

Preliminary chemical and mineralogical characterization of tailings from base metal sulfide deposits in Serbia and North Macedonia

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Abstract

Tailings of old mines often contain metals, which were not of economic interest or could not be recovered with the existing technology at the time of active mining. This is especially true for metals that often occur as by-products in Cu-Pb-Zn-(Ag-Au) ores as Sb, Mo, Ge, and In. A fundamental characterization of some tailings is presented in terms of their mineralogy and content of valuable metals which could be extracted to finance a possible remediation and improve the supply of the EU with critical metals. Tailings from active and abandoned mines in Serbia (Bor, porphyry Cu/Au; Krivelj, porphyry Cu/Au; Blagodat, hydrothermal Pb-Zn; Lece, epithermal Au; Rudnik, hydrothermal/skarn Pb-Zn) and North Macedonia (Sasa, Pb-Zn; Probištip, Pb-Zn; Bučim, porphyry Cu; Lojane, fault-bound vein-type low-temperature As, Sb, Cr at the contact of rhyolite and serpentinite) were studied. Analysis for major and trace elements used a multi-method approach (lithium borate fusion and ICP-MS/OES analysis, gravimetric analysis, instrumental neutron activation analysis, total digestion ICP-OES, infrared spectroscopy) with mineral identification by scanning electron microscopy. Concentrations of the major commodity elements (Cu, Pb, Zn, Au, Ag) varies within several orders of magnitude depending on mineralogy and ore type. Critical metals (Co, Ga, Ge, Sb) contents are low with some exceptions. Some tailings contain moderate to elevated potentially toxic element levels (As, Cd, Pb, Tl). For the sample from Probištip which yielded the highest valuable metal concentrations (>5000 ppm Pb, 4020 ppm Zn), a heavy mineral concentrate of the sand size fraction (0.06 mm to 0.5 mm) was produced and analyzed by SEM and LA-ICP-MS for additional rare phases and trace elements. In all tailings studied, additional milling would be needed to separate ore from gangue minerals. Increasing metal prices might facilitate feasibility studies for some of the localities in the future, despite the limited quantitative information about the characterized tailings.

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1. INTRODUCTION

Tailings are defined by LOTTERMOSER (2010) as “*the processing waste from a mill, washery or concentrator that removed the economic metals, minerals, mineral fuels or coal from the mined resource*”. Tailings of abandoned mines often contain significant amounts of metals, which could not be recovered with the existing technology at the time of mining, were not of economic interest, or were not analyzed at that time. The latter holds true for many high-tech metals like Ge, Ga, In, Te, Bi and rare earth elements (REE). Many of these metals are regarded as “critical” by the European Commission. A critical raw material has a high economic importance and a high supply risk in the EU (LØVIK et al. 2018). This study was conducted in the frame of the RIS KAVA RESEERVE project funded by the European Union. The objective of the RESEERVE project is creating a West Balkan Mineral Register to reduce exploration costs and investment risks in order to improve the self-supply of the European Union with critical metals. This study’s main scope is a fundamental characterization of some tailings in terms of their mineralogy and content of valuable metals which could be extracted to finance a possible remediation and improve the supply of the EU with critical metals.

Tailings in most cases comprise small to very small particles and hence expose a very large mineral surface area to the envi-

ronment. This mineral surface was mostly “fresh”, i.e., unweathered at the time of mining. This can present a hazard for the local environment, as leaching of toxic minerals and acid mine drainage can be greatly enhanced. This long ongoing weathering is also a threat to possible mining of the tailings as it may have changed the original ores significantly. Alternatively, large tailings can also represent an opportunity for recovering valuable metals needed for high-tech applications.

2. STUDY SITES

Material from the tailings dams of the Bor, Krivelj, Grot/Blagodat, Lece, Rudnik (all located in Serbia), and Sasa, Probištip, Bučim and Lojane (located in North Macedonia) mines were collected in order to gain an initial overview of their chemical and mineralogical composition and to estimate the potential for future metal recovery. Locations are shown in Fig. 1, while coordinates of the sampled locations, deposit status, the surface of the tailings and the quantity stored in the tailings are listed in Table 1.

Table 2 presents basic information on the ore deposit type, host rocks and reserves of the primary deposits related to the sampled tailing dams as provided in the literature. Concerning environmental hazards, the tailings of Probištip (acid mine drainage)

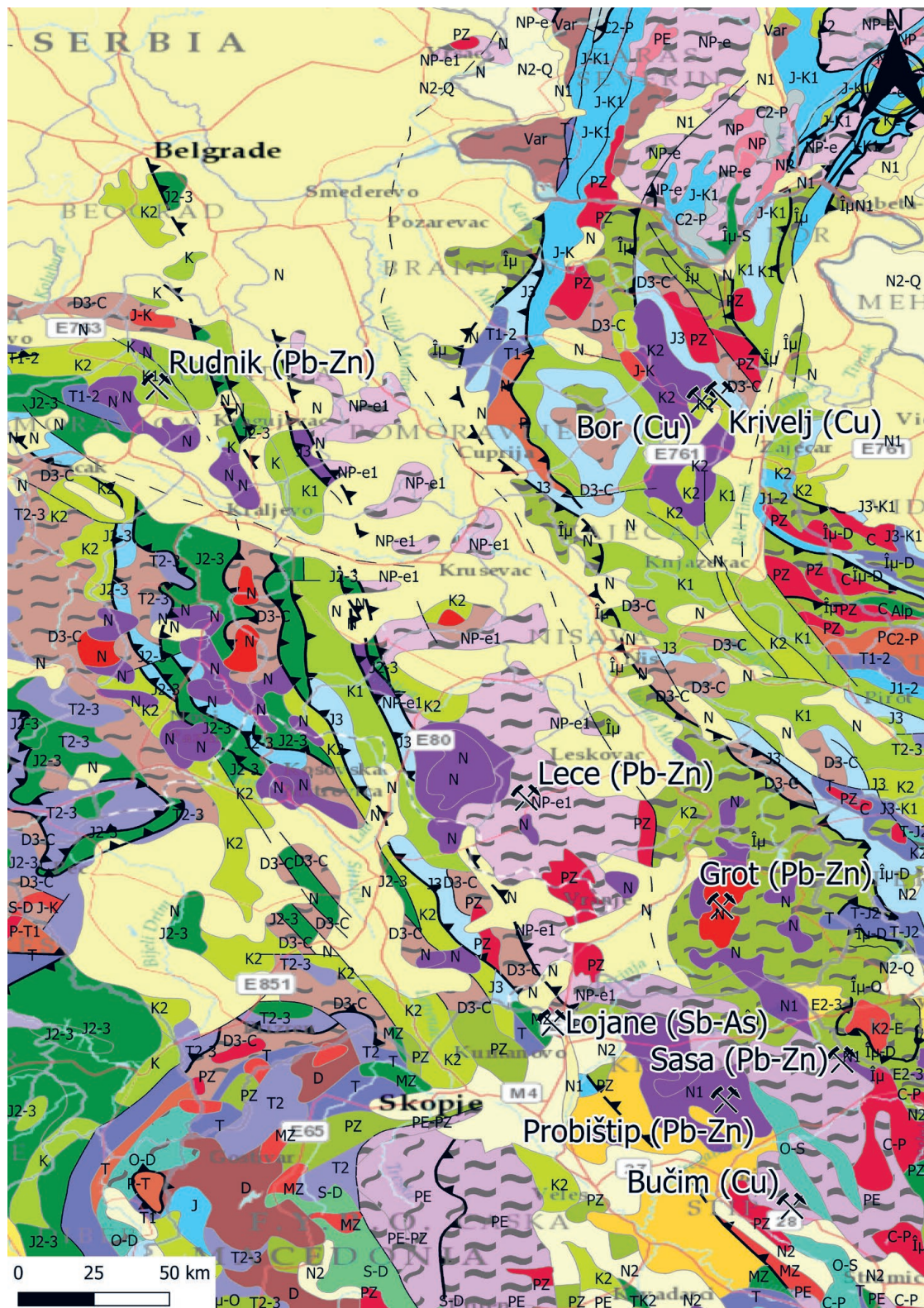


Figure 1. Overview map of the project area in Serbia and North Macedonia. The geological background map showing the abbreviated formation time of the geological units is modified from the IGME 5000 map (ASCH, 2005), details of the legend can be found there.

and Lojane (high concentrations of As and Sb in the tailings) must be noted. The localities Bor and Krivelj are both part of the same deposit.

2.1. Bor and Krivelj

The Bor deposit is part of the Bor Metallogenic Zone and formed as a porphyry copper deposit (JELENKOVIĆ et al. 2016).

It constitutes the type location of the Bor Metallogenetic Zone which is part of the Tethyan Eurasian Metallogenetic Belt (JANKOVIĆ 1977). The deposit formed in the Upper Cretaceous due to subduction related magmatism as part of the Banatic Magmatic Belt (JELENKOVIĆ et al. 2016 and references therein). Typical ore minerals are pyrite, enargite, tetrahedrite, bornite, and chalcopyrite. The reserves of the deposit are 130.5 million

Table 1. Country, WGS 84 (EPSG: 4326) coordinates, main elements, surface and quantity of material stored in the sampled tailings. All numbers are taken from GEOLOGICAL SURVEY OF SLOVENIA (2022).

Location	Country	Longitude	Latitude	Main elements	Surface (ha)	Quantity (Mt)
Lojane	N. Macedonia	21.66522	42.21793	Cr-Sb-As	3	0.5
Bučim	N. Macedonia	22.37727	41.67626	Cu	250	125
Sasa I	N. Macedonia	22.52203	42.11039	Pb-Zn	12	5
Sasa II	N. Macedonia	22.52664	42.10648	Pb-Zn	12	5
Sasa III	N. Macedonia	22.53272	42.10320	Pb-Zn	23	10
Probištip I	N. Macedonia	22.17857	41.99453	Pb-Zn	24	7
Probištip II	N. Macedonia	22.18053	41.98681	Pb-Zn	40	12
Probištip III	N. Macedonia	22.17795	41.97414	Pb-Zn	33	11
Bor I	Serbia	22.10574	44.07203	Cu	18	8
Bor II	Serbia	22.11171	44.06685	Cu	37	22
Krivelj I	Serbia	22.10699	44.13609	Cu	35	65
Krivelj II	Serbia	22.12033	44.13086	Cu	47	95
Grot	Serbia	22.16732	42.56455	Pb-Zn	26	5.5
Lece	Serbia	21.58800	42.88517	Pb-Zn	23	2.7
Rudnik	Serbia	20.48978	44.10877	Pb-Zn-Cu	41	8.7

Table 2. Overview and basic information of the ore deposits from which the evaluated tailings have been produced; SRB = Serbia, NMK = North Macedonia.

Locality	Commodity	Deposit type	Host rocks	Reserves (Mine)	Mining	Reference
Bor (SRB)	Cu, Au, Ag	High sulphidation porphyry Cu	Intermediary magmatites	14.5 Mt	Active	JELENKOVIĆ et al., 2008; JELENKOVIĆ et al., 2016
Krivelj (SRB)	Cu, Au, Ag	High sulphidation porphyry Cu	Intermediary magmatites	690 Mt	Active	JELENKOVIĆ et al., 2008; JELENKOVIĆ et al., 2016
Grot/Blagodot (SRB)	Pb, Zn	Hydrothermal Pb-Zn	Granitoids, gneisses, limestones	0.4 Mt	Inactive	JELENKOVIĆ et al., 2008; DJOKIĆ et al., 2012
Lece (SRB)	Pb, Zn, Au	Epithermal gold	Andesites with quartz veins	3.3 Mt	Active	JELENKOVIĆ et al., 2008
Rudnik (SRB)	Pb, Zn, Cu, Ag	Skarn	Limestones, Flysch, Quartzlatites	3 Mt	Active	JELENKOVIĆ et al., 2008
Sasa (NMK)	Pb-Zn	Skarn	Marble, schist	12.6 Mt	Active	STRMIĆ PALINKAS et al., 2013
Probištip (NMK)	Pb-Zn	Hydrothermal Pb-Zn	Intermediary Volcanics	9.8 Mt	Active	SERAFIMOVSKI et al., 2006; SPASOVSKI & SPASOVSKI, 2013; TASEV et al., 2018
Bučim (NMK)	Cu, Au, Ag	Porphyry Cu	Intermediary plutonites in gneisses	34 Mt	Active	SERAFIMOVSKI et al., 1996
Lojane (NMK)	As, Sb, Cr	Veins at contact of rhyolite and podiform chromite	Rhyolite and podiform chromite	0.3 Mt	Inactive	CASSARD et al., 2008; TASEV et al., 2017; KOLITSCH et al., 2018

tons at 0.56 % Cu, 0.24 g/t Au, and 1.66 g/t Ag; the inferred resources are 450.8 million tons at 0.49 % Cu, 0.1 g/t Au, and 1.72 g/t Ag (JELENKOVIĆ et al. 2008). The tailings of Bor (Fig. 2 a, b) cover an area of 55 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022). The Krivelj mine and its tailings dam covering an area of 82 ha and are located 3 km north of the Bor mine (Fig. 2 c) (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.2. Grot/Blagodot

The Blagodot deposit is a hydrothermal-replacement Pb-Zn deposit hosted by granitoids, gneisses, and limestones (JELENKOVIĆ et al. 2008). Characteristic ore minerals are galena, sphalerite, and pyrite (JELENKOVIĆ et al. 2008). DJOKIĆ et al. (2012) describe the ore as mainly composed of quartz followed by clay minerals, calcite, siderite, feldspars, and haematite; 17 % of the ore is sulfides, mainly pyrite, sphalerite, galena, and chalcopryrite. The Grot tailings dam hosts about 5.5 million tons of sand size fraction material (grain size around 0.5 mm) produced in the processing plant of the Blagodot ore field, which ceased production 100 years ago (DJOKIĆ et al. 2012). The tailings are heterogenous and metal contents range from 1500-18600 ppm Pb, 2300-4000 ppm Zn, 75-600 ppm Cu, 18-158 ppm As, and 7000-10000 ppm Mn, respectively (DJOKIĆ et al. 2012). The tailings of Grot (Fig. 2 d) cover an area of 26 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.3. Lece

The Lece mine is situated in the Lece volcanic complex in SE Serbia at the border of the Eastern Vardar Ophiolite zone and the Serbo-Macedonian unit (VELOJIĆ et al. 2018). The deposit is a high and low sulphidation epithermal gold mineralization hosted by andesites and quartz veins (JELENKOVIĆ et al. 2008), which formed during Oligocene-Miocene magmatism (VELOJIĆ et al. 2018). Ore minerals are galena, sphalerite, pyrite, and gold (JELENKOVIĆ et al. 2008). Reserves are 3.4 million tons at 1.8% Pb, 3.5% Zn, and 3.3 g/t Au (JELENKOVIĆ et al. 2008). The tailings of Lece (Fig. 3 a) cover an area of 23 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.4. Rudnik

The Rudnik deposit is a hydrothermal skarn Pb-Zn deposit hosted by limestones, flysch and quartz latites (JELENKOVIĆ et al. 2008). The deposit is part of the Šumadija metallogenetic zone in the Vardar zone and was formed by Oligocene-Miocene magmatism (STOJAVONIĆ et al. 2006) from fluids of magmatic origin (STOJAVONIĆ et al. 2018). The main ore minerals are galena, sphalerite, scheelite, chalcopryrite, cassiterite, and bismuthinite (STOJAVONIĆ et al. 2006). Resources are 3.4 Mt at a grade of 2% Pb, 2% Zn, 0.4% Cu, and 89 g/t Ag (JELENKOVIĆ et al.

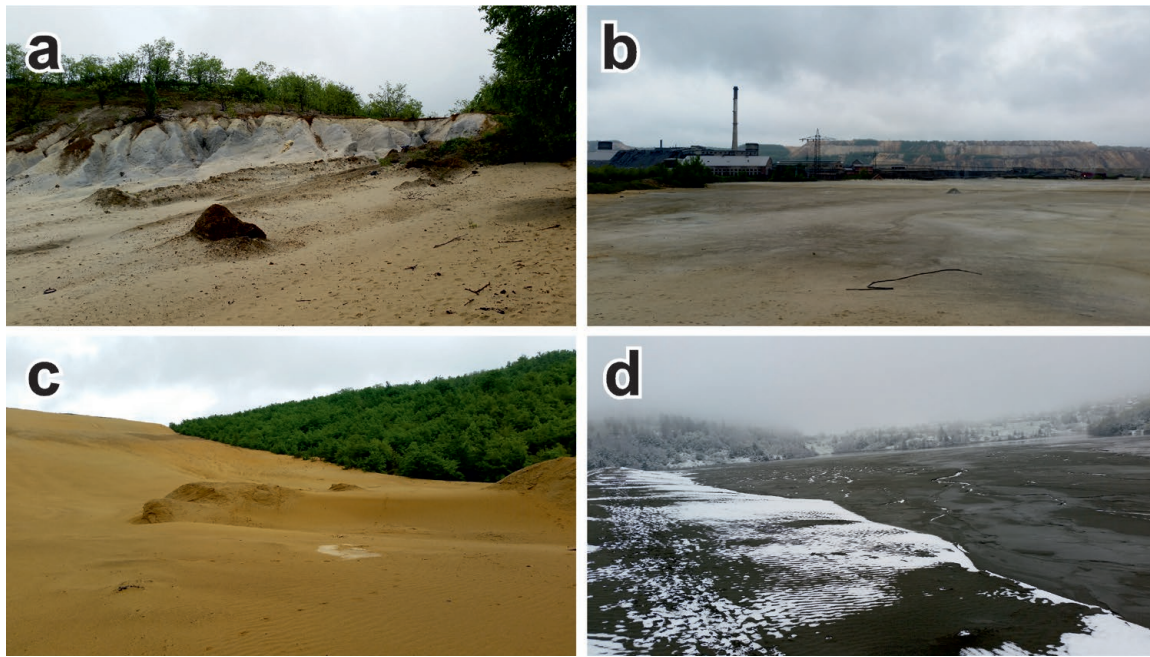


Figure 2. Field images of a, b - the Bor tailings; c - the Krivelj tailings; d - the Grot tailings.

2008). The tailings of Rudnik (Fig. 3 b) cover an area of 41 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.5. Sasa

The Sasa Pb-Zn deposit is classified as epigenetic-hydrothermal skarn mineralization related to Oligocene magmatism (TUFAR & ŠTRUCL 1984; STRIMIĆ PALINKAS et al. 2013). Hence the described minerals are typical skarn minerals: calc-silicates (pyroxenes, garnets, ilvaite, epidote), magnetite, pyrite, and pyrrothite, but there are also open-space filling hydrothermal minerals such as galena, sphalerite, pyrite, and minor chalcopyrite with abundant quartz and carbonates (STRIMIĆ PALINKAS et al. 2013). The reserves are 12.6 million tons at 7.5 % lead and zinc

(STRIMIĆ PALINKAS et al. 2013). The tailings of Sasa (Fig. 3 c) cover an area of 47 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.6. Probištip

The Probištip tailings dam comprises tailings of the Zletovo sub-volcanic hydrothermal Pb-Zn deposit related to Cenozoic volcanism (SERAFIMOVSKI et al. 2006). The deposit has been mined from medieval times until recently (SPASOVSKI & SPASOVSKI 2013). An apparently long ongoing problem is acid mine drainage as the river into which the mine dewaterers (SPASOVSKI & SPASOVSKI 2013) is called Kiselnica, which can be literally translated to “acid”. It is unknown, if this name refers to natural

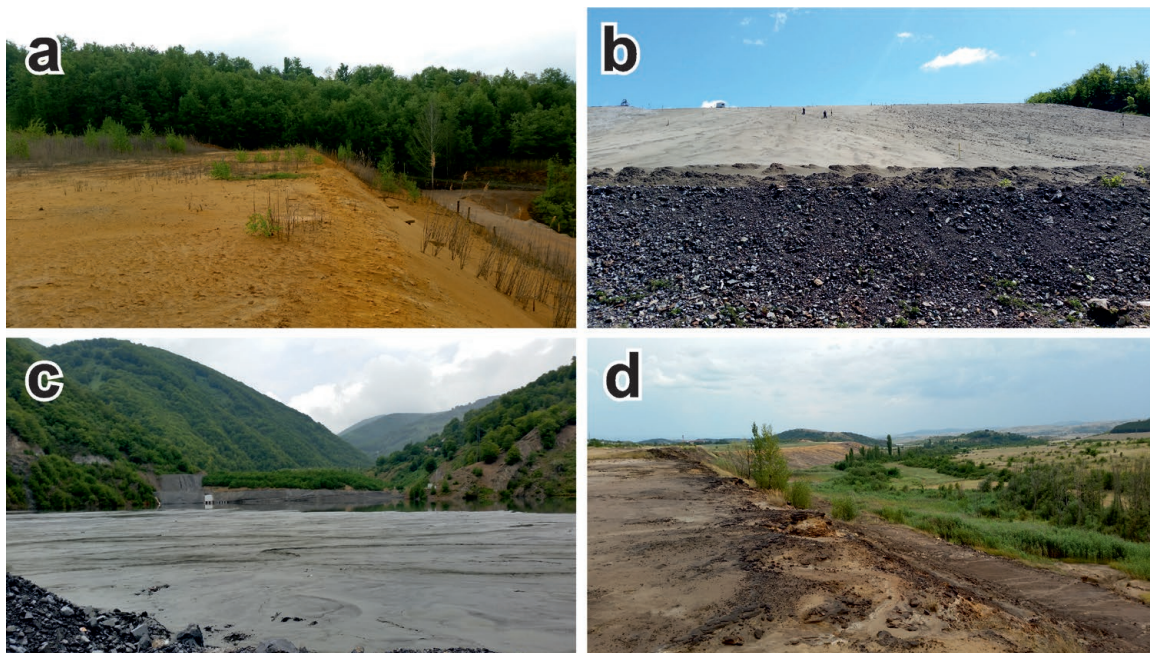


Figure 3. Field images of a - the Lece tailings; b - the Rudnik tailings; c - the Sasa tailings; d - the Probištip tailings.

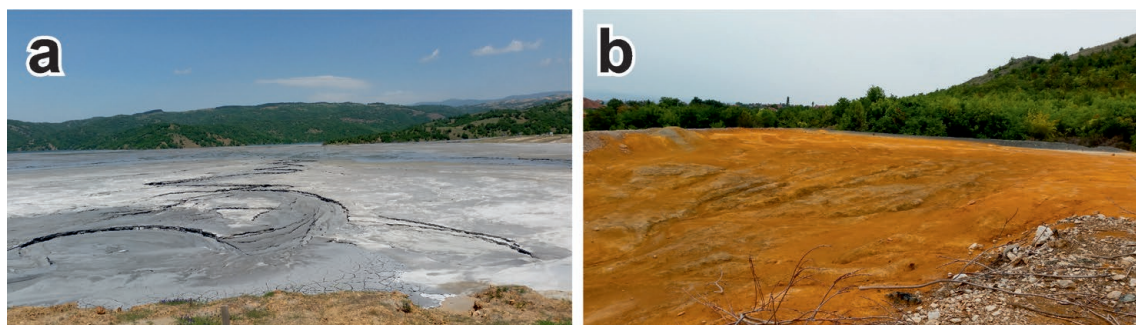


Figure 4. Field images of a - the Bučim tailings; b - the Lojane tailings.

acid drainage from the deposit, or acid mine drainage from the medieval mines. The main ore minerals are galena, sphalerite, pyrite, chalcopyrite, and siderite (SERAFIMOVSKI et al. 2006). The tailings dam (Fig. 3 d) covers an area of 97 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022) and hosts 4 million tons at an average thickness of 9.2 m and holds a metal content of 0.37 % Pb and 0.32 % Zn (SPASOVSKI & SPASOVSKI 2013).

2.7. Bučim

The Bučim deposit is a small porphyry Cu deposit hosted by latites and andesites intruded into gneisses during the Oligocene (SERAFIMOVSKI et al. 1996). The deposit is part of the Lece-Chalkidiki metallogenic zone. The main ore minerals are chalcopyrite, pyrite, magnetite, haematite, cubanite, vallerite, native gold, and bornite with chalcopyrite dominating (SERAFIMOVSKI et al. 1996). The deposit is still in production and reserves are 34 million tons at 0.267 % Cu (CASSARD et al. 2015). Additional precious metals are Au (0.35 g/t), and Ag (1 g/t) (SERAFIMOVSKI et al. 1996). The tailings of Bučim (Fig. 4 a) cover an area of 250 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

2.8. Lojane

Lojane is a former As, Sb, and Cr mine in Northern Macedonia, which was in operation from 1923-1979 (TASEV et al. 2017). Veins formed at the contact of rhyolite and podiform chromite bearing ophiolite (KOLITSCH et al. 2018). The main ore minerals are chromite and As and Sb phases: orpiment, realgar, and stibnite; additional phases include bravoite, vaesite, catterite, pyrite, marcasite, molybdenite, and pitchblende (TASEV et al. 2017). See KOLITSCH et al. (2018) for an exhaustive list of primary and secondary minerals. The reserves in the mine are estimated at 0.3 million tons (CASSARD et al. 2015). The completely unprotected tailings hold 3.5 million tons of which 15 000 tons are 50 % As concentrate (TASEV et al. 2017). Currently, the acid mine drainage potential is low, but the waste material is distributed by wind, surface water and groundwater (UIBLEIN 2021). The tailings of Lojane (Fig. 4 b) cover an area of 3 ha (GEOLOGICAL SURVEY OF SLOVENIA 2022).

3. METHODS

The 10 kg samples were collected by the Geological Survey of Slovenia from flotation tailings, which were already affected by remnants of vegetation. Representative samples were obtained by taking composite samples from the surface, trenches, and hand-drilled holes. At the facilities of the Geological Survey of Slovenia, the samples were dried at 40 °C, crushed and homogenized. The resulting fine sand-size material was embedded in resin and

polished for examination by reflected light microscopy and scanning-electron microscopy (SEM-EDX) employing a Zeiss Evo MA 10 with Bruker energy-dispersive analysis system. Additionally, for sample Pr01a from Probištip, a heavy mineral concentrate was produced by sieving the sample to a grain size between 60 µm and 500 µm, and separation with bromoform (density of 2.89 g/cm³). After washing and drying, the sample was embedded in resin and polished for examination by SEM-EDX. Subsequently, sphalerite identified in sample Pr01a was examined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), utilizing an ESI Nd:YAG laser ablation system coupled to a PerkinElmer NexION 2000 ICP-MS. LA-ICP-MS analyses were carried out at the Department of Applied Geosciences and Geophysics, Montanuniversität Leoben in Austria. Helium was used as carrier gas (flow rate of 0.75 L/min) and mixed with Ar during transport into the ICP-MS. A spot size of 50 µm was used for all analyses with an on-mineral fluency of 2-3 J/cm². Individual spot analyses are composed of 30s background collection (pre-ablation) followed by 60s of ablation and data collection. Thirty seconds of washout followed each laser ablation cycle. Twenty-nine isotopes were measured for each spot analysis: ³⁴S, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁵Cu, ⁶⁶Zn, ⁶⁷Zn, ⁷¹Ga, ⁷²Ge, ⁷⁴Ge, ⁷⁵As, ⁸²Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁹⁷Au, ²⁰¹Hg, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi.

Trace element quantification was done with the in-house sphalerite matrix-matched sinter pressed powder pellet reference material MUL-ZnS1 (ONUK et al. 2017) using ³⁴S as the internal standard. The MUL-ZnS1 is not suitable for quantification of Au, Tl and Hg, thus the USGS polysulfide MASS-1 (WILSON et al. 2002) was used for these elements. To ensure the quality of the analyses, the MASS-1 was used for quality control. The Iolite 4 software (PATON et al. 2011) was utilized for data reduction of the measured count signals into concentrations and detection limits. Detection limits were calculated using the 'Howell et al. 2010' method found in the Iolite 4 software. Instrumental drift correction was done by repeatedly measuring the reference materials. Time-resolved count signals of the different isotopes were scrutinized during data reduction to identify possible inclusions within the ablated sphalerite.

Major and trace elements of all samples were analyzed by a commercial laboratory (Activation Laboratories, Canada) using the packages 4B-INAA(Litho), 4B1, 4F-C, S, 4F-CO2, 4LITHO (1-10).

4. RESULTS

All samples showed traces of organic material (mainly plant roots) and signs of advanced weathering (mostly reddish colours and the typical smell of weathered sulfides) and have a grain size

Table 3. Mineral abundances and locking of sulfides by deposit. Potential ore minerals are in bold.

Locality	Very abundant minerals	Abundant minerals	Rare minerals	Accessories	Grain size/ Grain size sulfides	Locking of sulfides
Bor (SRB)	Quartz, plagioclase, orthoclase	Biotite, FeOx, pyrite, kaolinite, rutile	Chalcopyrite, baryte, titanomagnetite	Alunite, colusite, enargite	0-300 µm/10-50 µm	Mostly intergrown with quartz
Krivelj (SRB)	Quartz, plagioclase, orthoclase	Biotite, FeOx, pyrite, chalcopyrite , chlorite, rutile, galena , ilmenite	Baryte , apatite, allanite, hematite, magnetite, phlogopite, xenotime, zircon		1-200 µm/1-50 µm	Free and intergrown with quartz
Grot/Blagodot (SRB)	Quartz, pyrite	Biotite, FeOx, calcite, siderite, rutile, jacobsite	Plagioclase, orthoclase, chlorite, pyroxene, apatite, sphalerite , hematite, titanite	Zircon	10-300 µm/10-30 µm	Free and intergrown with quartz
Lece (SRB)	Quartz, plagioclase, orthoclase	FeOx	Baryte, galena, sphalerite , kaolinite, rutile, titanomagnetite, zircon	Hematite, Fe-sulfates, tetrahedrite-(Zn)	0-200 µm/0-30 µm	Inclusions in quartz
Rudnik (SRB)	Amphibole, quartz	Andradite, pyroxene, chlorite, FeOx, orthoclase, titanite	Galena , ilmenite, pyrrhotite, sphalerite , zircon	Anglesite	5-200 µm/5-20 µm	Mostly present as inclusions in silicates
Sasa (NMK)	Kaolinite, Quartz	Augite, chlorite, orthopyroxene, clinopyroxene, epidote, andradite garnet, FeOx, galena , Mn-calcite, muscovite, orthoclase, pyrite	Apatite, pyrrhotite , rutile, siderite, sphalerite	Monazite, rhodonite, zircon	5-200 µm/5-200 µm	Free and intergrown with silicates
Probištip (NMK)	Epidote, quartz	Baryte, calcite, chlorite, Mn-calcite, FeOx, galena , orthoclase, plagioclase, pyrite, rhodochrosite, Mn-siderite	Albite, phlogopite, pyrrhotite , rutile, sphalerite	Chalcopyrite, magnetite, manganosite	10-300 µm/10-100 µm	Pyrite is mostly free and hosts inclusions of the other sulfides
Bučim (NMK)	FeOx, orthoclase, plagioclase, quartz	Biotite, phlogopite, pyrite, titanite	Apatite, chalcopyrite , epidote, ilmenite, pyrrhotite, rutile, zircon	Molybdenite , xenotime	5-200 µm/5-200 µm	Free and intergrown with silicates
Lojane (NMK)	FeOx, olivine, quartz, realgar	Albite, ankerite, dimorphite , dolomite, magnesite, orthoclase, plagioclase, pyrite, siderite	Angelellite, cervantite, chromite , enstatite, muscovite, phlogopite, stibnite, wakabayashilite		5-200 µm/5-200 µm	Mostly free

in the silt to fine-sand range (0.002 mm to 0.2 mm). Many grains had weathered rims and showed fractures probably related to processing. The weathered rusty iron-rich rims are indicated as FeOx as the determination of the water/OH content is not possible using SEM analysis and a full characterization of those phases was not relevant for this study. Table 3 presents the minerals identified by SEM in each sample. Mineral abundances were estimated qualitatively based on the SEM analyses. Rare minerals were identified a few times (less than 10) per sample and accessory minerals were only identified once or twice per sample. Mineral formulae of uncommon minerals are given in the Appendix.

In all cases except for Grot/Blagodot and Lojane, the samples were dominated by large silicate grains, mainly quartz and feldspars. In the case of Grot/Blagodot, the sample was dominated by large grains of quartz and pyrite. The sample from Lojane was dominated by iron oxides, olivine, quartz, and realgar. In Figs. 5 - 7, representative mineral associations of the tailings samples are illustrated using back-scattered electron images (BSE).

4.1. Bor and Krivelj

The samples from Bor and Krivelj (Fig. 5a, b) show a bimodal grain size distribution and mainly comprise large silicate grains of quartz, plagioclase, and orthoclase in the 100 µm to 300 µm range. In the smaller size class of <5 µm to 50 µm, biotite, iron oxides, pyrite, kaolinite, and rutile are abundant in the Bor tailings. In the Krivelj tailings, biotite, FeOx, pyrite, chalcopyrite, galena, chlorite, rutile, and ilmenite prevail. Rare minerals in the Bor tailings are chalcopyrite, baryte, and titanomagnetite with alunite, colusite, and enargite as accessories. Rare minerals in the Krivelj tailings are baryte, apatite, allanite, haematite, magnetite, phlogopite, xenotime, and zircon.

In the Bor tailings, the sulfides are mostly intergrown with quartz. In the Krivelj tailing, part of the sulfides occur as free grains. In both tailings, the sulfides have a grain size of 1 µm to 50 µm.

4.2. Grot/Blagodot

The sample from Grot (Fig. 5c) shows a polymodal size distribution with 100 µm to 300 µm, 25 µm to 50 µm, and < 10 µm size classes. The two larger size classes are dominated by quartz and pyrite, which forms liberated grains of up to 50 µm and also occurs as inclusions in quartz. Abundant minerals in the two smaller size classes are biotite, FeOx, calcite, siderite, rutile, and jacobsite. Rare minerals are baryte, apatite, allanite, haematite, magnetite, phlogopite, xenotime, and zircon. The sulfides reach a grain size of 10 µm to 30 µm and may be present as liberated grains and as inclusions in quartz.

4.3. Lece

The sample from Lece (Fig. 5d) shows a bimodal grain size distribution with the majority (by volume) of grains in the 50 - 200 µm size range and a fine fraction of < 5 µm. The main minerals are quartz, plagioclase, and orthoclase along with FeOx as an abundant phase. Baryte, galena, sphalerite, kaolinite, rutile, titanomagnetite, and zircon are rare minerals. Haematite, Fe-sulfates, and tetrahedrite-(Zn) are present as accessories. The sulfides attain a grain size of <5 µm to 30 µm and are mainly present as inclusions in quartz.

4.4. Rudnik

The sample from Rudnik (Fig. 6a) shows a bimodal grain size distribution with the majority (by volume) of grains in the 30 µm to 200 µm size range and a fine fraction with a size of ~ 5 µm.

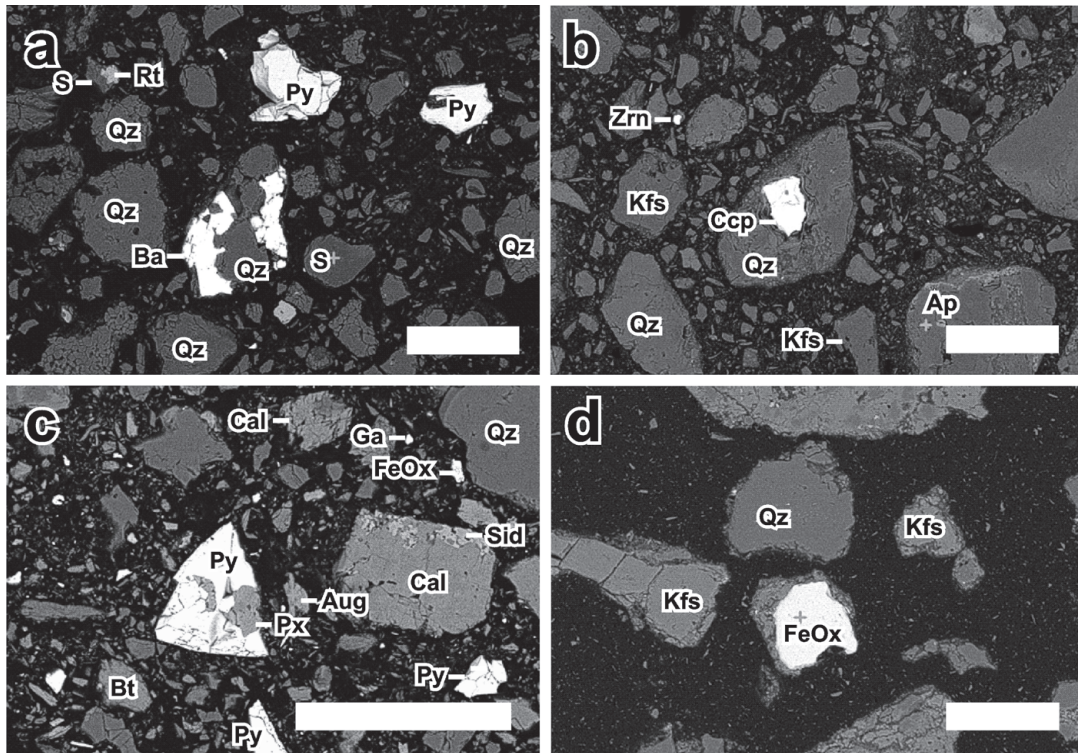


Figure 5. Overview BSE images of tailings samples. a - Bor; b - Krivelj; c - Grot; d - Lece. Abbreviations: Aug = augite, Ba = baryte, Bt = biotite, Cal = calcite, FeOx = iron oxides, Ga = galena, Kfs = K-feldspar, Px = pyroxene, Py = pyrite, Qz = quartz, Rt = rutile, S = sulfate, Sid = siderite. The scale bar has a length of 100 µm.

The main minerals are amphibole and quartz. Abundant minerals are andradite, pyroxene, chlorite, FeOx, orthoclase, and titanite. Rare minerals are galena, ilmenite, pyrrhotite, sphalerite, and zircon. The sulfides have a grain size of 5 µm to 30 µm and are mainly present as inclusions in quartz.

4.5. Sasa

The sample from Sasa (Fig. 6b) shows a bimodal grain size distribution with the majority of grains in the 30 - 200 µm size range and a fine fraction with a size of ~ 5 µm. The main minerals are kaolinite and quartz. Abundant minerals are chlorite, orthopy-

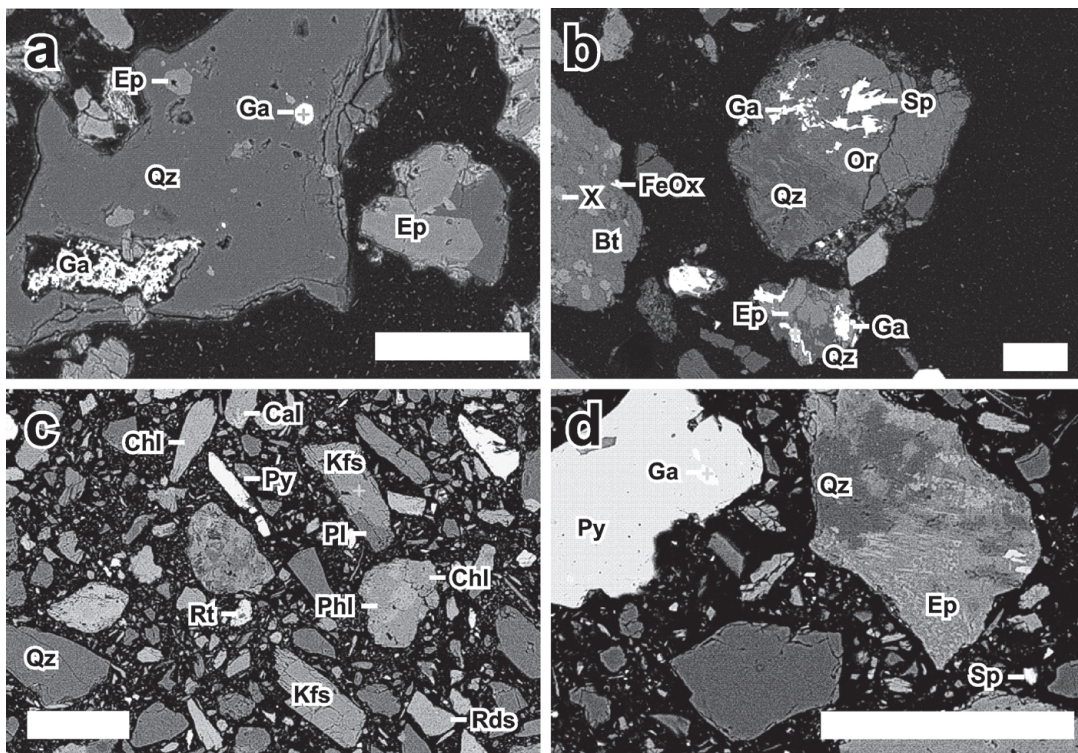


Figure 6. a - Overview BSE image of the sample from Rudnik; Detail BSE images of the samples from: b - Sasa; c, d - Probištip. Abbreviations: Bt = biotite, Cal = calcite, Chl = chlorite, Ep = epidote, FeOx = iron oxides, Ga = galena, Kfs = K-feldspar, Or = orthoclase, Phl = phlogopite, Pl = plagioclase, Py = pyrite, Qz = quartz, Rds = rhodosite, Rt = rutile, Sp = sphalerite, X = Xenotime. The scale bar has a length of 100 µm.

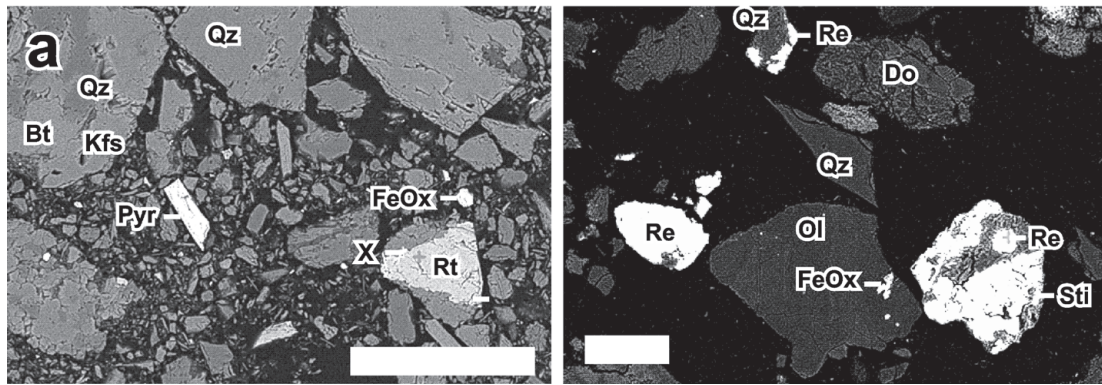


Figure 7. Overview BSE images of: a - the sample from Bučim; b - the sample from Lojane. Abbreviations: Bt = biotite, Do = dolomite, FeOx = iron oxides, Kfs = K-feldspar, Ol = olivine, Pyr = pyrrhotite, Qz = quartz, Re = realgar, Rt = rutile, Sti = stibnite, X = xenotime. The scale bar has a length of 100 µm.

roxene, clinopyroxene (e.g., augite), orthoclase, muscovite, epidote, FeOx, galena, andradite garnet, Mn-calcite, and pyrite. Rare minerals are apatite, rutile, siderite, pyrrhotite, and sphalerite. Accessories are monazite, rhodonite, and zircon. The grain size of sulfides that are either liberated or intergrown with silicates, ranges from 5 µm to 200 µm.

4.6. Probištip

The grain size of the sample from Probištip (Fig. 6c, d) ranges from 10 - 300 µm. The main minerals are epidote and quartz. Abundant minerals are baryte, calcite, Mn-calcite, rhodochrosite, Mn-siderite, FeOx, galena, pyrite, chlorite, orthoclase, and plagioclase. Rare minerals include albite, phlogopite, rutile, pyrrhotite, and sphalerite. Accessories are chalcocopyrite, magnetite, and manganosite. Pyrite forms mostly free grains and may host sulfide inclusions.

4.7. Bučim

The sample from Bučim (Fig. 7a) shows a bimodal grain size distribution with 50 - 200 µm and < 5 µm size classes. The main minerals are FeOx, orthoclase, plagioclase, and quartz. Abundant minerals are biotite, phlogopite, pyrite, and titanite. Rare minerals are apatite, chalcocopyrite, epidote, ilmenite, pyrrhotite, rutile, and zircon. Accessories are molybdenite and xenotime. The sulfides have grain sizes from 5 - 200 µm and occur either as liberated grains or intergrown with silicates.

4.8. Lojane

The sample from Lojane (Fig. 7b) shows a bimodal size distribution with 50 - 200 µm and 5 - 20 µm size classes. The main minerals are FeOx, olivine, quartz, orpiment and realgar. Abundant minerals are albite, ankerite, dimorphite, dolomite, magnesite, orthoclase, plagioclase, pyrite, and siderite. Rare minerals are angelellite, cervantite, chromite, enstatite, muscovite, phlogopite, stibnite, and wakabayashilite. The sulfides are mostly free and present in all size classes.

5. BULK CHEMICAL ANALYSES

Table 4 presents the analytical whole-rock data of the samples. In the following, the measured concentrations of the major commodity metals Cu, Zn, Pb, Ag and Au are briefly described, along with the levels of critical metals to the EU (Co, Ga, Ge, In, Sb) (LØVIK et al. 2018) and potentially toxic trace elements (As, Cd, Tl).

The Bor and Krivelj tailings show expected similarities as they originate from the same deposit. However, the sample from Krivelj shows a higher amount of Cu (560 ppm), whereas S concentrations are higher in the Bor sample, indicating a higher proportion of pyrite. Based on the SEM analyses, Cu is mainly hosted by chalcocopyrite. Concentrations of Au are higher in Bor (0.3 ppm) than in Krivelj (0.04 ppm). Compared to more massive Cu-Zn-Pb sulfide ores, the concentrations of critical metals are generally low with 3 ppm Co, 15 ppm Ga, 2 ppm Ge, 0.4 ppm Sb, < 0.2 ppm In for Krivelj, with the values for Bor even being slightly lower.

The Grot/Blagodot tailings contain Pb (3870 ppm) and Zn (2980 ppm), Cu (96 ppm) and REE (60 ppm Ce). Lead and Zn are hosted by galena and sphalerite, respectively. Cu bearing minerals were not observed. Critical element concentrations are low, but potentially toxic elements are slightly elevated (101 ppm As, 16 ppm Cd, 7 ppm Tl). The concentrations of Au (0.08 ppm) and Ag (<1 ppm) are too low to regard these elements as potential bonuses for a case for reprocessing.

The Lece tailings contain 455 ppm Zn, 1680 ppm Pb, 0.5 ppm Au, but also 722 ppm As and 9.3 ppm Tl. Zinc is present in sphalerite, Pb in galena, and Ba (600 ppm) in baryte. No As-bearing minerals were discovered by SEM analysis, suggesting that As is hosted by Fe oxide or other secondary phases. The low S concentrations (0.2%) indicate that pyrite is only of very minor importance. Among the critical metals, only Sb is of importance, showing concentrations of 75 ppm.

The Rudnik tailings contain 160 ppm Cr, 230 ppm Cu, 540 ppm Zn, and 1710 ppm Pb. No Cr or Cu bearing minerals were found, but as serpentinites are present in the deposit (STOJAVONIĆ et al. 2018), such Cr contents can be expected. It remains unclear though, which mineral phase hosts the Cr (probably chromite or Cr-bearing chlorite). Zinc is hosted by sphalerite; Pb is mainly hosted by galena, and additionally by anglesite. Precious metal concentrations are low (5.7 ppm Ag, <2 ppb Au), as well as high-tech metals. Among the potentially toxic elements, As has a concentration of 67 ppm, whereas Cd and Tl are below 1 ppm. The Rudnik sample carries the highest concentration of Bi (11 ppm) analyzed in this study.

The Sasa tailings contain 4540 ppm Pb, 1900 Zn ppm, 90 ppb Au, 240 ppm Cu, and 520 ppm Ba. Zinc is present as sphalerite, Pb as galena, and Ce (54 ppm) mainly in monazite. From the literature (STRIMIĆ PALINKAS et al. 2013) it can be expected that Cu is present in chalcocopyrite and Ba in baryte. Among the high-tech metals, Ge attains the highest value recorded in this

Table 4. Chemical analysis data. DL = detection limit; methods: FUS-ICP = lithium borate fusion and ICP-MS/OES analysis; GRAV = gravimetric; INAA = instrumental neutron activation analysis; TD-ICP = total digestion ICP-OES; CO2 = infrared spectroscopy.

Analyte	Unit	DL	Method	Bor	Krivelj	Grot/ Blagodot	Lece	Rudnik	Sasa	Probištip	Bučim	Lojane
SiO ₂	%	0.01	FUS-ICP	65.65	62.73	52.83	82.16	37.25	45.72	56.79	64.45	35.57
Al ₂ O ₃	%	0.01	FUS-ICP	12.1	14.74	9.47	6.77	7.86	8.03	8.31	13.61	3.29
Fe ₂ O ₃ (T)	%	0.01	FUS-ICP	2.7	5.5	11.36	3.41	18.12	16.22	13.45	6.35	4.79
MnO	%	0.001	FUS-ICP	0.005	0.029	1.379	0.015	0.287	1.265	3.918	0.087	0.073
MgO	%	0.01	FUS-ICP	0.04	1.66	2.01	0.05	2.1	1.92	0.29	2.28	4.81
CaO	%	0.01	FUS-ICP	0.56	3.22	9.35	0.05	15.77	10.96	0.94	2.45	5.32
Na ₂ O	%	0.01	FUS-ICP	0.78	2.66	0.71	0.19	0.26	0.19	0.06	2.83	0.22
K ₂ O	%	0.01	FUS-ICP	1.06	1.73	1.91	3.65	0.63	1.1	1.99	4.54	0.7
TiO ₂	%	0.001	FUS-ICP	0.485	0.468	0.844	0.242	0.382	0.51	0.376	0.669	0.281
P ₂ O ₅	%	0.01	FUS-ICP	0.11	0.14	0.34	0.08	0.08	0.39	0.14	0.25	0.03
LOI	%		GRAV	16.74	7.64	7.45	2.57	11.9	11.62	10.86	2.88	30.27
Total	%	0.01	FUS-ICP	100.2	100.5	97.66	99.2	94.62	97.91	97.13	100.4	85.35
CO ₂	%	0.01	CO ₂	0.03	0.06	5.86	< 0.01	0.13	1.15	4.09	0.89	8.25
Au	ppb	2	INAA	351	39	77	508	< 2	90	77	88	< 2
Ag	ppm	0.3	TD-ICP	1.1	< 0.3	1	2.3	5.7	5.1	17	< 0.3	< 0.3
As	ppm	0.5	INAA	22.5	4.8	101	690	66.6	301	306	47.7	> 10000
Ba	ppm	2	FUS-ICP	897	275	531	595	103	522	6070	723	340
Be	ppm	1	FUS-ICP	< 1	2	3	1	2	4	2	3	2
Bi	ppm	0.4	FUS-MS	0.4	< 0.4	< 0.4	< 0.4	11.3	3.3	2.7	1.3	< 0.4
Br	ppm	0.5	INAA	2.3	2.3	5	4	2.8	1.3	3.2	2.5	< 0.5
Cd	ppm	0.5	TD-ICP	< 0.5	< 0.5	16.3	< 0.5	0.9	15.9	18.2	< 0.5	< 0.5
Ce	ppm	0.1	FUS-MS	10.3	21.1	59.9	15.1	36.9	54.1	42.9	74.1	14.5
Co	ppm	1	FUS-MS	2	3	17	2	11	13	8	16	60
Cr	ppm	5	INAA	12	21	73	34	151	54	24	44	1710
Cs	ppm	0.5	FUS-MS	< 0.5	0.5	8.1	6.4	6	3.8	13.1	2.3	17.3
Cu	ppm	1	TD-ICP	177	562	96	47	226	240	302	361	27
Dy	ppm	0.1	FUS-MS	0.2	1.6	4.1	0.8	2.7	3.7	4.6	4.7	1.9
Er	ppm	0.1	FUS-MS	0.2	1	2.1	0.5	1.5	2	2.9	2.6	1.1
Eu	ppm	0.05	FUS-MS	0.15	0.53	1.52	0.34	0.78	1.11	1.34	1.27	0.4
Ga	ppm	1	FUS-MS	10	15	17	9	14	17	17	19	5
Gd	ppm	0.1	FUS-MS	0.3	1.5	4.8	0.8	3	4.1	4.1	5.3	1.8
Ge	ppm	1	FUS-MS	3	2	3	2	3	5	2	2	3
Hf	ppm	0.2	FUS-MS	1.4	2.3	3.9	1.6	2.3	2.9	3.7	5.4	1.6
Ho	ppm	0.1	FUS-MS	< 0.1	0.3	0.7	0.2	0.5	0.7	0.9	0.9	0.4
In	ppm	0.2	FUS-MS	< 0.2	< 0.2	< 0.2	< 0.2	0.3	1.4	9.1	< 0.2	< 0.2
Ir	ppb	5	INAA	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
La	ppm	0.1	FUS-MS	5.5	10.3	29.3	9.3	20.9	27.6	22.8	44.2	7.3
Lu	ppm	0.01	FUS-MS	0.06	0.19	0.3	0.09	0.24	0.32	0.43	0.42	0.17
Mo	ppm	2	FUS-MS	2	16	4	< 2	< 2	4	7	11	79
Nb	ppm	1	FUS-MS	3	4	20	3	7	13	7	10	5
Nd	ppm	0.1	FUS-MS	3.6	9.9	27.5	5.8	17.9	24.1	18.8	30	7.5
Ni	ppm	1	TD-ICP	1	4	62	4	63	40	13	28	1090
Pb	ppm	5	FUS-MS	51	8	2710	1420	1710	3560	4640	39	89
Pr	ppm	0.05	FUS-MS	1.07	2.49	6.82	1.63	4.61	6.31	4.89	8.15	1.79
Rb	ppm	2	FUS-MS	2	31	126	132	50	71	111	124	42
S	%	0.001	TD-ICP	5.88	1.18	3.07	0.238	4.5	5.85	2.67	0.658	8.26
Sb	ppm	0.2	INAA	1.2	0.4	3.6	75.4	13.8	5.5	23.6	9.5	> 10000
Sc	ppm	0.1	INAA	7.4	9.9	9.3	4.6	9.2	8.8	9.8	12.5	10.5
Se	ppm	3	INAA	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Sm	ppm	0.1	FUS-MS	0.4	1.8	5.6	1	3.4	4.7	4.1	6.1	1.7
Sn	ppm	1	FUS-MS	3	1	2	1	18	24	3	5	1
Sr	ppm	2	FUS-ICP	1205	553	253	138	379	173	304	319	80
Ta	ppm	0.1	FUS-MS	0.2	0.3	1.4	0.3	0.6	0.9	0.7	1	0.4
Tb	ppm	0.1	FUS-MS	< 0.1	0.3	0.8	0.1	0.5	0.7	0.8	0.9	0.3
Th	ppm	0.1	FUS-MS	1.4	2.8	5.5	4	5.9	6.5	12.9	21	2.5
Tl	ppm	0.1	FUS-MS	0.3	1.6	7.3	9.3	0.5	3.4	8.5	3.3	38.6
Tm	ppm	0.05	FUS-MS	< 0.05	0.16	0.28	0.08	0.21	0.29	0.43	0.35	0.16
U	ppm	0.1	FUS-MS	0.5	1	3.1	1.7	1.5	3.8	10.2	8.1	19.6
V	ppm	5	FUS-ICP	119	139	104	53	81	134	89	135	48
W	ppm	1	FUS-MS	4	< 1	25	10	18	29	4	6	45
Y	ppm	1	FUS-ICP	2	8	20	4	14	20	26	24	10
Yb	ppm	0.1	FUS-MS	0.3	1.1	1.9	0.6	1.4	1.9	2.9	2.5	1.1
Zn	ppm	1	TD-ICP	4	20	2980	455	509	1660	4020	35	50
Zr	ppm	2	FUS-ICP	49	82	145	63	79	102	131	190	55
ΣREE	ppm			31.5	70.2	174.9	44.9	117.4	160.4	147.7	218.0	60.6

Table 5. Statistical results of LA-ICP-MS analysis on sphalerite particles (n = 25) from the Probištip tailings. Element contents in ppm.

Isotope	Median	Min	max
⁵⁵ Mn	95	<11	1167
⁵⁷ Fe	4696	531	67696
⁵⁹ Co	<1.4	<1.4	54
⁶⁰ Ni	<4	<4	<4
⁶³ Cu	459	11	2903
⁷¹ Ga	2.5	<1.1	494
⁷⁴ Ge	3.7	<3	25
⁷⁵ As	19	<5	1815
⁹⁵ Mo	<1.2	<1.2	<1.2
¹⁰⁷ Ag	13	<0.6	701
¹¹¹ Cd	4153	1359	11183
¹¹⁵ In	7.4	<0.2	443
¹¹⁸ Sn	2.4	<2	59
¹²¹ Sb	16	<0.5	2188
²⁰² Hg	44	22	465
²⁰⁵ Tl	<0.2	<0.2	46
²⁰⁸ Pb	21	<0.3	15334
²⁰⁹ Bi	<0.2	<0.2	<0.2

study (5 ppm). It is most likely substituted into the sphalerite structure, along with low concentrations of In (1.4 ppm). Toxic element concentrations are moderate (300 ppm As, 16 ppm Cd, 3.4 ppm Tl). Both the Rudnik and Sasa tailings contain elevated Sn (18 and 24 ppm, respectively).

The Probištip tailings have considerable concentrations of Pb (>5000 ppm) and Zn (4020 ppm) with some Cu (300 ppm). Copper is hosted by chalcopyrite, Pb by galena (especially its alteration product cerussite), and Zn is hosted by sphalerite. Silver concentrations (17 ppm) are the highest reported from the selection of samples analyzed in this study. As shown later, Ag is partly hosted by sphalerite. The Probištip sample carries moderate As (306 ppm), Cd (18 ppm) and Tl (8.5 ppm), and low concentrations of high-tech metals except for In (9.1 ppm) which reaches the maximum concentration in the sample set studied.

The Bučim tailings contain some Cu (360 ppm) and Ba (723 ppm). Cu is hosted by chalcopyrite and Ba is likely to be hosted by baryte. Weak Au concentrations (0.09 ppm) do not increase the economic value of the material. Concentrations of toxic elements are low (<50 ppm As), as are those of the high-tech metals.

The Lojane tailings contain very high amounts of As (>2000 ppm) and Sb (>10000 ppm), as well as Cr (1710 ppm). Arsenic is primarily hosted by realgar, and antimony by stibnite, but both are also present in numerous sulfides, arsenates and oxides. Cr is hosted by chromite and Ni (1090 ppm) is likely hosted by bravoite

and vaesite. The analyzed sample reveals 8.3 % S, 60 ppm Co, 79 ppm Mo, and 45 ppm W. Copper is low (30 ppm), and further high-tech elements (Ga, Ge, In) are close to or below detection limit. The Lojane tailings differ from all the above as they do not provide any options to recover Cu, Pb, Au and Ag. The potential is clearly dominated by Sb and As with minor Ni and Co.

6. SPHALERITE TRACE ELEMENT DATA

Chemical analysis of the tailings sample from Probištip indicated elevated concentrations of combined Zn and Pb, at 2.7 % S. The polished section contained a variety of ore minerals, including galena, sphalerite and chalcopyrite. Sphalerite is often an important host of minor and trace elements. Therefore, it was decided to perform preliminary trace element analyses on sphalerite using LA-ICP-MS. Data presented in Table 5 indicate low median concentrations of Fe (0.47%), with some higher concentrations reaching 6.8%, and moderate Cd (0.41%) reaching more than 1% in cases. Element spectra over the time of analysis in the majority of cases do not show significant spikes that would point to invisible inclusions. In most sphalerite particles, Cu contents are elevated, most probably due to fine exsolution of and intergrowth with chalcopyrite. The median contents of typical by-product elements in sphalerite are 3.7 ppm Ge, 2.5 ppm Ga and 7.4 ppm In. Compared with the large dataset of COOK et al. (2009) of trace elements in sphalerites, Ga and Ge are in the expected range, while In is clearly below the median. The median content of Ag is 13 ppm but ranges up to 700 ppm in single particles.

7. DISCUSSION AND CONCLUSIONS

Besides mineralogical and chemical differences, the analyzed tailings from nine sites in southeastern Europe have some features in common: First, their predominant grain-size is in the sand-silt range (0.002 mm to 0.5 mm), many show a bimodal size distribution and, their composition is quite variable as expected from the literature. The first point is positive in the context of the possible recovery of the metals since mining fine-grained material needs little specialized equipment, and even the processing is more energy/cost-efficient as most of the necessary preparation steps as crushing or milling have been done previously during former operations. However, as shown in Table 3, most of the sulfides have a small grain size compared to the gangue minerals and are often intergrown with or present as inclusions in the latter, respectively.

There are several possible explanations for the bimodal size distribution. For tailings of flotation plants, a fairly uniform grain size should be expected; this would be the larger size class observed. The smaller size class in the range of < 10 µm could represent dust that was not removed prior to flotation, abrasion prod-

Table 6. Summary of potentially valuable elements and element carrier minerals in the tailings samples.

Locality	Major commodity metals	Precious metals	EU-critical metals	Toxic metals	Main metal-bearing minerals for recovery
Bor (SRB)	Cu	Au			Pyrite, chalcopyrite, colusite, enargite
Krivelj (SRB)	Cu	(Au)			Pyrite, chalcopyrite, galena
Grot/Blagodot (SRB)	Pb, Zn	(Au)		As, Cd, Tl	Pyrite, sphalerite
Lece (SRB)	Pb, Zn	Au	Sb	As, Tl	Fe oxides(?), baryte, galena, sphalerite, tetrahedrite
Rudnik (SRB)	Pb, Zn (Cu)	Ag		(As)	Galena, pyrrhotite, sphalerite, anglesite
Sasa (NMK)	Pb, Zn (Cu)	Au	Ge (In)	As	Galena, pyrrhotite, sphalerite
Probištip (NMK)	Pb, Zn, Cu	Ag	In	As	Galena, pyrrhotite, sphalerite, chalcopyrite
Bučim (NMK)	(Cu)				Chalcopyrite, molybdenite
Lojane (NMK)	Sb, Cr, Ni		Sb, Co	As	Realgar, orpiment, stibnite and other Sb-As phases

ucts originating from the flotation and subsequent processes, dust that was removed before flotation but mixed before or during dumping in the tailings dam, or in situ formed weathering products including clay minerals. As a final possibility, analytical bias may have been introduced during crushing, sample preparation, or an unfavourable cutting plane of the polished section could be responsible for the observed bimodal size distribution. As most samples with a bimodal size distribution show a different mineralogy in the various size classes, an unfavourable cutting plane or an effect of crushing is unlikely. Given the attempts to gather and prepare representative samples during all steps from sampling to preparation, it can be assumed, that the bimodal size distribution is really present in the sampled tailings.

The high spatial variability poses problems for mining and processing, some of which may be tackled using geophysical methods to investigate the shape of the tailings bodies which in some cases were just dumped to fill valleys. More problems are likely to be caused by the chemical variability, even at the sample scale, as the tailings are far from homogeneous. All the available reports on these tailings draw attention to their enormous inhomogeneity (KOLITSCH et al. 2018). In an extreme case, for the Lojane tailings, there are even reports of “*numerous heaps of black and white powder*” consisting of stibnite concentrate and arsenolite (As_2O_3) thought to be remnants of 2500 wooden barrels stored at the smelter (TASEV et al. 2017). At the same place a tailings pile and a concentrate storage pond are reported, the latter holding approximately 15 000 tons of 50 % As concentrate (TASEV et al. 2017).

From an economic point of view, the metal contents analyzed in the tailings samples do not indicate a high potential for mining because they are comparatively low. However, given the easy access and likely low mining costs, some of the tailings may become economic if metal prices increase due to foreseen future shortages for base and critical high-tech metals. In any case, a possible and in many cases ecologically worthwhile remediation could at least partly be financed by the recovery of some valuable metals. In Table 6, we provide a summary of the potential identified using whole-rock chemical and in-situ mineralogical and mineral chemical analyses.

The highest total metal concentrations were found in the sample from the Probištip tailings with 0.4% Zn, >0.5% ppm Pb and 300 ppm Cu; however, those grades are still low compared to commercial mines. Unfortunately, the sulfide phases such as sphalerite do not carry elevated trace element concentrations that would economically support re-mining and processing the material. The base metal sulfides are often locked in pyrite which is mostly present as free grains. This poses challenges for reprocessing, but it should be kept in mind, that modern processing plants are significantly more powerful in every aspect than in the past.

Additionally, it should be considered worthwhile to process the Lojane tailings dam as this would not only reveal considerable amounts of As and Sb, but also protect the local environment from further toxification. Increasing metal prices might facilitate feasibility studies for some of the localities in the near future.

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