

MINERALOGY OF NEUTRAL MINE DRAINAGE IN THE TAILINGS OF SIDERITE-Cu ORES IN EASTERN SLOVAKIA

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ABSTRACT

This work presents the results of investigation of the primary minerals and their weathering products of two tailing ponds near the villages of Rudňany and Slovinky in eastern Slovakia. The tailings are near-neutral or slightly alkaline (pH = 7.2–8.8) because the acidity generated by the decomposition of the sulfides is efficiently neutralized by the abundant carbonate minerals. The most frequent primary gangue minerals are siderite, quartz, barite, and muscovite. The prevailing

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primary sulfide minerals in both tailing ponds are pyrite and chalcopyrite; less common are tetrahedrite and arsenopyrite. The most frequent secondary and tertiary (*i.e.*, formed in the tailings, not in the oxidation zone of the deposits) minerals at both localities are iron oxides, either goethite or poorly crystalline hydrous ferric oxide. Other minerals (cuprite, malachite, delafossite; identified by X-ray microdiffraction or Raman spectroscopy) are minor or rare and occur only in Slovinky. The iron oxide minerals are enriched in a suite of elements, including Cu, Si, Ca, Zn, As, Mg, and Mn. The transformations of the poorly crystalline hydrous ferric oxide to goethite and maturation of goethite is controlled by both high-valence tetrahedral cations (Si, As, P) and lower-valence octahedral cations (Cu), as shown by the measurements of the size of coherently diffracting domains in goethite and the chemical composition of goethite. The iron oxide minerals, by virtue of their adsorption capacity, prevent separate minerals of many metals and metalloids (Cu, Ca, As, Sb) from nucleating and growing, and therefore control the entire neutral mine drainage (NMD) system. Geochemical modeling of the discharged waters shows that all common Cu and ferric arsenate minerals are strongly undersaturated, confirming the central role of iron oxide phases in the NMD system.

Keywords: tailing ponds, goethite, weathering products, Cu-Fe deposits.

INTRODUCTION

Weathering of copper ores is usually associated with eye-catching and spectacular aggregates with hues of green and blue. Copper carbonates, sulfates, phosphates, and arsenates display their stunning colors and possess unique structures with topologies unlike those shown by other divalent cations. This difference is due to the strong Jahn-Teller distortion of the coordination polyhedra which host Cu^{2+} (see Burns & Hawthorne 1996). Iron sulfide ores, on the other hand, decompose to rusty masses of iron oxides. If the primary mineralization is dominated by iron sulfide minerals (pyrite, marcasite, pyrrhotite), acid mine drainage (AMD) ensues and contaminates underground and surface streams (*e.g.*, Plumlee *et al.* 1999, Nordstrom & Alpers 1999). In certain cases, however, the acidity generated by the decomposition of the sulfides can be efficiently compensated by the buffering capacity of carbonate minerals, and less commonly feldspars (*e.g.*, Cravotta *et al.* 1999, Sracek *et al.* 2011, Majzlan *et al.* 2011). This neutral mine drainage (NMD) does not negatively impact the living conditions of aquatic fauna through acidity, but still poses a danger because some metals or metalloids may be transported in a dissolved form even at near-neutral conditions. Interestingly, one such metal is copper, as the common copper carbonate and sulfate minerals precipitate at relatively high pH (*e.g.*, Zittlau *et al.* 2013). At strongly to mildly acidic conditions, the solubility of copper in sulfate-rich aqueous media is very high and chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) precipitates only if the activities of Cu^{2+} and sulfate reach formidable levels. Because of the incompatibility of Cu^{2+} and other cations (see above), Cu^{2+} is also not incorporated in the many ferric sulfate or ferric oxide minerals which form from AMD or NMD. Hence, Cu-rich NMD offers a unique geochemical and mineralogical window to the interplay between highly insoluble (at near-neutral pH) phases of Fe(III) and relatively mobile Cu(II). Studies of such systems may provide valuable evidence of the

mobility of copper and associated elements under conditions when weathering products are abundant but the aqueous phase remains enriched in a variety of potentially toxic metals and metalloids.

Metals and metalloids can be incorporated into structures of secondary and tertiary mineral phases or adsorbed on their surfaces in the form of outer- or inner-sphere complexes. The mode of association is an important factor in determining the risk of release of the potentially toxic elements into the adjacent water systems. Surface complexes can be released back to the pore solution if conditions such as pH, Eh, or temperature are changed. The incorporation of elements into structures of minerals leads to a long-term immobilization and can be reversed only if the entire volume of a mineral is dissolved or transformed (Mitsunobu *et al.* 2010). Ferrihydrite is a very common iron oxide mineral in natural settings (Jambor & Dutrizac 1998) and it can adsorb or incorporate a number of elements or molecules. The adsorption of tetrahedral ions, such as phosphate or arsenate, is strong and has been studied in a detail (Waychunas *et al.* 1993, Persson *et al.* 1996, among others). The octahedral ions, such as Sb^{5+} , can be incorporated into the disordered structure of ferrihydrite (Mitsunobu *et al.* 2010, Bolanz *et al.* 2013). The presence of tetrahedrally or octahedrally coordinated impurities can then hinder the transformation of ferrihydrite to well-crystallized iron oxide minerals, mostly goethite ($\alpha\text{-FeOOH}$) (*e.g.*, Bolanz *et al.* 2013). The fate of the incorporated or adsorbed elements during the transformation to goethite is not always clear.

The simple crystal structure of goethite has been shown to take up divalent Ni, Zn, Cu, and Cd, trivalent Cr, V, Mn, Ga, Co, and Sc, and tetravalent Pb and Ge cations under natural conditions (Stiers & Schwertmann 1985, Vandenberghe *et al.* 1986, Cornell & Giovanoli 1988, Fazey *et al.* 1991, Singh & Gilkes 1992, Vempati *et al.* 1995, Gasser *et al.* 1999, Manceau *et al.* 2000, Scheinost *et al.* 2001, Sileo *et al.* 2001, 2003, Singh *et al.* 2002, Trivedi *et al.* 2004, Alvarez *et al.* 2005). The incorporated

elements cause changes in the nucleation process and crystal growth, modify the lattice parameters, and influence crystal habits and reactivity (Alvarez *et al.* 2007).

This study is based on a detailed characterization of the weathering products in the tailing ponds from two deposits, Slovinky and Rudňany, in Slovakia using selected analytical methods: electron microprobe analysis (EMPA) and micro-X-ray diffraction (μ -XRD) including full-profile analysis. The goal of this study is to determine the distribution of metals and metalloids among the weathering phases and indirectly evaluate the immobilization and release potential for the toxic elements. We assess the influence of minor elements in the iron oxides on the transformation from poorly to well-crystallized phases. This work describes the mineral composition of the studied tailings, since a geochemical study of the tailings in Rudňany has already been published (Hiller *et al.* 2013) and a geochemical study of Slovinky is in preparation. pH values of both tailings vary from near-neutral to weakly alkaline due to neutralization of the acidic solutions by the abundant carbonates. pH values of the Rudňany tailings vary from 7.16 to 8.12 (Hiller *et al.* 2013), those of the Slovinky tailings from 7.54 to 8.7 (Tóth *et al.* 2013).

Part of the published geochemical information is re-used here to discuss the presence or absence of certain minerals in the tailings, based on modeling with the software suite PHREEQC. The observed mineralogy is compared to the expected mineral composition based on equilibrium thermodynamic predictions.

CHARACTERIZATION OF THE STUDIED FE-CU DEPOSITS

The Rudňany deposit is situated in the northern part of the Spišsko-Gemerské rudohorie Mountains, ~12 km east of the city of Spišská Nová Ves. The first written record of mining here dates back to 1332. The exploitation concentrated mainly on Fe and later on Cu and Ag ores. Since 1945, the Rudňany deposit has been an important producer of siderite ores, barite, and sulfide concentrate (Cu, Hg, Sb, Ag, and Bi). Between 1945 and 1982 the deposit produced 32.1 metric million tonnes of siderite-barite-tetrahedrite [(FeCO₃, BaSO₄, (Cu,Fe)₁₂Sb₄S₁₃)] ores (Cambel *et al.* 1985). Mining ceased in 1993 (Grecula *et al.* 1995), but barite is currently still extracted from the old tailing pond.

The Rudňany ore field is represented by the siderite-barite-sulfidic type of veins. Sulfide minerals are represented by tetrahedrite [schwazite, (Cu,Hg)₁₂Sb₄S₁₃], chalcopyrite (CuFeS₂), pyrite (FeS₂), with rare arsenopyrite (FeAsS), sphalerite (ZnS), and cinnabar (HgS). Common Fe-bearing minerals are siderite with up to 2.68 wt.% MnO and 6.66 wt.% MgO (Bernard 1961,

Rojkovič 1979, Cambel *et al.* 1985, Chovan *et al.* 1994) and hematite (Fe₂O₃). Most of the ore bodies are hosted by Carboniferous conglomerates, carbonaceous schists, mafic pyroclastics, and sandstones. The lowermost parts of the veins are located mostly in the Early Paleozoic phyllitic formation (chloritic-sericitic and graphitic slates, metabasalts) and the upper parts of the ore bodies usually terminate in the basal Permian conglomerates, sandstones, and slates (Grecula *et al.* 1995).

The flotation processing plant was in operation since 1963 and produced siderite, barite, and sulfide concentrate. The waste was deposited onto a tailings pond (Fig. 1a) in the village of Markušovce, and in 2005 the pond held 9,901,160 tonnes of mining waste (Jančura *et al.* 2005). Because the ores were mined in Rudňany, we will refer to this tailings pond as Rudňany and not Markušovce (note that Hiller *et al.* 2013 described the same tailings pond as Markušovce). The impoundment is located in front of the mouth of the Markušovská dolina valley to the valley of Rudniansky creek, 476 m above sea level. The length of the impoundment is approximately 1085 m and the width is in the range of 160–340 m. The surface area of the impoundment is 35 ha (Jančura *et al.* 2005). The tailings are separated from the carbonate bedrock by an impermeable clay layer at their base.

The Slovinky deposit is situated in the northern part of the Spišsko-Gemerské rudohorie Mountains, ~28 km east of the village of Rudňany. Medieval exploitation targeted predominantly Cu, later Au and Ag. In 1897, exploitation of Cu ores came to a halt and was replaced by mining of Fe ores until 1925. From then until 1993, the mine produced Cu, Au, and Ag concentrate (Grecula *et al.* 1995).

The siderite-quartz (FeCO₃-SiO₂) veins contain abundant sulfide and sulfosalt minerals such as chalcopyrite, tetrahedrite, arsenopyrite, and pyrite, and rarely galena (PbS), sphalerite, bornite (Cu₅FeS₄), bourmonite (CuPbSbS₃), jamesonite (FePb₄Sb₆S₁₄), tennantite [(Cu,Fe)₁₂As₄S₁₃], and stibnite (Sb₂S₃) (Regásek 1967a, 1967b). Siderite has elevated MgO content (Chovan *et al.* 1994, Piovarczy & Badárová 1987). The ore veins are hosted by Paleozoic green phyllites and metarhyolites (Grecula *et al.* 1995).

Mine waste was deposited into a tailing pond from 1967 to 1993. The pond (Fig. 1b) is located in the valley of Slovinský creek, 543 m above sea level, and it contains 4,700,000 tonnes of mine waste. The height of the dam is 113 m. Since 1993, 5–6 meters of slag has been deposited onto the tailings. The slag originated from the Kovohuty plant in the nearby village of Krompachy, where ores and materials from different sources were processed. Analyses of the slags document elevated contents of some elements (mainly Cu, Pb, Zn, Ni, Co, Cr, Ba, and W) (Šottník *et al.* 2011).

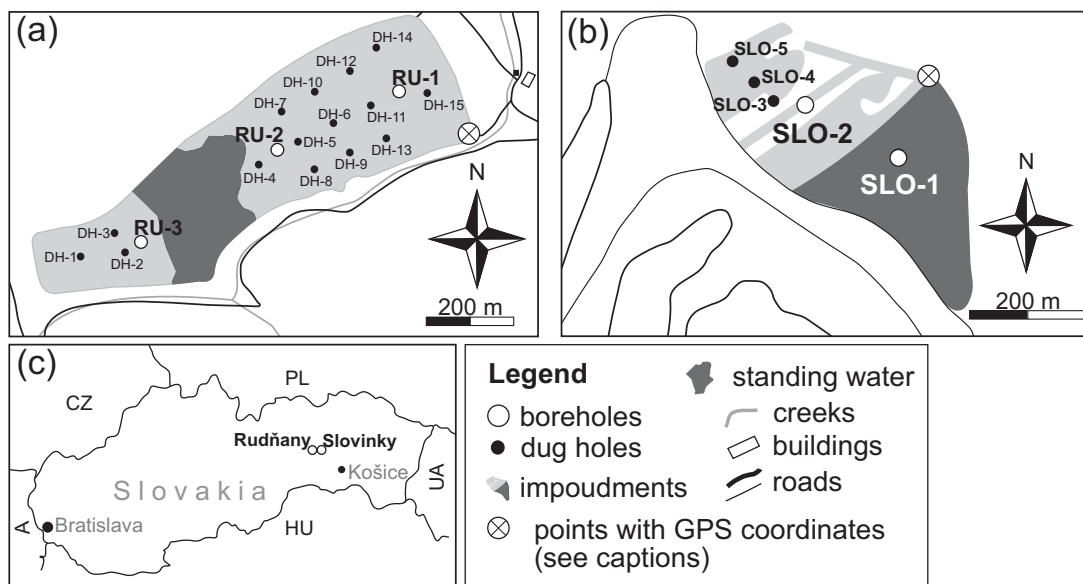


FIG. 1. Schematic maps of the studied tailings ponds: (a) Rudňany and (b) Slovinky. Map (c) shows the position of the sites in Slovakia. The GPS coordinates for the points shown on the maps are: Rudňany latitude (N) $48^{\circ}53'55.80''$, longitude (E) $20^{\circ}38'55.02''$; Slovinky latitude (N) $48^{\circ}53'20.32''$, longitude (E) $20^{\circ}52'09.66''$.

The climate of both regions is moderately warm and humid. The average temperature of the coolest month, January, is -5 to -6 °C and the average temperature of the warmest month, July, is 16 to 18 °C. The average annual precipitation is 550–600 mm.

MATERIALS AND METHODS

Samples of the tailing material in Rudňany were collected in the form of drill cores from three boreholes (RU-1, RU-2, and RU-3) situated from the NE to the SW part of the tailings pond (Fig. 1a). An additional 28 samples were collected from manually dug holes (DH-1 up to DH-15). At the Slovinky deposit, samples of tailings were collected from drill cores (SLO-1 – SE part of impoundment and SLO-2 – middle part of impoundment) and from three dug holes (SLO-3, 4, 5) (Fig. 1b). The main criteria for selection during the sampling were color, content of sandy and clayey particles, and water saturation of the tailings. The tailings were frozen in the field, transported to the laboratories in the Department of Mineralogy and Petrology (Bratislava, Slovakia), defrosted and air-dried under laboratory conditions (temperature of 22 ± 2 °C), homogenized, and sieved (<1 mm).

Tailing samples for electron microprobe analyses and for micro-X-ray diffraction (μ -XRD) were homogenized and separated into light and heavy fractions by panning in water or in ethanol. Selected heavy-grain

concentrates were prepared for further study in the form of standard thin and polished sections, to be inspected in transmitted and reflected polarized light, respectively (Department of Mineralogy and Petrology, Bratislava, Slovakia).

Primary minerals and the products of their oxidation in the environment of the tailings ponds were subsequently analyzed with a Cameca SX-100 electron microprobe operated in wavelength-dispersive mode (WDS) under the conditions of 20 kV, 20 nA, and beam size of 1–5 μ m (Geological Institute of Dionýz Štúr in Bratislava, Slovakia). The following lines, standards, and crystals were used for the analyzed elements: Mg ($K\alpha$, forsterite, TAP); Al ($K\alpha$, Al_2O_3 , TAP); Si ($K\alpha$, SiO_2 , TAP); S, Fe, Cu ($K\alpha$, $CuFeS_2$, PET); P ($K\alpha$, GaP, PET); Ca ($K\alpha$, wollastonite, PET); Mn ($K\alpha$, Mn, LIF); Co ($K\alpha$, Co, LIF); Ni ($K\alpha$, Ni, LIF); Zn ($K\alpha$, ZnS, LIF), Pb ($M\alpha$, PbS, PET); Sb ($L\beta$, Sb_2S_3 , PET); As ($L\beta$, FeAsS, TAP). The counting time on each peak was 20 s, on background 10 s (20 s for Sb).

The μ -XRD data were collected at the X-ray beamline of the Synchrotron Radiation Laboratory for Environmental Studies (SUL-X) of the synchrotron radiation source ANKA (Karlsruhe Institute of Technology, KIT, Germany). A silicon (111) crystal pair with a fixed beam exit was used as a monochromator. The μ -XRD data were acquired in transmission mode with a Photonic Science CCD detector XDI VHR-2 150 in 4×4 binning mode. The samples

were thin grain mounts in epoxy detached from the supporting glass. For these experiments, the beamline was operated at a constant energy of 14 keV ($\lambda = 0.886$ Å). Powdered Si (NIST 640d) was used as the calibrant for the d values. All acquired images were integrated with the program Fit2D (Hammersley *et al.* 1996) and the 1D XRD patterns were further used for full-profile refinement with the program GSAS (Larson & von Dreele 1994) and DIFFRAC^{plus} TOPAS (Bruker 2010) after a background subtraction. As in the case of in-house powder XRD patterns, background parameters, lattice parameters, shift parameter, preferred orientation, and Lorentzian peak broadening (parameter LX) were refined. All of the μ -XRD patterns were, before the refinement, evaluated by DIFFRAC^{plus} EVA software using the PDF4 database.

Thermodynamic modeling was done with the software package PHREEQC version 3.1.0 (Parkhurst & Appelo 1999). The thermodynamic database was augmented with data for As-rich hydrous ferric oxide (Majzlan 2011) and Cu sulfate minerals (Zittlau *et al.* 2013). Analytical data for water samples were taken from Hiller *et al.* (2013) who described the sampling, treatment, and analytical procedures in detail.

RESULTS AND DISCUSSION

The tailings at both studied sites consist of alternating layers of sandy and clayey material with different thicknesses of individual layers from some cm to more than 3 m. Mineral composition (graphically shown in Fig. S1, electronic supplementary information, available from the MAC Depository of Unpublished Data, Document CM52_10.3749/canmin.1400020) of the tailings is influenced by geological settings, lithological background, and mineral composition of the primary ore.

Mineral composition of the tailing impoundment at Rudňany

Siderite is the most common mineral in the tailing material, as a result of its abundant occurrence in the primary mineral assemblage, followed by quartz and barite. Another common carbonate mineral in the tailings is dolomite. The silicate minerals present are muscovite, chlorite, illite, and kaolinite.

Mineral composition of the tailing impoundment in Slovinky

The top layer of the tailing impoundment in the area of borehole SLO-1 (0–100 cm) is formed of slag, composed mostly of amorphous glasses. Flotation waste collected from boreholes SLO-1 and SLO-2 is composed mostly of quartz, siderite, and muscovite. Gypsum is also common, but the content of chlorite and clay minerals is relatively low.

Weathering products

Primary minerals in the tailings may succumb to weathering and oxidation and transform into new minerals. Some do not, however, and persist because their oxidation or hydration is too slow or perhaps thermodynamically not driven. An example of such a case is hematite found in the tailings but known to belong to the primary mineralization. The newly formed minerals are oxidized and often hydrated but should not be confused with the secondary minerals formed in the oxidation zone of the deposit. Therefore, one should, when possible, distinguish the secondary minerals and the tertiary minerals formed at the expense of the primary minerals, and perhaps also the secondary minerals, *in situ* in the tailings. The tertiary minerals occur as rims on primary minerals (Fig. 2a, b) and in some cases fill cracks in the primary minerals (Fig. 2b). Another morphological type of weathering products are completely oxidized grains with or without relics of the original mineral(s) (Fig. 2c, d). The composition of the rims and grains is different (Fig. 3). The rims are strongly influenced by the original mineral, but the difference lies also in elements which do not occur in the original minerals, for example, Ca or Mg. Rims are much richer in Ca and somewhat richer in Mg than the grains. Iron oxide phases without relics of primary minerals are the most common phases; iron oxides associated with the relics of arsenopyrite and tetrahedrite are rare. The last type of weathering product is represented by minerals cementing primary ore and gangue minerals and their decomposition products (Fig. 2e, f). It is not clear whether these minerals, mostly malachite, are secondary or tertiary.

Poorly crystalline Fe oxides and goethite (α -FeOOH)

The oxidation rims are mostly developed around pyrite, less frequently around chalcopyrite, and rarely around arsenopyrite. Oxidation rims were mostly observed at Slovinky; at Rudňany, they were found only in the uppermost layers of the tailings (0–50 cm). Our μ -XRD data reveal that the oxidation rims formed on pyrite grains (Fig. 2a) consist mostly of amorphous Fe oxides and rarely of poorly crystalline goethite. The chemical composition of the oxidation rims is to some extent dictated by the primary ore mineral. Various elements are detected in rims on pyrite (Cu, As, Si, Ca, Zn, Mg, Pb, Sb) (Table 1, Fig. 3). It is interesting to note that the rims on pyrite are enriched in Cu but not As (Fig. 4). It seems that the Fe oxides scavenge Cu from the pore waters in the tailings; arsenic is not scavenged, in contrast to other sites we investigated previously (Majzlan *et al.* 2011). This apparent indifference of the iron oxide compounds to arsenic, however, is probably a consequence of relatively small amounts of arsenic

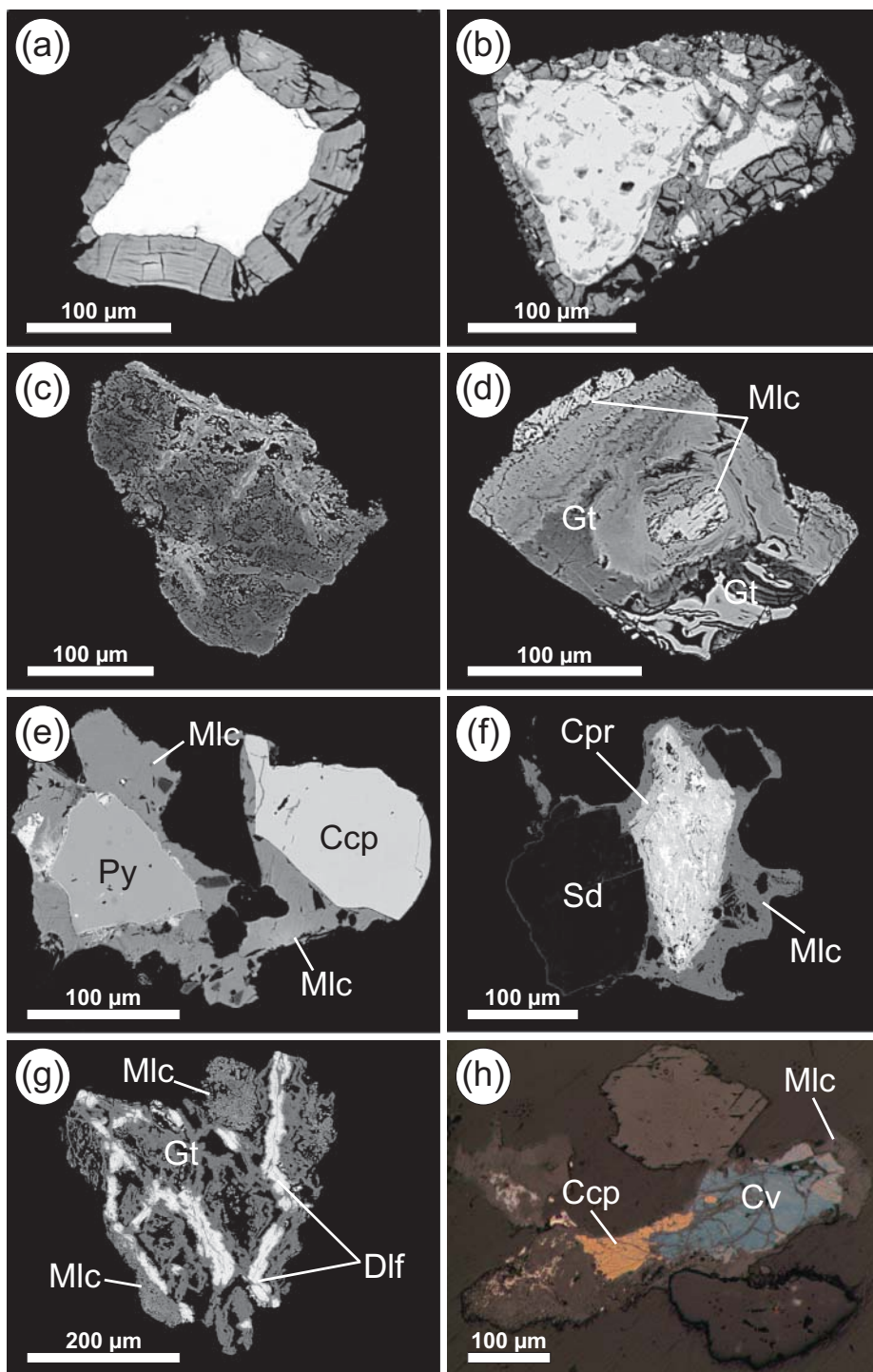


FIG. 2. Selected back-scattered electron (BSE, a–g) and reflected-light (h) images of mineral phases from the tailings: (a) oxidation rim on pyrite, (b) oxidation rim on chalcopyrite, (c) goethite produced by weathering of siderite, (d) zonal grain of goethite (Gt) with malachite (Mlc), (e) malachite (Mlc) cementing pyrite (Py) and chalcopyrite (Ccp), (f) native copper replaced by cuprite (Cpr) with cementing malachite (Mlc), (g) botryoidal aggregates of delafossite (Dlf) with goethite (Gt) and radial malachite (Mlc), (h) chalcopyrite (Ccp) replaced by covellite (Cv) with malachite (Mlc).

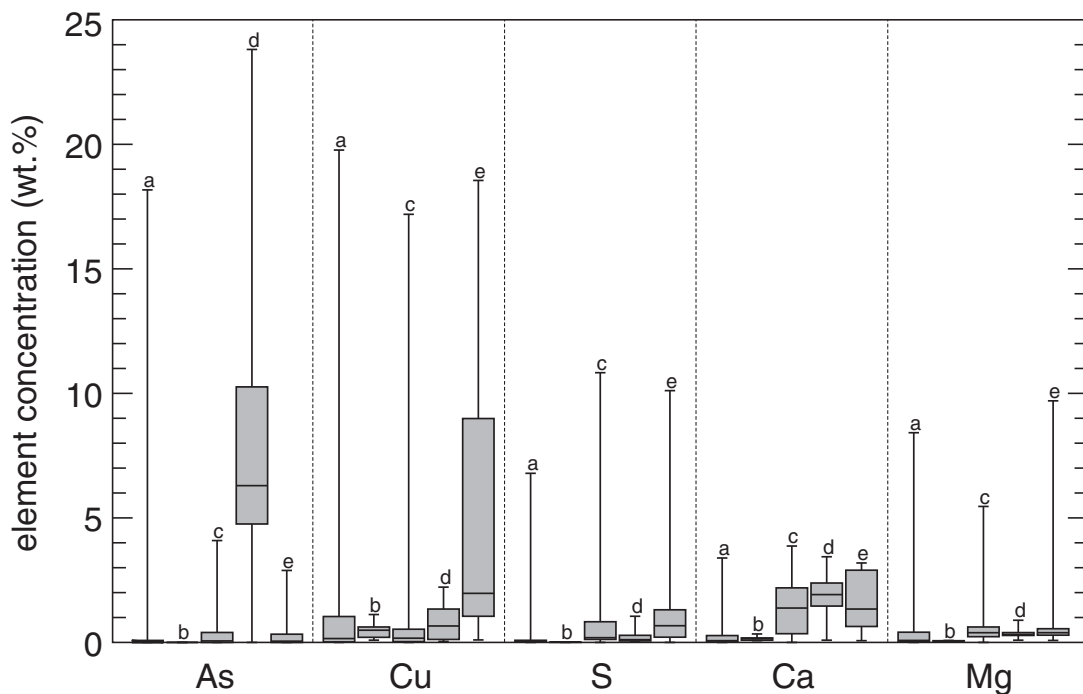


FIG. 3. Box-and-whiskers diagrams of selected elements in (a) Fe-dominated grains, (b) Mn-dominated grains, (c) rims on pyrite, (d) rims on arsenopyrite, and (e) rims on chalcopyrite. Note that in some cases, the boxes and whiskers are missing because all measured values were 0.00. The bottom and top of the box represent the first and third quartiles, the band inside the box is the median. The whiskers represent the minimal and maximal value within each data set.

within the tailing ponds, not specific properties of iron oxide phases or the environment of the impoundment.

Rims on arsenopyrite grains (Table 2, Fig. 4) are composed mostly of amorphous Fe oxide compounds with As content higher than in the rims on pyrite (Fig. 3). Only in a single instance was the μ -XRD pattern interpreted as goethite, but this rim, interestingly, was significantly depleted in As. Higher content of As commonly causes the formation of amorphous Fe oxide phases at near-neutral conditions or scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) at acidic conditions (Courtin-Nomadel *et al.* 2010, Murciego *et al.* 2011, Lalinská-Voleková *et al.* 2012).

Iron oxides with higher As content (up to 18.2 wt.%) were found as a separate phase or in association with arsenopyrite. Our data confirm that these phases are X-ray amorphous. Courtin-Nomadel *et al.* (2010) found that the amorphous or poorly crystalline hydrous ferric arsenate (HFA) is among the first products precipitated when arsenopyrite is oxidized.

The most frequent crystalline weathering product is goethite, which was identified in all studied samples. The texture of goethite grains is compact or rarely zonal (Fig. 2d). Goethite is found in the form

of separate grains or attached to other minerals such as barite, siderite, hematite, malachite, or silicates. Goethite grains were also observed in association with chalcopyrite, tetrahedrite, and siderite in samples collected from the dump at Rudňany.

According to the EMP analyses, grains of goethite have significant concentrations of Si, Mg, Mn, Cu, Zn, Sb, and As (Table 3), significant in the sense that it exceeds what would be expected from incorporation of these elements into the crystal structure of goethite. The size of the coherently diffracting domains of goethite (derived from XRD data) varies from 5.3 to 60.8 nm (Fig. 5a). Examples of the μ -XRD patterns and the models for three goethite grains with different chemical composition are shown in Figures 5b, c, and d. The lattice parameter a ranges from 4.526(9) Å to 4.69(2) Å, whereas b and c vary between 9.84(2) and 10.09(3) Å and 2.950(6) and 3.056(9) Å, respectively. Correspondingly, the unit-cell volume V ranges from 137.05(5) to 141.9(7) Å³ (Table 3).

Variations of the calculated lattice parameters and unit-cell volume can be caused by substitutions at the octahedral Fe^{3+} sites. Incorporation of Mn, Cu, Zn, Al, As, and Sb into the structure of goethite has been previously reported, mostly in synthetic but also in

TABLE 1. SELECTED EMP COMPOSITIONS OF RIMS ON PYRITE GRAINS* AND FOUR COMPOSITIONS WITH LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	Mg	Al	Si	S	Ca	Mn	Fe	Co	Cu	Zn	Pb	Sb	As	O	Total	a (Å)	b (Å)	c (Å)	V (Å ³)
SLO-2_0-100_15	0.27	0.07	1.76	0.29	1.33	0.15	53.64	0.06	0.53	0.58	0.05	0.16	1.49	27.51	87.94	4.661(8)	10.03(2)	2.955(7)	138.1(3)
RU-01_0-50_5	0.79	<d.l.	0.70	0.21	2.43	0.05	55.19	0.06	0.13	0.05	0.01	0.05	0.87	26.93	87.53	4.618(2)	9.953(6)	3.024(1)	139.0(1)
RU-01_0-50_12	0.54	<d.l.	0.25	0.17	2.14	0.06	50.94	0.05	0.18	0.01	<d.l.	0.03	0.67	24.16	79.45	4.60(1)	10.02(2)	3.03(1)	139.9(7)
RU-01_0-50_17 with Qz	0.54	<d.l.	0.56	0.16	2.76	<d.l.	49.59	0.07	0.02	0.01	0.02	0.02	<d.l.	23.81	77.75	4.65(2)	9.8(2)	3.0(10)	137.7(5)
SLO-2_0-100_7	1.02	1.00	4.00	0.06	0.44	0.19	49.35	0.05	2.09	1.96	0.20	0.09	<d.l.	28.84	89.46				
S-3_11	0.91	0.02	0.73	0.09	0.88	0.04	55.55	0.14	0.93	<d.l.	0.91	0.06	1.60	27.07	88.99				
S-3_17	0.28	<d.l.	0.33	0.96	0.29	0.05	46.12	0.04	17.19	0.02	0.06	0.29	0.26	26.61	92.57				
SLO-4_8	0.23	0.01	2.24	0.12	1.62	0.02	50.80	0.05	2.51	2.28	0.03	0.12	0.19	26.76	87.03				
RUS-01_20-100_9	1.92	0.02	0.21	0.03	0.85	3.56	53.15	0.08	<d.l.	<d.l.	0.08	0.06	<d.l.	26.86	86.82				
RUS-1_100-200_10	0.54	0.01	0.32	2.36	3.87	<d.l.	48.09	0.06	<d.l.	<d.l.	0.01	<d.l.	<d.l.	26.49	81.75				
Average (108 analyses)	0.56	0.06	0.97	0.89	1.42	0.27	52.72	0.07	1.01	0.26	0.06	0.12	0.36						
Maximum	5.46	1.00	4.00	10.83	3.87	3.56	69.67	0.62	17.19	2.28	0.91	0.68	4.09						
Minimum	0.02	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	36.34	0.03	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.						

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt.%.

*Results of 10 analyses out of 108 are reported. Symbols: Qz: quartz.

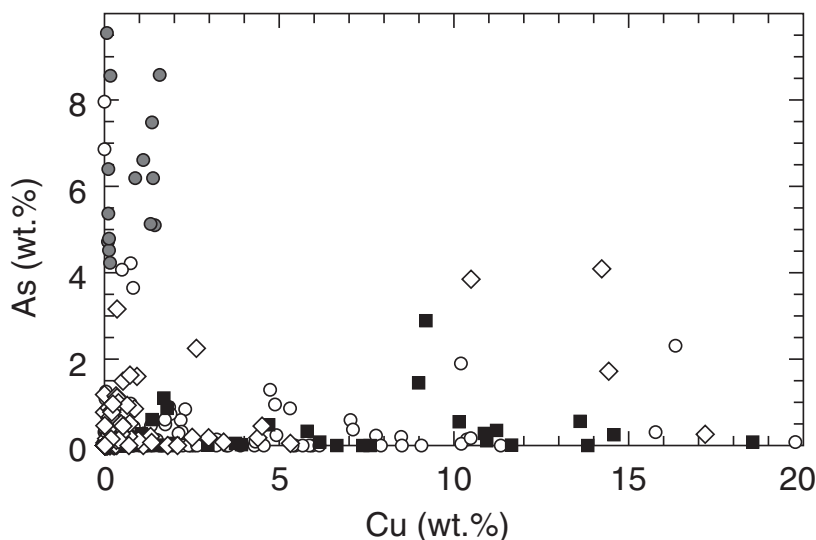


FIG. 4. A diagram of Cu and As content in the grains of iron oxides (white circles), rims on pyrite (white diamonds), rims on arsenopyrite (grey circles), and rims on chalcopyrite (solid squares). All data from spot EMP analyses.

natural goethite (*e.g.*, Manceau *et al.* 2000, Sileo *et al.* 2001, Alvarez *et al.* 2007, Majzlan *et al.* 2011). Substitution of different cations has a diverse effect on the goethite structure. In single-metal substituted goethite, incorporation of Cr reduces the unit-cell volume while that of Zn, Cd, and Pb causes its expansion (Kaur *et al.* 2009). Moreover, incorporation of cations such as Cd, Zn, Cu, Ni, and Co has a strong impact on the lattice parameter *a* (Gerth 1989). Trivalent Mn has the same ionic radius as Fe^{3+} (Shannon 1976), but it does not readily fit into the structure of goethite owing to the Jahn-Teller effect, and it causes an increase of the *a* and decrease of the *b* parameters (Cornell & Schwertmann 2003). In contrast, the incorporation of V^{3+} with almost identical ionic radius as Fe^{3+} and Mn^{3+} does not induce any change in lattice parameters compared to pure goethite (Schwertmann & Pfab 1994).

There is no significant correlation, however, between lattice parameters of goethite and the content of any element analyzed in our samples. The lack of correlation is probably a consequence of the multiple substitutions in our natural samples and the interplay among the substituting cations in the structure, for example, clustering. Therefore, the influence of cations with smaller ionic radii than Fe^{3+} (*e.g.*, Sb, As, Al) may be compensated by the presence of the cations with larger ionic radii (*e.g.*, Cu, Zn). This effect of simultaneous incorporation of several distinct cations has been previously observed for synthetic goethite (Kaur *et al.* 2009). Some cations or portions thereof may be incorporated directly into the structure of goethite. A certain portion of the metals and

metalloids may be adsorbed to the surface of the goethite (Grolimund *et al.* 2000, Kulik 2009).

The average Si content in the spot EMP analyses in the goethite grains is 0.99 wt.% and the highest content is 17.61 wt.%. Gómez *et al.* (2011) presumed that silicate ions are adsorbed on the surface of goethite or fill the voids between the crystallites that constitute the goethite crystal, rather than by incorporation of the silicate ions into the goethite structure.

The increased contents of Mn and Mg in goethite can be tracked back to the presence and dissolution of carbonate minerals, especially siderite (Fig. 6). We assume that most of the goethite is a product of siderite oxidation (Fig. 2c), but upon weathering, Mn and Mg are mobilized and, in general, Fe oxide phases contain lower concentrations of these elements than the parent minerals (Fig. 6). A few goethite grains originated from the oxidation of sulfide minerals. The highest content of Mg is 8.4 wt.%, with an average content of 0.6 wt.%. The average content of Mn in goethite is 0.8 wt.% and the maximum value is 13.7 wt.%. Calcium content is up to 3.4 wt.% (average 0.5 wt.%).

Goethite grains are often enriched in Cu and rarely in Zn. The Cu and Zn contents of the Fe oxide phases attains 11.3 wt.% (average 0.9 wt.%) and 1.6 wt.% (average 0.1 wt.%), respectively. Manceau *et al.* (2000) observed that Cu and Zn have the same local structure arrangement in natural and synthetic goethite. With the exception of the Cu polyhedron, which is distorted by the Jahn-Teller effect, (Cu,Zn)–O and (Cu,Zn)–Fe distances are similar to Fe–O and Fe–Fe distances in goethite. No significant steric effect was

TABLE 2. SELECTED EMP COMPOSITIONS OF RIMS ON ARSENOPYRITE GRAINS* AND ONE COMPOSITION WITH LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	Mg	Al	Si	S	Ca	Fe	Cu	Pb	Sb	As	O	Total	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
RU-01_0-50_7	0.65	<d.l.	0.26	0.11	2.42	58.11	0.44	<d.l.	0.01	<d.l.	26.98	89.09	4.610(2)	9.954(5)	3.024(1)	138.74(5)
RU-01_0-50_9	0.89	0.01	0.19	0.06	2.58	39.16	0.07	<d.l.	<d.l.	9.55	23.91	76.58				
RUS-01_100-200_11	0.49	<d.l.	0.10	0.52	1.87	32.36	1.69	0.21	<d.l.	23.81	29.18	90.55				
RUS-01_100-200_12	0.33	0.04	0.31	1.05	1.72	44.31	1.04	0.37	0.38	14.15	29.94	93.80				
RUS-01_100-200_20	0.29	<d.l.	0.41	0.13	1.84	50.88	0.10	1.38	0.03	4.72	26.15	86.00				
RUS-01_100-200_25	0.24	0.59	1.49	0.31	1.21	47.04	1.44	0.15	0.28	5.10	26.78	84.80				
RUS-01_100-200_27	0.32	0.56	2.25	0.04	0.87	44.94	1.32	0.12	0.16	5.13	26.17	82.00				
RUS-1_100-200_3	0.39	<d.l.	0.03	0.53	2.01	31.07	2.22	0.16	0.06	22.38	27.96	87.15				
RUS-1_100-200_11	0.23	0.10	0.39	0.04	1.07	50.42	1.11	0.44	0.48	6.61	26.99	88.20				
RUS-1_100-200_12	0.31	<d.l.	0.20	0.13	3.44	46.20	0.88	0.12	0.09	6.19	25.49	83.24				
Average (24 analyses)	0.37	0.11	0.51	0.21	1.94	46.60	0.76	0.26	0.15	7.94						
Maximum	0.89	0.59	2.25	1.05	3.44	58.11	2.22	1.38	0.48	23.81						
Minimum	0.09	<d.l.	0.03	0.02	0.09	31.07	0.04	<d.l.	<d.l.	<d.l.						

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt. %.

*Results of 10 analyses out of 24 are reported.

TABLE 3. SELECTED EMP COMPOSITIONS OF GOETHITE GRAINS* AND LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	Mg	Al	Si	Ca	Mn	Fe	Cu	Zn	Pb	Sb	As	O	Total	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
SLO-2_300-400_3	2.76	0.02	2.66	0.23	3.29	49.39	0.11	0.00	0.02	0.10	0.02	28.30	87.02	4.633(3)	9.92(1)	3.038(3)	139.6(1)
SLO-2_300-400_8-with Mlc, Qz	0.38	0.15	3.36	0.52	0.59	48.70	7.04	0.28	1.20	0.32	0.59	28.40	91.86	4.632(3)	9.92(1)	3.038(3)	139.6(1)
SLO-2_300-400_33	1.73	0.42	1.88	0.41	13.68	36.54	2.56	0.11	0.88	0.04	0.00	28.30	86.64	4.632(3)	9.92(1)	3.037(3)	139.5(1)
SLO-2_0-100_21-with Dlf, Mlc	0.04	0.02	0.90	0.01	0.18	52.58	4.29	0.02	0.02	0.03	0.00	25.01	83.25	4.597(3)	9.971(5)	3.027(1)	138.72(6)
SLO-4S_5-with Mlc, Qz	0.30	0.29	0.72	0.14	2.95	44.08	7.77	0.74	0.18	0.18	0.23	24.68	82.59	4.68(1)	9.84(2)	3.023(5)	139.3(2)
SLO-4S_30-with Cpr	0.48	0.47	1.90	0.19	0.18	53.29	1.50	1.59	0.17	0.21	0.13	27.02	87.28	4.612(6)	9.97(3)	3.008(6)	138.3(3)
RU-1 1900-2100_17	0.56	<d.l.	1.83	0.30	0.61	51.95	2.31	0.05	0.07	0.61	0.84	27.42	87.24	4.637(3)	10.019(8)	3.040(2)	141.2(2)
RU-1 1900-2100_2-with Brt	<d.l.	0.01	1.09	0.17	0.34	57.19	0.75	0.02	0.03	0.84	0.97	27.17	88.71	4.622(3)	9.997(7)	3.033(2)	140.1(2)
RU3-1400-1600_21	0.02	0.17	1.28	0.04	0.21	54.81	0.02	<d.l.	0.03	0.04	<d.l.	26.16	84.25	4.618(2)	9.976(4)	3.025(1)	139.35(6)
RU-3_0-40_19	0.22	<d.l.	0.25	0.30	14.18	44.90	<d.l.	<d.l.	0.05	<d.l.	<d.l.	28.17	88.14	4.604(3)	9.954(7)	3.019(2)	138.35(9)

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt. %.

*Results of 10 analyses out of 72 are reported. Symbols: Mlc: malachite, Qz: quartz, Dlf: Delafossite, Cpr: cuprite, Brt: barite.

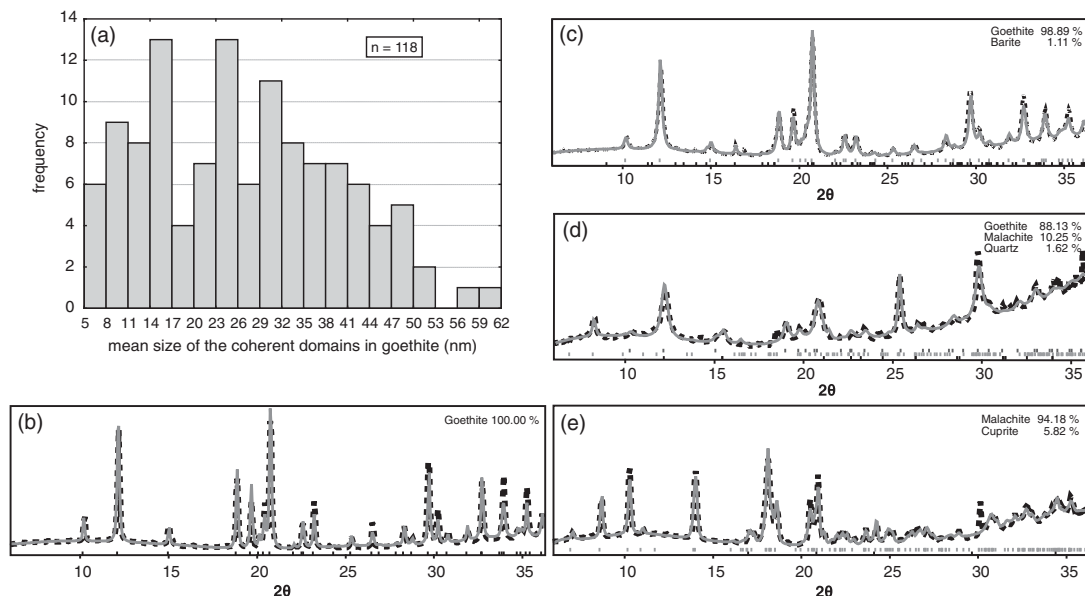


FIG. 5. (a) Histogram of the mean size of the coherent domains in goethite. (b–e) micro-X-ray diffraction patterns ($\lambda = 0.886 \text{ \AA}$) with the results of full-profile refinement (dotted curve – data, solid gray curve – fit). Ticks below the patterns indicate the position of calculated peaks. The minerals and their quantitative abundance are listed in the upper right-hand corner of each panel. (b) Goethite (sample RU1_1900-2100_11); (c) goethite with elevated content of Si up to 1.57 wt.%, Cu up to 1.33 wt.%, Sb up to 1.27 wt.%, As up to 0.97 wt.%, and Ca up to 0.61 wt.% and barite (sample RU1_1900-2100_10); (d) goethite with elevated content of Cu up to 11.34 wt.%, Pb up to 1.20 wt.%, As and Mn up to 0.59 wt.%, malachite and quartz (sample SLO2_300-400_AG3); (e) malachite with cuprite (sample SLO4S_7c).

observed around Cu (0.73 $\text{\AA}$) and Zn (0.74 $\text{\AA}$) in spite of the $\sim 14\%$ increase in ionic radii compared to Fe^{3+} (0.645 $\text{\AA}$). The Sb content of the goethite grains attains 3.9 wt.%, average 0.4 wt.%. The average value of As in the goethite grains is 0.1 wt.%, with maximum content up to 1.0 wt.%.

Gerth (1989) indicated that high concentration of Cu (9 mol.%) preferentially induces the nucleation of hematite over goethite. The product consists of aggregates with a hematite core and outgrowths of goethite (Feitknecht & Michaelis 1962, Gerth 1989). In our samples from the Rudňany dump, only two grains of goethite with hematite were identified using μ -XRD. The Cu content of these grains attains 3.5 wt.%.

The rims developed around chalcopyrite (Fig. 2b) are generally thin and the measurements with the μ -XRD beam were difficult to interpret because most of the signal came from chalcopyrite. Only in three cases were we able to identify these rims as goethite. The chemical composition of the chalcopyrite rims is affected by the primary ore mineral composition and elements which are adsorbed or incorporated into these rims (Table 4). The rims on chalcopyrite are mostly enriched in Cu and to a lesser extent in As (Fig. 4).

Transformation between poorly crystalline Fe oxides and goethite

The minerals in the tailings ponds offer a snapshot of processes which operate within the ponds. We possess no information about the temporal scales of these processes, but the data provide evidence about what controls these processes.

Ferrihydrite is a common precursor for many crystalline oxides. If prepared in the laboratory, the transformation of ferrihydrite to goethite or hematite can be followed (e.g., Schwertmann *et al.* 2004, Vu *et al.* 2008). It is also well known that impurities slow the transformation, especially phosphate (e.g., Paige *et al.* 1997) or arsenate (e.g., Das *et al.* 2011, Bolanz *et al.* 2013). The studied tailings are a natural laboratory where the previously published observations from laboratory beakers and bottles can be compared with natural settings.

The effect of the tetrahedral oxyanions silicate, arsenate, and phosphate upon the crystallinity of goethite is clearly seen in Figure 7a. The Figure shows that the mean size of the coherently diffracting domains decreases with increasing Si + As + Sb + P. The data define a wedge-like cluster bordered by the

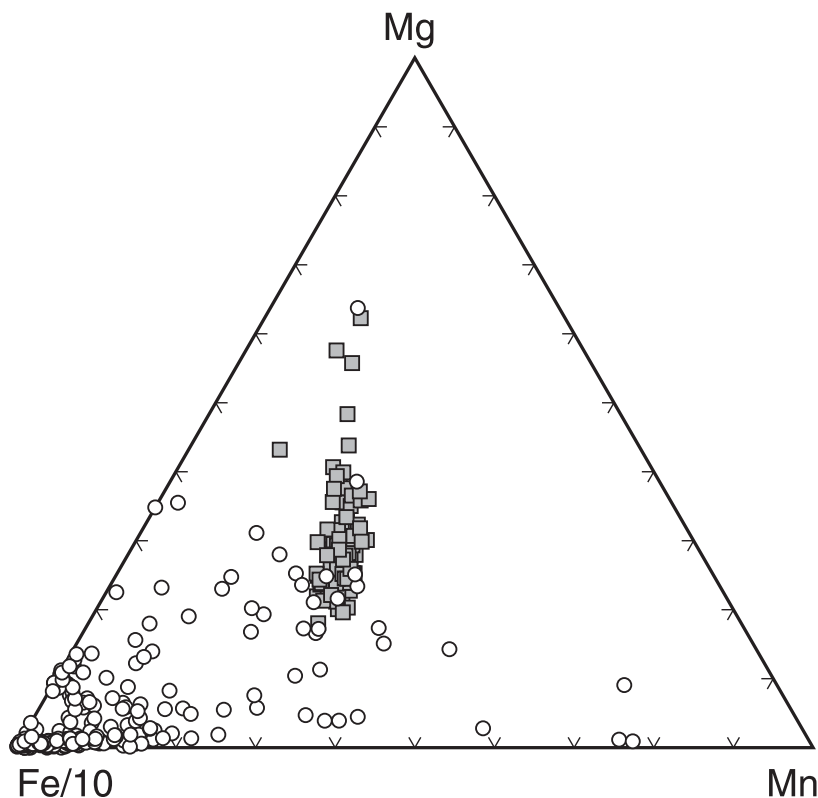


FIG. 6. A Fe10–Mn–Mg triangular plot for the primary siderite from Rudňany (squares, data from Cambel *et al.* 1985) and the Fe oxide phases from the tailings pond at Rudňany (circles, this study).

dashed line in Figure 7a. The line appears to level off at approximately 4 wt.% Si + As + Sb + P. It should be also noted that silicon is the most abundant element among the three; arsenic is the second most abundant, and phosphorus has the lowest concentrations. Yet all three elements display a wedge-like data distribution similar to that in Figure 7a (see also Fig. S2). This distribution confirms that the tetrahedral high-charge cations slow down the transformation of the poorly crystalline iron oxide compounds to goethite. The wedge-like data distribution is a snapshot of the crystallinity of the iron oxide phases, where the data points move upwards (in Fig. 7a) with time. In other words, this Figure also captures samples with low content of impurities and low crystallinity, but these samples are “young”. They will mature and attain the highest crystallinity observed in our samples.

Although the association of the tetrahedral high-charge cations (*e.g.*, As⁵⁺, P⁵⁺) with iron oxides has been well documented in the literature (*e.g.*, Guan *et al.* 2009, Das *et al.* 2011, Bolanz *et al.* 2013), the impact of octahedral, lower-charge cations has not been inspected in comparable depth. Our samples

offer the possibility of doing so. Of the octahedral lower-charge cations, copper is abundant in the studied samples. The other cations are not so abundant and the distributions are restricted to relatively low concentrations, although they appear to be wedge-like. Copper, an abundant impurity, shows a well-defined wedge-like distribution (Fig. 7b). This distribution, however, levels off at ~15 wt.% Cu, suggesting that the divalent cations also hinder the transformation, but not to the same extent as the tetrahedral cations.

Products of tetrahedrite weathering

We also observed rims on tetrahedrite and separate grains with tetrahedrite relics. Scarce rims on tetrahedrite were observed only in samples from the Rudňany dump. The copper content of the rims on the tetrahedrite varies from 33.4 to 60.7 wt.%; in terms of other elements Sb attains 11.5 wt.% (average 5.9 wt.%), Hg up to 6.1 wt.% (2.1 wt.%), As up to 2.2 wt.% (1.5 wt.%), Fe up to 2.0 wt.% (1.1 wt.%),

TABLE 4. SELECTED EMP COMPOSITIONS OF RIMS ON CHACOPYRITE GRAINS* AND THREE COMPOSITIONS WITH LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	Mg	Al	Si	S	Ca	Mn	Fe	Cu	Zn	Pb	Sb	As	Hg	O	Total	a (Å)	b (Å)	c (Å)	V (Å ³)
SLO-2_300-400_17	9.70	<d.l.	0.01	<d.l.	0.11	2.03	31.67	0.10	0.01	0.00	0.02	<d.l.	<d.l.	21.30	65.03	4.633(3)	9.92(1)	3.038(3)	139.6(1)
SLO-2_300-400_26	0.86	0.05	1.17	9.86	0.64	0.08	37.64	18.55	0.18	0.07	4.85	0.08	<d.l.	39.60	113.71	4.615(5)	9.92(2)	3.030(3)	138.7(1)
SLO-2_300-400_27	0.68	0.06	1.41	0.17	0.72	0.13	38.13	10.15	0.47	0.08	9.71	0.55	<d.l.	25.33	87.68	4.632(3)	9.92(1)	3.038(3)	139.5(1)
SLO-2_300-400_28	0.55	0.01	1.20	0.18	0.69	0.09	35.47	10.87	0.60	0.18	15.04	0.28	<d.l.	25.62	90.88				
SLO-2_300-400_40	0.90	0.22	2.93	5.17	0.68	0.34	40.84	13.61	0.55	0.58	0.55	0.56	<d.l.	34.08	101.12				
SLO-2_300-400_18	0.88	0.02	6.22	0.99	0.35	0.13	39.47	11.22	0.04	0.22	1.13	0.35	<d.l.	29.81	90.92				
SLO-4_13	0.22	0.09	2.68	0.11	1.34	<d.l.	48.06	6.16	0.60	0.17	0.03	0.08	0.04	26.44	86.10				
RUS-12_20-100_12	0.41	<d.l.	1.00	0.92	3.19	<d.l.	52.28	1.26	0.03	0.07	0.04	<d.l.	<d.l.	26.90	86.16				
RU-2_0-100_31	0.08	0.19	0.07	0.15	0.07	0.63	56.35	0.37	0.01	0.04	<d.l.	<d.l.	<d.l.	25.27	83.31				
RU-3_0-40_9	0.21	0.24	1.27	0.21	0.86	0.08	44.17	7.60	0.00	0.00	0.06	<d.l.	1.60	23.65	80.10				
Average (48 analyses)	0.65	0.07	1.21	1.78	1.63	0.16	46.00	4.86	0.09	0.07	0.88	0.26	0.21						
Maximum	9.70	0.76	6.22	10.11	3.19	2.03	56.35	18.55	0.60	0.58	15.04	2.89	1.60						
Minimum	0.08	<d.l.	0.01	<d.l.	0.07	<d.l.	31.67	0.10	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.						

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt.%.

*Results of 10 analyses out of 48 are reported.

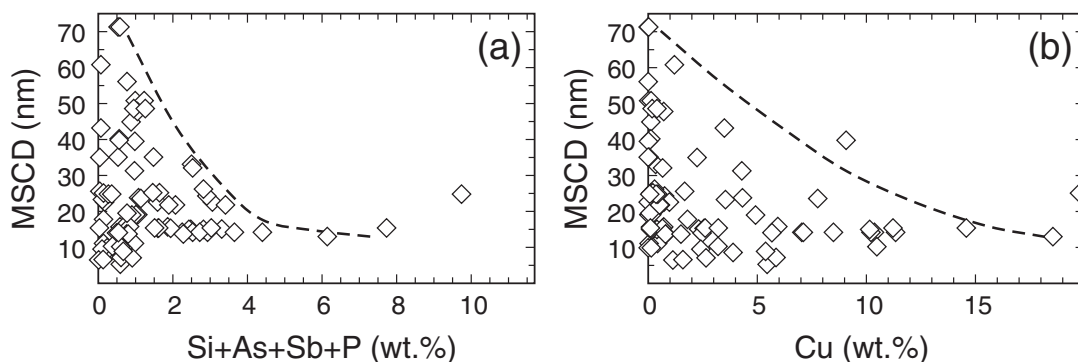


FIG. 7. Mean size of the coherently diffracting domains (MSCD) of goethite as a function of chemical composition of the goethite samples (measured by spot EMP analyses). In some cases, several spot analyses were made in an area scanned by μ -XRD and each of the EMP analyses is shown as a separate data point. The dashed curves are a guide for the eye, showing the wedge-like distribution of the data.

and Mg up to 1.7 wt.% (1.1 wt.%). The rims also contain remnants of S (up to 6.1 wt.%).

Products of tetrahedrite oxidation are rarely observed. They are represented by Fe oxides with remnants of Cu, Sb, As, Hg, and S, and elements that are adsorbed from pore solutions (Ca and Mg). We do not have μ -XRD data to identify these weathering products.

Other minerals

Delafossite, CuFeO_2 , was found only in the Slovinky tailing pond in borehole SLO-2 where it occurs in the upper part of the tailings (depths 0–100 cm and 300–400 cm). The grain size varies from 120 to 300 μm . The mineral is compact, zoned or botryoidal, and forms veinlets and relics in goethite and malachite (Fig. 2g). It was identified by EMP analyses and micro-Raman spectroscopy (as reported in Kučerová *et al.* 2013).

Malachite, $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$, is a less common relic from the oxidation zones of the deposits, identified in the Slovinky tailing pond and at the Rudňany dump. It was found in association with chalcopyrite and goethite in the Rudňany dump. At Slovinky, malachite was found only between 0–50 cm depth. Malachite alone or with goethite cements other minerals, *e.g.*, native Cu, pyrite, chalcopyrite, quartz, and siderite (Fig. 2e, f). Separate grains or radial aggregates of malachite were found rarely at Slovinky.

Cuprite, Cu_2O , was observed only in association with malachite. Cuprite is probably formed by oxidation of native copper (Fig. 2f) or chalcopyrite. The chemical composition and lattice parameters of malachite and cuprite are listed in Tables 5 and 6, respectively. In spite of the common occurrence of these minerals in the oxidized zone of many Cu

deposits, malachite and cuprite were not found in the tailings at Rudňany.

Covellite, CuS , was found rarely in samples of Slovinky and Rudňany tailings as blue coatings on chalcopyrite surfaces (Fig. 2h). Covellite is a common weathering product of Cu ores. Alpers & Brimhall (1989) and Jang & Wadsworth (1994) assumed that covellite represents the first stage of chalcopyrite replacement. Dold & Fontboté (2001) found that in their samples chalcopyrite was replaced by chalcocite (Cu_2S), digenite (Cu_9S_5), and/or covellite (CuS).

Observed versus expected mineralogy

The observed mineralogical composition of both tailings ponds is relatively simple. Primary minerals are well known from the hydrothermal veins or the country rocks. The secondary and tertiary minerals are mostly represented by X-ray amorphous Fe oxides phases or goethite. Minerals of Cu, either oxides or carbonates, are less common and less abundant. The observed mineralogy can be confronted with thermodynamic predictions based on saturation indices (SI) of the individual minerals in the aqueous solutions discharged from the tailings pond. These data were presented for three samples by Hiller *et al.* (2013, their Table 5). The redox state of the waters was not reported, therefore we assume that the water samples lie in the predominant fields of the highest oxidation state for all major redox-active cations (these waters precipitated masses of ochreous, Fe-rich precipitates). Results of the SI calculations are graphically presented in Figure 8.

There is a striking difference between several groups of minerals. All Fe oxide phases, be they X-ray amorphous, poorly crystalline, or crystalline, appear to be supersaturated in these samples. A likely explanation is the very small size of the particles,

TABLE 5. SELECTED EMP COMPOSITIONS OF MALACHITE* AND LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	Mg	Ca	Mn	Fe	Ni	Cu	Zn	Pb	As	O	Total	a (Å)	b (Å)	c (Å)	β	V (Å ³)
SLO-4S_7c-with Cpr	0.18	0.17	0.09	0.73	0.64	49.32	2.61	0.25	0.72	14.48	69.49	9.511(8)	11.939(9)	3.217(2)	98.71(6)	361.1(5)
SLO-4S_9	0.12	0.10	0.06	0.74	0.17	55.62	1.65	0.02	<d.l.	15.18	73.89	9.484(7)	11.990(7)	3.212(2)	98.36(5)	361.37(5)
SLO-4S_9b	0.31	0.16	0.10	0.49	0.15	51.73	1.19	0.48	0.06	14.27	69.22	9.500(9)	11.964(1)	3.226(2)	98.52(6)	362.66(6)
SLO-4S_14	0.41	0.11	0.04	0.58	0.04	51.97	1.66	0.02	<d.l.	14.65	69.99	9.635(5)	11.805(4)	3.221(2)	98.48(6)	362.38(5)
SLO-4S_12	1.22	0.17	0.18	1.11	0.06	55.04	0.57	0.02	0.04	15.71	74.35	9.515(5)	11.960(5)	3.232(1)	98.84(2)	363.46(3)
POR-3_34-with Ccp	0.07	0.02	<d.l.	1.37	<d.l.	57.28	0.05	<d.l.	<d.l.	15.85	75.20	9.562(9)	11.946(10)	3.237(2)	99.04(7)	365.19(7)
POR-3_35-with Ccp	0.07	0.01	0.01	1.07	0.01	57.57	0.02	<d.l.	<d.l.	15.59	74.79	9.353(3)	11.643(9)	3.219(6)	98.72(6)	346.44(3)

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt.%.
 *Results of 7 analyses out of 20 are reported. Symbols: Cpr: cuprite, Ccp: chalcopyrite.

TABLE 6. SELECTED EMP COMPOSITIONS OF CUPRITE* AND LATTICE PARAMETERS FROM SYNCHROTRON μ -XRD

	SiO ₂	P ₂ O ₅	Fe ₂ O ₃	Cu ₂ O	PbO	Sb ₂ O ₅	SnO	Total	a (Å)	V (Å ³)
SLO-4S_10	1.01	0.42	0.63	95.00	0.03	<d.l.	<d.l.	97.10	4.2550(6)	77.04(3)
SLO-4S_15-with Mlc	0.06	0.20	0.08	97.70	<d.l.	0.04	<d.l.	98.08	4.2674(3)	77.71(2)
SLO-4S_16-with Mlc	0.07	0.45	0.19	94.72	0.22	0.85	1.76	98.25	4.1876(6)	73.43(3)
SLO-4S_18	0.13	0.21	0.32	99.01	0.03	0.07	0.43	100.20	4.2786(7)	78.33(3)

<d.l.: less than detection limit. The compositions, determined with an electron microprobe, are quoted in wt.%.
 *Results of 4 analyses out of 9 are reported. Symbols: Mlc: malachite.

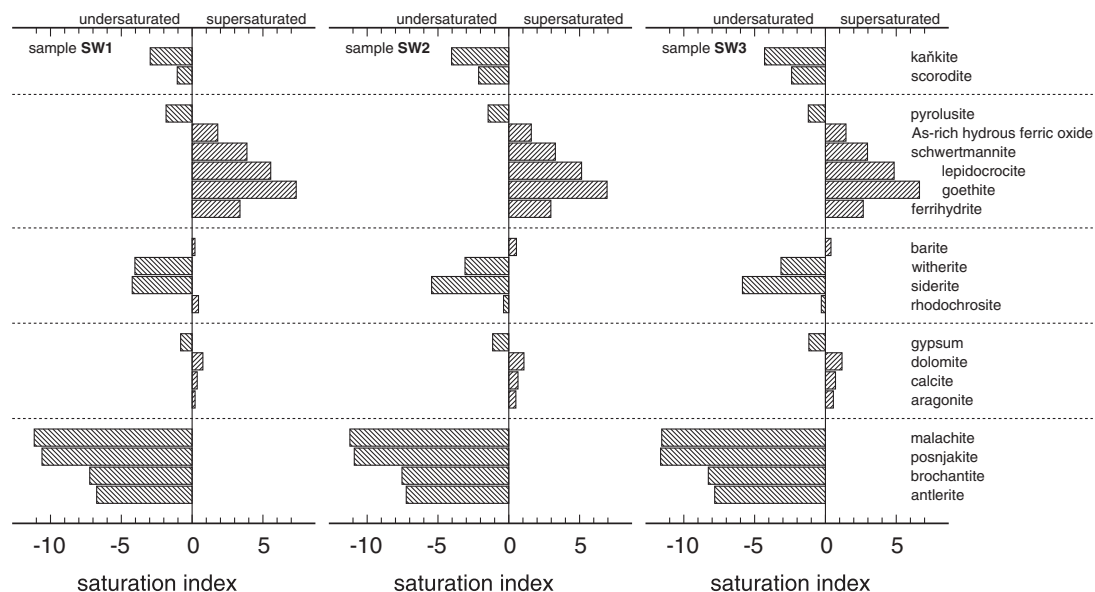


FIG. 8. Saturation indices of minerals relevant to the tailings pond at Rudnaňý calculated for the analyses of water discharged from the tailings pond (data from Hiller *et al.* 2013).

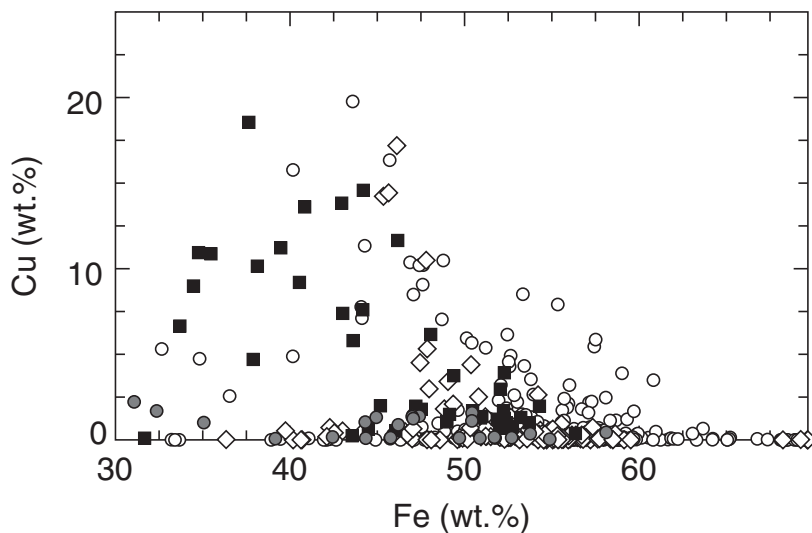


FIG. 9. A diagram of Fe and Cu content of the grains of iron oxides (white circles), rims on pyrite (white diamonds), rims on arsenopyrite (grey circles), and rims on chalcopyrite (solid squares). All data from spot EMP analyses.

therefore their ability to pass through the $0.45\ \mu\text{m}$ filters (used by Hiller *et al.* 2013) and be counted as “dissolved” iron. On the other hand, the carbonates and sulfates of copper are all substantially undersaturated even though the concentration of copper in the bulk tailings and in the iron oxides (Fig. 9) can be

quite high. The iron oxide compounds, therefore, act as a potent adsorber not only for arsenate or antimonate, but also for copper. The studied system, although relatively rich in copper, produces hardly any separate Cu minerals. We conclude that the observed Cu minerals, such as delafosite, malachite, and cuprite,

are relics from the oxidation zone of the deposit (*i.e.*, they are secondary minerals). The iron oxide phases dominate and control the entire mineralogy and geochemistry of the system. They adsorb or incorporate an entire suite of elements, thus preventing other minerals from nucleation and growth, leading to undersaturation of some minerals in the aqueous phase (Fig. 8). The crystallinity and maturation of the iron oxide compounds, in turn, is strongly influenced by the chemical impurities.

CONCLUSIONS

The tailings ponds at both studied sites represent weathering and oxidation of the abundant primary siderite, with local enrichment in barite and the sulfide minerals pyrite, chalcopyrite, and tetrahedrite. We determined that (1) the tailings are near-neutral or slightly alkaline because the acidity generated by the decomposition of the sulfides is efficiently neutralized by the abundant carbonate minerals; (2) the tertiary mineralogical composition of the tailings is dominated by poorly crystalline hydrous ferric oxide and goethite and other minerals are minor or rare; (3) the transformation of the poorly crystalline hydrous ferric oxide to goethite and maturation of the goethite is controlled by both high-valence tetrahedral cations (Si, As, P) and lower-valence octahedral cations (Cu); and (4) the iron oxide phases adsorb an entire suite of elements, including cations such as Cu, Ca, and Mn. The iron oxide compounds, by the virtue of their adsorption capacity, prevent separate minerals of these metals from nucleating and growing, and therefore control the entire NMD system.

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