background



FIGURE 5. Rims on an arsenopyrite crystal, a backscattered electron (BSE) image and the corresponding element distribution maps. Representative chemical analyses on the rims on arsenopyrite are given in Table 2.



FIGURE 6. Rims on a pyrite crystal, a backscattered electron (BSE) image and the corresponding element distribution maps. Representative chemical analyses on the rims on pyrite are given in Table 2.

quantitatively. The background arises mainly from scattering from the underlying epoxy. Because of the varying thickness of this component, we were able to construct the background only by interpolating between points located in the angular regions without peaks. In this way, the information about X-ray amorphous compounds in the sample was lost. Some artifacts remained even when using this procedure, especially at ~13 and $20 \ ^2\Theta$ (Fig. 11). These artifacts then interfered with the Rietveld analyses and were responsible for the poor match between the measured and calculated patterns in these angular regions.

The μ -XRD experiments show that the grains can be subdivided into three large groups. The grains rich in Fe with low As

and low to moderate Sb concentration (e.g., grain PK6-B, Table 2) diffract well and the diffraction peaks can be indexed with the orthorhombic unit cell of goethite, α -FeOOH (Fig. 11a). The diffraction rings of goethite are continuous, suggesting that the goethite particles are very small. A steady companion in many grains is quartz, which was not seen in an optical microscope or an electron microprobe. In many of these grains, another minor phase, most likely dolomite, was detected.

The grains in which As prevails over Sb (e.g., grain PK6-G, Table 2) are X-ray amorphous. Only quartz peaks are occasionally present. The rings that correspond to these peaks are continuous but narrow, suggesting that many well-ordered and



FIGURE 7. (a) A grain composed of goethite and quartz (grain PK6-B, see Table 2 for the chemical composition); (b) grain made of poorly crystalline tripuhyite (PK6-D); (c) two grains; the porous one on the left probably originated by in situ transformation of primary Sb sulfide, and the compact and zoned one on the right probably precipitated from aqueous solutions. The chemical composition of the compact grain (PK6-Nb) is given in Table 2.

	Fe ₂ O ₃	As ₂ O ₅	Sb₂O₅	CaO	MnO ₂	SO₃	SiO ₂	AI_2O_3	Σ
Grains									
Borehole-grain ID	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)	mean(1σ)
Note (n)	min-max	min-max	min-max	min-max	min-max	min-max	min-max	min-max	min-max
PK6-A (4)	80.22(1.67)	0.05(0.04)	1.82(0.30)	0.41(0.03)	0.28(0.03)	0.39(0.04)	4.61(0.43)	1.50(1.81)	89.29(0.90)
	77.76-81.31	0-0.08	1.52-2.24	0.37-0.43	0.24-0.31	0.36-0.45	4.28-5.21	0.47-4.21	88.46-90.57
PK6-B (7)	65.93(5.10)	2.95(1.01)	12.79(3.93)	1.20(0.27)	0.31(0.12)	0.74(0.39)	2.1(0.27)	3.83(0.48)	89.84(0.96)
	59.60-75.76	1.00-3.98	7.84-19.25	0.65-1.43	0.12-0.48	0.16-1.31	1.78-2.48	3.02-4.57	88.55-91.06
PK6-D (7)	37.28(3.27)	0.59(0.05)	51.46(3.71)	1.05(0.05)	0.18(0.04)	0.22(0.04)	1.15(0.10)	3.39(0.06)	95.32(0.53)
	33.57-43.36	0.50-0.65	44.51-55.5	1.00-1.15	0.14-0.23	0.15-0.28	0.99-1.30	3.32-3.52	94.57-96.15
PK6-Nb	64.25(3.95)	7.60(0.22)	14.52(2.19)	2.12(0.10)	0.75(0.03)	1.79(2.58)	0.33(0.08)	2.36(1.09)	93.71(1.62)
Fe-rich (4)	59.42-68.49	7.41-7.86	11.88-17.10	2.03-2.25	0.71-0.78	0.41-5.65	0.21-0.39	0.78-3.20	91.42-95.10
PK6-Nb	33.98(6.20)	7.82(2.70)	43.40(8.25)	2.77(0.81)	0.62(0.14)	0.25(0.13)	1.76(2.19)	2.81(2.60)	93.40(6.01)
Sb rich (8)	25.84-42.96	4.33-10.79	25.14-51.17	1.84-3.78	0.37-0.80	0.17-0.57	0.28-5.86	0.79-6.85	79.74–98.48
PK6-Nc	80.46(2.83)	0.05(0.01)	0.17(0.01)	0.15(0.08)	1.53(1.60)	0.07(0.03)	3.99(0.63)	0.03(0.04)	86.45(1.81)
oxide (3)	77.19-82.23	0.04-0.05	0.16-0.18	0.09-0.24	0.39-3.36	0.04-0.10	3.27-4.42	0.01-0.08	84.39-87.76
PK6-Nc	59.18	0.00	0.06	1.16	7.01	0.00	0.03	0.01	67.44
carbonate (1)									
PK6-G (9)	63.50(5.52)	13.13(2.14)	6.36(1.95)	2.51(0.40)	0.40(0.10)	1.42(0.15)	0.80(0.08)	1.36(0.27)	89.48(2.88)
	55.8-74.23	7.70–14.52	2.23-8.33	1.54-2.84	0.19-0.58	1.20-1.72	0.70-0.90	0.64-1.53	84.01-94.73
Rims									
Borehole-rim ID									
Parent sulfide (n)									
PK7-H	66.76(5.01)	1.97(1.41)	7.21(1.68)	2.15(0.25)	0.15(0.09)	3.53(2.86)	1.2(0.28)	0.07(0.10)	83.03(4.92)
pyrite (9)	57.47–71.97	0.21-4.64	4.24-9.13	1.76–2.45	0.08-0.34	1.60-10.7	0.82-1.69	0.01-0.32	77.14-88.46
PK8-B	62.81(3.53)	9.43(4.18)	5.62(1.60)	1.39(0.09)	0.07(0.03)	3.34(0.60)	0.61(0.39)	0.17(0.12)	83.44(4.28)
pyrite (3)	60.20-66.83	4.98-13.28	3.82-6.87	1.30–1.48	0.04-0.10	2.77-3.97	0.38-1.06	0.09-0.31	78.64-86.87
PK8-C	71.28(2.38)	0.47(0.21)	4.68(0.20)	0.86(0.25)	0.06(0.04)	9.34(1.67)	0.71(0.13)	0.07(0.03)	87.45(0.98)
pyrite (4)	69.19–74.55	0.19–0.67	4.44-4.91	0.55-1.16	0.02-0.11	7.76–11.66	0.52-0.78	0.04-0.10	86.52-88.66
PK7-A	42.05(3.60)	22.66(3.92)	7.11(3.59)	3.95(0.46)	0.06(0.08)	0.61(0.34)	1.19(0.91)	0.27(0.46)	77.90(7.56)
arsenopyrite (12)	36.21-48.55	18.05-32.11	3.60-14.78	3.33-4.80	0.00-0.31	0.32-1.40	0.35-3.38	0.03-1.71	67.10-88.69
PK7-M	44.48(2.2)	23.32(2.02)	6.22(2.35)	4.29(0.47)	0.04(0.05)	0.63(0.22)	0.73(0.22)	0.12(0.10)	79.85(3.92)
arsenopyrite (22)	40.88-49.38	18.84–25.92	2.53-12.06	3.55-5.34	0.00-0.22	0.26-1.12	0.28-1.21	0.00-0.51	71.64-87.15
PK8-C	43.30(2.92)	27.60(4.38)	3.33(1.03)	3.42(0.57)	0.05(0.02)	1.56(0.82)	0.34(0.13)	0.78(0.54)	80.38(3.66)
arsenopyrite (5)	39.25-46.73	24.33-35.22	1.59–4.18	3.00-4.35	0.02-0.06	0.81-2.81	0.11-0.45	0.14-1.43	75.76-84.00
PK8-D	42.51(2.43)	11.38(1.32)	16.38(3.05)	2.99(0.28)	0.03(0.01)	8.11(3.85)	0.99(0.44)	0.43(0.36)	82.82(6.82)
gudmundite (12)	37.63-45.63	9.22-13.02	11.00-21.71	2.50-3.62	0.01-0.05	2.69–12.91	0.55–1.99	0.13-1.02	67.79–90.23
Notes: All data in wt	%. <i>n</i> is the num	ber of analyses	averaged. The m	neasured eleme	ents were recalc	ulated to oxides	with an assume	ed oxidation sta	te; these may no
pe valid in all cases									

 TABLE 2.
 Representative EMP analyses of the grains and rims (from more than 800 analyses) from the impoundments in Pezinok



FIGURE 8. A triangular plot of the chemical compositions of the rims and grains in the tailings (circles, electron microprobe analyses) and the ochres (HFO, diamonds) discharged from the impoundments (bulk measurements by atomic absorption spectrometry). The symbol size is scaled to the CaO concentration. Red circles = rims on arsenopyrite; yellow circles = rims on pyrite; orange circles = rims on gudmundite; blue circles = rims on berthierite; green circles = grains; orange diamonds = discharged ochres. The lines represent constant Fe/As (wt/wt%) ratios.



FIGURE 9. Concentrations of CaO and MgO in spot EMP analyses. Apart from a few outliers, the two oxides show good correlation.

small quartz crystallites are present.

The grains, which contain a significant amount of Sb in addition to Fe (e.g., grain PK6-D; Table 2; Fig. 7), are poorly crystalline and the broad peaks can be indexed with the unit cell of tripuhyite, FeSbO₄ (Fig. 11b). The tripuhyite rings are broad and continuous. We were not able to model the peak shape satisfactorily, resulting in a relatively poor match of the measured and calculated patterns (Fig. 11). Occasionally, quartz or dolomite may be present. Tripuhyite is a relatively uncommon mineral present in weathering zones of Sb deposits (Shlain et al. 1971; Klempert et al. 1971; Shulikovskaya et al. 1976; Blokhina 1986;



FIGURE 10. Extended X-ray absorption fine-structure (EXAFS) spectra at the As K edge from two grains: grain PK6-B with less Sb (black solid curve) and grain PK6-D with more Sb (gray dashed curve). The chemical compositions of the grains are listed in Table 2; the backscattered electron photographs are shown in Figure 7.



FIGURE 11. X-ray diffraction patterns of (**a**) goethite+quartz, (**b**) tripuhyite, integrated from the 2D Debye-Scherrer rings (crosses) with the results of Rietveld refinement (calculated curve = solid line). The ticks below the patterns show the calculated positions of the XRD peaks for the phases present. The pattern of tripuhyite was refined with the structural model of Berlepsch et al. (2003). The single unindexed sharp peak at d = 2.88 Å in the panel (**b**) belongs to dolomite.

Sergeev et al. 1993; Szakall et al. 2000). In some instances, it is abundant and has been proposed as a guide in prospecting for Sb deposits (Blokhina 1986). Tripuhyite is accompanied



FIGURE 12. The 2D X-ray diffraction pattern showing the spotty nature of the siderite rings and the continuous goethite rings. The inset shows a BSE image of the analyzed grain (grain PK6-Nc, see Table 2 for its composition). The darker gray small grains are siderite crystals, the lighter mass is goethite.

in these deposits by the more common secondary Sb minerals such as stibiconite, cervantite, and senarmontite, and is probably a weathering product of stibnite-pyrite ores or berthierite ores. It is also possible that this inconspicuous mineral is often overlooked or misidentified.

A rare mineral detected in the studied grains is siderite. This mineral was identified only in one grain by both the EMP analyses and μ -XRD (grain PK6-Nc; Table 2). Here it is intergrown with goethite (Fig. 12). In a few other diffraction patterns of the grains, only the peak at d = 2.8 Å was noted in the μ -XRD patterns; this peak may belong to siderite. The Debye-Scherrer rings of siderite are spotty as opposed to the continuous rings of goethite (Fig. 12). The many minute, randomly oriented siderite crystals are dispersed in the goethite matrix. This mode of occurrence differs from hydrothermal carbonates, which are usually coarse-grained and are dominated by the dolomite-ankerite compositions. Therefore, we conclude that the siderite detected by μ -XRD experiments belongs to the newly formed minerals in the impoundments.

Transmission electron microscopy. The minerals identified by the μ -XRD experiments were further examined by transmission electron microscopy. In agreement with μ -XRD, the grains with dominant Fe and low to moderate Sb contain mostly goethite. The lath-like crystals of goethite coalesce into larger aggregates of an overall size rarely exceeding 150 nm (Fig. 13a). The individual coherently diffracting domains must be significantly smaller as documented by almost continuous rings in the electron diffraction patterns. Spot energy-dispersive



FIGURE 13. TEM microphotographs of (**a**) a goethite aggregate in one of the Fe-rich grains (PK-6, grain A, see Table 2 for its composition); (**b**) an illite platelet embedded in the goethite aggregate (PK-6, grain A); (**c**) an aggregate of the goethite nanocrystals with the corresponding spacing of the lattice fringes; the inset shows the electron diffraction pattern (PK-6, grain D, see Table 2 for the chemical analyses of this grain); (**d**) an aggregate of tripuhyite nanocrystals with the corresponding spacing of the lattice fringes; the inset shows the electron diffraction pattern (PK-6, grain D, see Table 2 for the chemical analyses of this grain); (**d**) an aggregate of tripuhyite nanocrystals with the corresponding spacing of the lattice fringes; the inset shows the electron diffraction pattern (PK-6, grain D).

 TABLE 3.
 Description of the samples used for the microbiological determinations in this study

	•
Sample	Description and chemical composition
PE-1	Thick orange mud from a sedimentation trap below
	the upper impoundment
	~50 wt% Fe ₂ O ₃ , 20 wt% As ₂ O ₅ , 0.5 wt% Sb ₂ O ₅
PE-2, PE-3	Sandy-silty material from the side of the lower impoundment
	~5 wt% Fe, 0.6 wt% As, 0.6 wt% Sb
PE-6	Thick orange mud dripping from a drainage pipe from
	the lower impoundment
	~50 wt% Fe ₂ O ₃ , 25 wt% As ₂ O ₅ , 2.5 wt% Sb ₂ O ₅
Notes: The c	hemical compositions of the samples were taken from repeated he material taken from the sampling locations

analyses of these aggregates, acquired with the TEM, did not differ appreciably from the wavelength-dispersive electron microprobe analyses. The goethite mass appears to be chemically homogeneous. A mineral not identified by either EMP or μ -XRD is a sheet silicate found in the form of platelets up to 100 nm thick (Fig. 13b). The basal spacing of ~10 Å indicates that the mineral belongs to the illite group. Because the grain size is much bigger than for goethite and the crystallinity is rather good, these illite platelets are most likely detrital, produced during grinding of the ores. It is not clear whether they serve as nucleation sites for the Fe-As-Sb oxides or they are incorporated into these minerals accidentally.

The grains with high Fe and Sb content contain tripulyite and goethite. In these grains, the former mineral was identified by μ -XRD, but the latter was not. Goethite is found only in some areas as aggregates of randomly oriented domains up to ~10 nm in size (Fig. 13c). The orientation of the lattice fringes changes from one domain to the other. On the contrary, the domains of tripulyite (3–10 nm in size) (Fig. 13d) appear to have some common orientation as the lattice fringes change only by a small angle from one domain to the other.

Microbiology of the tailings. Four samples from the tailings and their discharge products (Fig. 1; Table 3) were analyzed with restriction fragment length polymorphism (RFLP) to assess the microbial diversity of the waste form. These experiments were conducted to estimate whether the physiology of the detected microbial species could influence the weathering kinetics of the primary minerals and hence could impact the formation of the tertiary minerals.

All samples contained a multitude of different microbial phyla (Table 4). Archaea were neither detectable using a standard primer set for the amplification of archaeal 16S rRNA genes nor using catalyzed reporter deposition fluorescence in situ microscopy (CARD-FISH) [probe: ARCH915, Stahl et al. (1991)]. Most of the bacterial species we identified via sequencing and subsequent alignment to genebank entries are similar to other bacteria that were detected in arsenic-polluted environments (Macur et al. 2001; Ellis et al. 2003; Cai et al. 2009). Bacteria evolved two different resistance strategies to survive in areas heavily contaminated by arsenic. Arsenate that is taken up by the cells due to its similarity to the phosphate ion is reduced intracellularly to arsenite and subsequently transported out of the cytoplasm (Rosen 2002; Mukhopadhyay et al. 2002). Under neutral or acidic pH, arsenite resembles the organic compound glycerol and therefore enters the cell via aquaglyceroporins. Especially in aerobic environments contaminated by arsenic, bacteria employ aerobic arsenite reductases as a defense mechanism (Silver and Phung 2005). Although arsenate is highly soluble, it precipitates with calcium or insoluble iron compounds. Hence, oxidation to the seemingly more bioavailable arsenate can be a resistance strategy in the presence of compounds on which arsenate absorbs. Several bacterial strains belonging to the Oxalobacteraceae are known to carry arsenic resistance system (ars)-genes for cytoplasmic arsenate reduction (Cai et al. 2009; Muller et al. 2007). We detected 16S rRNA gene sequences of members of the Oxalobacteraceae in high clone numbers in PE-2 (clones MKM18, 20, 24, 27) but also in PE-6 (clone MKM55). In contrast, Sphingomonadaceae are known for their capability to reduce arsenate or oxidize arsenite (Macur et al. 2001; Kinegam et al. 2008). Clones belonging to the Sphingomonadaceae were detected in sample PE-1 (clone MKM1). We observed that a high percentage of the collected 16S rRNA samples were most closely related to strictly aerobic heterotrophic bacteria, such as Sphingomonas (MKM1), Caulobacter (MKM28), or Janthinobacterium (MKM18, MKM27, MKM20, MKM24, MKM55) strains (Poindexter 1964; Gillis and De Ley 1992; Balkwill et al. 2006). However, with the exception of PE-2, clone libraries from all other sites contained sequences that were most closely related to 16S rRNA genes from Geobacter (PE-1: MKM2; PE-3: MKM33) or Rhodoferax (PE-6: MKM42) species that are known dissimilatory iron reducing bacteria (Finneran et al. 2003; Islam et al. 2005). This may imply that, due to metabolic oxygen consumption, dissimilatory iron reduction could take place near the top of the tailings. This finding is in line with the detection of siderite (FeCO₃) in the tailings material, since siderite is a secondary ferrous iron mineral formed by ironreducing organisms. Furthermore, we found signatures of organisms related to lithotrophic bacteria that can gain energy via an oxidation of reduced sulfur compounds such as Sulfuricurvum (PE-1: MKM4), Alkalilimnicola (PE-2: MKM19), and Acidithiobacillus strains (PE-2: MKM21), and organisms belonging to the Ectothiorhodospiraceae (PE-3: MKM30). This suggests a biotic sulfate and ferric iron production in the tailings (Robertson and Kuenen 1991; Pronk and Johnson 1992; Oremland et al. 2002; Kodama and Watanabe 2004). The similarity of the clone MKM21 to Acidithiobacillus ferrooxidans was surprising since Acidithiobacillus strains are acidophilic and therefore grow under low-pH conditions (Kuenen et al. 1992). If the signature MKM21 belongs to an acidophilic organism, then it is predicted that acidophilic areas exist in the mainly pH-neutral tailings. Such areas could be present only as local gradients on the decomposing sulfide grains. It should further be noted that 16S rRNA genes that cannot be assigned to known isolated bacteria were also frequently found. These sequences represented 23% of the total number of analyzed sequences in sample PE-6. So far, we cannot speculate on the ecological niche of these organisms found in the tailings.

CONCLUDING REMARKS

The spot EMP analyses, µ-XRD, and TEM results document the different behavior of As and Sb in the tailings. Arsenate significantly modifies the structure of iron oxides and inhibits their crystallization or transformation to crystalline phases. This phenomenon has been observed repeatedly in field or labora-

TABLE 4.	RFLP results c	obtained from the	samples PF-1	> 3 and 6
	IN LI ICAULAU			and u

Sample	e Phylogenetic	Clone type	Related organism or clone	Similarity score	Number of related group clones/
					total number
PE-1	α -Proteobacteria	MKM1 [HM047808]	Sphingomonas sp. [AB110635]]	1130	9/40 (22.5%)
		MKM14 [HM047826]	Gluconacetobacter liquefaciens [NR_026132	1463	1/40 (2.5%)
		MKM16 [HM047828]	Rhodobacter sp. [FM956479]	919	1/40 (2.5%)
	γ-Proteobacteria	MKM5 [HM047817]	Aquicella siphonis [NR_025764]]	1513	1/40 (2.5%)
		MKM12 [HM047824]	Proteinimicrobium ihbtica [AM746627	1275	1/40 (2.5%)
	δ-Proteobacteria	MKM2 [HM047809]	Geobacter sp. [EF527233]	1062	7/40 (17.5%)
	ε-Proteobacteria	MKM4 [HM047816]	Sulfuricurvum kujiense [AB080643]	1685	5/40 (12.5%)
	Firmicutes	MKM3 [HM047815] MKM9 [HM047821]	Erysipelothrix rhusiopathiae [AB055910]	1090–1286	6/40 (15%)
		MKM15 [HM047827]	Clostridium cellulolyticum [CP001348]	942	1/40 (2.5%)
	Bacteroidetes	MKM11 [HM047823]	Pedobacter insulae [EF100697]	1733	1/40 (2.5%)
		MKM7 [HM047819]	Bacteroidetes bacterium [AF550591]	1211	1/40 (2.5%)
		MKM13 [HM047825]	Parabacteroides gordonii [AB470345]	1147	1/40 (2.5%)
	Chlorobi	MKM8 [HM047820]	Ignavibacterium album [AB478415]	1225	1/40 (2.5%)
		MKM10* [HM047822]	Chlorobi bacterium [DQ676339]	1397	2/40 (5%)
	TM6	MKM6* [HM047818]	Uncultured bacterium [AY043958]	1306	2/40 (5%)
PE-2	α -Proteobacterium	MKM25 [HM047835]	Blastochloris sp. [AB250618]	1136	2/38 (5.2%)
	β-Proteobacteria (Oxalobacteraceae)	MKM18 [HM047814]		1245–1871	19/38 (50%)
		MKM27 [HM047837]	Janthinobacterium lividum [AB428446]		
		MKM20 [HM047830]			
		MKM24 [HM047834]		740	4.0 (2.0 (2.6 2.0 ())
	γ-Proteobacteria	MKM1/*[HM04/813]	Hydrocarboniphaga effusa [AY 363244]	/12	10/38 (26.3%)
		MKM19 [HM047829]	Aikaiiiimnicola enriicnii [CP000453]	1341	3/38 (7.8%)
	Firmicutos		Acialitiobacillus letrooxidaris [AJ459800]	1299	1/38 (2.6%)
	Nitrochico		Nitrospira marina [V926604]	1065	1/30 (2.0%)
	Verrucemicrobia	NIKIVIZO [[[]IVI047630]	Uncultured bactorium [EI502020]	1110	1/36 (2.0%)
DF-3	a-Proteobacteria	MKM22 [HM047833]	Caulobacter sp. [DQ337540]	1033	5/33 (2.0%)
I L-J	u-Hoteobacteria	MKM38 [HM047845]	Kaistia sp. [AM409363]	1376	1/33 (30%)
	B-Proteobacteria	MKM37 [HM047838]	Bacterium Ellin6067 [AY234719]	1445	2/33 (6 1%)
	procoducteria	MKM30 [HM047840]	Iron-oxidizing acidophile m1	1260	6/33 (18.2%)
	v-Proteobacteria	MKM29 [HM047839]	Shiaella flexneri [CP001383]	1748	1/33 (3%)
	1. Fotobbacteria	MKM31 [HM047843]	Legionella dresdeniensis [AM747393]	1543	2/33 (6.1%)
		MKM39 [HM047841]	Acinetobacter radioresistens [AY568493]	1864	2/33 (6.1%)
	δ-Proteobacteria	MKM33* [HM047847]	Geobacter sp. [CP001390]	639	6/33 (18%)
	Chloroflexi	MKM32 [HM047846]	Leptolinea tardivitalis [AB109438]	1225	1/33 (3%)
	Actinobacteria	MKM40 [HM047844]	Propionibacterium acnes [AE017283]	1770	1/33 (3%)
		MKM34 [HM047848]	Unknown Actinomycete [X68459]	1086	2/33 (6.1%)
		MKM35* [HM047849]	llumatobacter sp. sw-xj83[GQ302523]	1157	2/33 (6.1%)
	Planctomycetes	MKM41 [HM047842]	Planctomyces sp. [X81948]	1029	1/33 (3%)
	TM7	MKM36* [HM047850]	Uncultured bacterium [GU410601]	861	1/33 (3%)
PE-6	β-Proteobacteria	MKM42 [HM047811]	Rhodoferax ferrireducens [AM265401]	1149	3/30 (10%)
		MKM55 [HM047852]	Janthinobacterium sp. [GU244361]	1585	2/30 (6.7%)
		MKM45 [HM047855]	Methylibium sp. [FJ464985]	1208	1/30 (3.3%)
		MKM51* [HM047812]	Uncultured marine bacterium [FJ825812]	742	6/30 (20%)
	Actinobacteria	MKM50 [HM047864]	Planktophilia limnetica [FJ428831]	1399	1/30 (3.3%)
		MKM48 [HM047860]	Solirubrobacter soli [AB245334]	1052	2/30 (6.7%)
	Acidobacteria	MKM43 [HM047854]	Halophaga toetida [X77215]	1253	3/30 (10%)
	Verrucomicrobia	IVIKIVI53 [HM04/857]	Bacterium Ellin514 [AY960///]	996	2/30 (6./%)
	Chioroflexi		Bellillinea calaitistulae [AB243672]	1199	1/30 (3.3%)
	Planctomycetes		Pirellula sp. [X81947]	1297	1/30 (3.3%)
	Bacteroldetes		LUNDUCLEE SP. [FJ598048]	905 1 1047	1/30 (3.3%)
	OPTI	IVINIVI44^ [HIVIU4/853]	Uncultured candidate division OP11 bacterium [GU236005	154/	2/30 (6.7%)
	NIKP10	IVINIVI49" [HIVIU4/863]	Uncultured candidate division OPTT bacterium [EU266851	1220	2/30 (6./%)
			Uncultured candidate division TM6 bacterium [DO676273]	1320	1/20 (2.2%)
	Linclassified bacteria	MKMA7* [MM0A7050]	Uncultured bacterium [EE515472]	1204	1/30 (3.3%)
			oncurren bacterrunn [EF313473]	1370	1/ 30 (3.370)

Notes: Genebank numbers are given in square brackets. All MKM sequences were first aligned to the nucleotide collection using the blastn algorithm. Uncultured/ environmental sequences were excluded in the initial sequence search. Sequence alignments were repeated with uncultured/environmental sequences in the database if the highest similarity score to isolated bacteria was below 900. These MKM sequences are marked with an asterisk.

tory studies (Voegelin 2010 and references therein). Antimony, on the other hand, does not interfere with the crystallization of the iron oxides to such an extent. In the systems with low to moderate Sb concentration, goethite crystallizes. Simultaneous high concentrations of Fe and Sb lead to the formation of poorly crystalline tripuhyite. It is also possible that this inconspicuous mineral is often overlooked or misidentified. In the absence of Fe, antimony produces minerals with a distinctly higher concentration of Ca (Fig. 8).

The two tailing impoundments in Pezinok offer a possibility to study the mineralogical, geochemical, and microbiological aspects of iron, arsenic, and antimony cycling under oxidizing and neutral (with respect to pH) conditions. The primary ore minerals oxidize and decompose in two oxidation zones, at the top and the bottom of the impoundments. Observations in polarized light, electron microprobe, and the XAS data [including the XAS data presented by Majzlan et al. (2007)] indicate that the redox-active elements achieve their highest oxidation state rapidly. The acidity generated by the weathering of the sulfides is neutralized by the reaction with ubiquitous carbonates. The presence of Sb in the weathering rims on arsenopyrite (FeAsS), that of As in the rims on berthierite (FeSb₂S₄), and both As and Sb in the rims on pyrite (FeS₂) shows that both Sb and As are mobile and can be transported, at least over small distances, by the aqueous media. The formation of grains with zoned textures and widely variable chemical composition indicates that Fe is also mobile. Since Fe³⁺ is insoluble under circumneutral pH values, iron is probably brought by the aqueous solutions from the reduced inactive zone. Upon oxidation, the iron oxides adsorb or react with As and Sb and form various minerals. Another indication of the active redox processes is the occurrence of siderite and goethite in some of the analyzed grains.

Geochemically, As and Sb behave in quite different ways. Arsenic cannot be accommodated in the weathering products beyond an Fe/As ratio (wt/wt%) of ~1.5, at least in the samples studied here. Even the weathering rims on arsenopyrite, a mineral with an Fe/As ratio of 0.75, do not attain Fe/As ratios lower than 1.5. In the grains of the tertiary minerals, the Fe/As ratio is higher than 3.0. It seems that the capacity of iron oxides to accommodate As is exhausted and this element is carried out of the impoundments into the discharged hydrous ferric oxides. A similar limit for the incorporation of the tetrahedral phosphate anion into hydrous ferric oxide was reported by Thibault et al. (2009) where they described the phosphate-rich hydrous ferric oxide as a "solid-solution end-member." Although it is difficult to present the system phosphate (or arsenate)-hydrous ferric oxide as a true solid solution, the conclusions of a limiting ratio between Fe and tetrahedral anions seems to hold for both phosphate and arsenate.

Antimony, on the other hand, is largely retained in the impoundment. The grains of the tertiary minerals can accommodate any Fe/Sb ratio. These trends of As and Sb separation can be easily spotted also in a comparison of the chemical composition of the tailings and the ochreous HFO (Fig. 2). In the tailings, the concentrations of As and Sb are roughly comparable but in the discharged HFO, As clearly dominates. This conclusion also agrees with the findings of Flynn et al. (2003) who reported that "Sb is relatively unreactive and immobile" and co-contaminants, As and Cu in their case, were more mobile and dangerous to the environment. Similarly, Ettler et al. (2010) described soils polluted by Sb and As and consistently found that As is more mobile than Sb.

Another intriguing finding of this study is that even the most heavily contaminated samples are populated by diverse communities of microorganisms. Among our collection of 16S rRNA gene signatures, we find sequences that are most closely related to arsenic resistant aerobic heterotrophic species, as well as dissimilatory iron reducers, and sulfur oxidizers. The detection of sequences that are most closely related to typical obligatory anaerobic organisms like *Geobacter* species might imply that aerobic bacteria are highly metabolically active and hence consume oxygen within the surface of the tailings. This evidence for physiological activity of the bacterial community allows one to suggest that the microorganisms may play an important, if not dominant role in the mobilization or immobilization of the elements from the tailings. Almost a third of the 16S

rRNA genes found in the samples cannot be assigned to known and sequenced organisms, meaning that these extreme environments are inhabited by living forms that await to be discovered, isolated, and described.

This study also documents that a detailed mineralogical knowledge is necessary to describe a mobility and association of an element with minerals or materials present. Unless the weathering products are concentrated and inspected thoroughly, minerals like nanocrystalline tripuhyite will escape identification. Conclusions of sequential extraction studies (e.g., Gál et al. 2006) that Sb is associated with Fe oxides can be easily challenged. Antimony does associate with Fe but also forms distinct minerals, whose solubility in the extractants may vary widely as a function of the crystallinity and surface area of those minerals. Another aspect of antimony speciation in the environment is its redox activity (Mitsunobu et al. 2010), which has not been addressed here but should be kept in mind.

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