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ARTICLE

SECONDARY ARSENATES FROM THE ĽUBIETOVÁ-SVÄTODUŠNÁ COPPER DEPOSIT IN SLOVAKIA

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Abstract: In the vicinity of Lubietová in the Banská Bystrica region in Slovakia, copper was mined in three deposits: Podlipa, Svätodušná, and Kolba. The study concerns the association of secondary arsenates of the Lubietová-Svätodušná copper deposit. The Lubietová-Svätodušná deposit contains a large number of secondary minerals, formed as a result of weathering in the hypergene zone. Among them, copper arsenates are the most important, due to the rare occurrence of some of them. Four secondary arsenates have been characterized: chalcophyllite, euchroite, olivenite and pharmacosiderite. The minerals were identified using X-ray diffraction (XRD), whereas observations under a scanning electron microscope (SEM) and chemical analysis (EDS) showed that some of them are heterogeneous, contain different substitutions, and show significant variability in the content of individual elements within single specimens.

Keywords: secondary minerals; arsenates; euchroite; Ľubietová-Svätodušná, copper

1. Introduction

Arsenic is a highly toxic element. It occurs in nature in various forms and at various oxidation states. Its toxicity and mobility in the environment depend on both its chemical form and the form of occurrence [1]. Heaps rich in arsenic are particularly dangerous to the natural environment. This element can be transported from them by rainwater, running water and industrial sewage over very long distances. Usually, the sources of arsenic are sulfur salts and metal arsenides such as arsenopyrite, cobaltite, nickelite; arsenic sulfides, e.g. realgar and arsenic oxides [2]. An example of such a dump is the heap created because of mining the copper deposit Ľubietová-Svätodušná in the Slovak Republic. In addition to primary minerals, secondary minerals also occur there, mainly arsenates, although sulphates and carbonates also appear. This heap is the place where euchroite $Cu_2(AsO_4)(OH) \cdot 3H_2O$ was first found and described [3] vide [4].

Despite many studies, descriptions and characteristics of these arsenates [4–16] and continuous interest in this topic, the conditions and processes that had to occur in the Ľubietová-Svätodušná deposit heap for these minerals to form and co-occur together have not yet been fully described [17]. In this work, the arsenates occurring in the heap were characterized in order to use them for further research on the conditions of formation of such secondary arsenates' associations.

2. Location

The village and commune of Ľubietová is located in the central part of the Slovak Republic. It is located 15 km east of Banská Bystrica [4]. Administratively, it is located in the Banská Bystrica district in the Banská Bystrica region. The Ľubietová-Svätodušná deposit is located about 5 km from the center of the village [18], in the upper part of the Peklo Valley, on the southwestern slope of Kolba (1 162.1 m MSL) (Fig. 1).

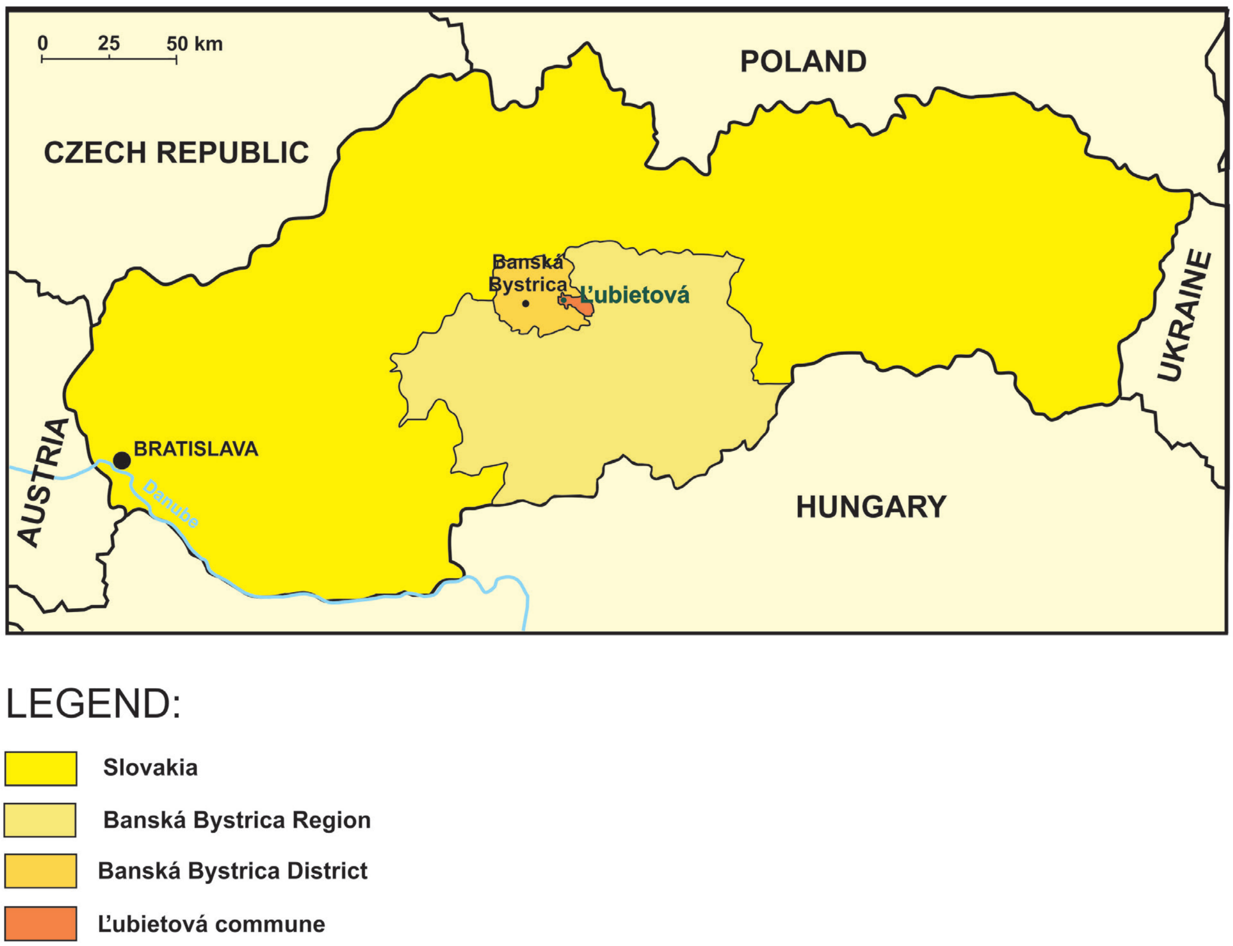


Fig. 1. Location of Ľubietová in Slovakia

3. Geology of research area

The studied area is located on the border of Mesozoic and late Paleozoic formations and crystalline complexes of Fatricum and northern Veporicum, as well as Neogene and Quaternary volcanites (Fig. 2). Fatricum represents a system of nappes lying close to the surface, covering Tatricum. It consists of Permian and Mesozoic sequences, with local relics of crystalline basement. Veporicum also consists of a crystalline basement and late Paleozoic and Mesozoic cover.

The cover formations are divided into northern and southern. The northern one is mainly composed of Permian clastic sediments and Mesozoic sediments. The southern one is composed of Upper Carboniferous, Permian and Triassic sediments. The crystalline basement has a complicated internal structure. There are both granitoid units with highly metamorphosed rocks and units of weakly metamorphosed Early Paleozoic rocks. Volcanites are associated with andesitic volcanism. In central Slovakia, it lasted from the early Badenian to the Pannonian. It was preceded by acidic, rhyodacitic-rhyolitic volcanism. The last stage of volcanic activity in Slovakia was alkaline basaltic volcanism (Pannonian, Pliocene and Pleistocene) [19].

The geological substratum of the studied area is very diverse. The Hron Valley is filled with sandy gravels [21]. In the south, the area is built of neogenous, volcanic rocks of the Poľana Massif, such as pyroclasts (tuffs and tuffites) with a composition of pyroxene andesites, lying on rhyodacitic tuffs and pyroxene andesites. The tuffs and andesites cover the Paleozoic rocks of the Ľubietová crystalline rock (Veporicum). The crystalline rock is composed of gneisses, schists, migmatites, amphibolites and Vepor granitoids. The crystalline rock is covered by Permian sediments such as variegated schists, arkosic and greywacke sandstones and quartz porphyries. The Permian rocks are covered by layers of quartzites, Lower Triassic schists, and Middle and Upper Triassic dolomites. They are considered to be a sedimentary series belonging to the Veporicum. In the western part of the area, Neogene sediments (sands, sandstones and gravels) appear [4].

The Ľubietová deposit is a hydrothermal-vein copper deposit and it is located in the Permian formations of the Ľubietová ridge [5]. This deposit is epigenetic, Upper Cretaceous and is associated with the Alpine orogeny. Genetically, it is related to the tectonic-metamorphic and tectonic-magmatic processes of that period [22], see [4]. The greater part of the Ľubietová deposit is associated with arkosic rocks.

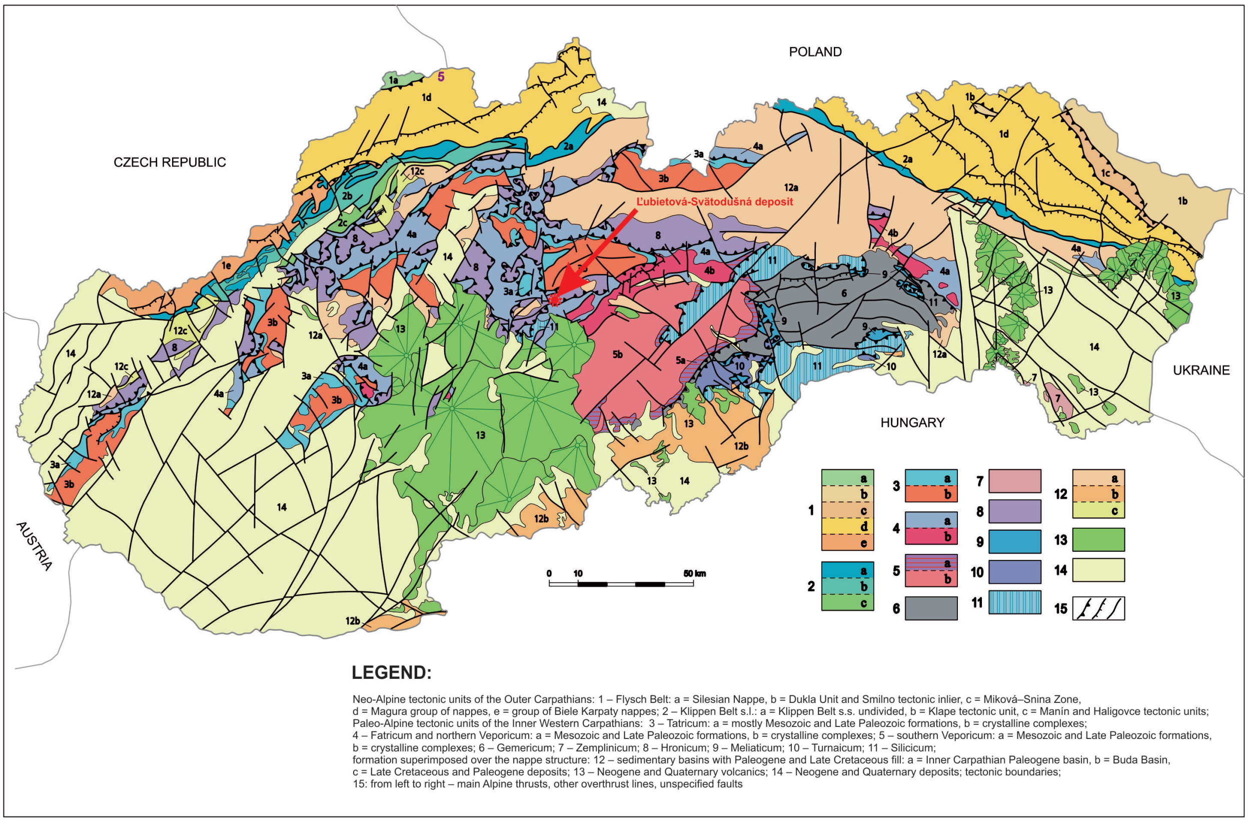


Fig. 2. Location of the Ľubietová-Svätodušná deposit at the simplified geological map of Slovakia (after [19], according to the General geological map of the Slovak Republic 1:200,000 [20])

Currently, the underground parts of the deposit are almost inaccessible and material for research was collected from numerous dumps. The largest spoil heaps are located above the Podlipa settlement and in the Peklo Valley (the Ľubietová-Svätodušná deposit, the Kolba deposit) [5].

In the Ľubietová-Svätodušná deposit, mineralization occurs mainly in quartz or quartz-carbonate veins. The primary minerals are [4, 5, 11]:

- ankerite $Ca(Fe^{2+},Mg)[CO_3]_2$,
- arsenopyrite FeAsS,
- chalcopyrite $CuFeS_2$,
- cobaltite CoAsS,
- Fe-bearing magnesite $(Mg,Fe)CO_3$,
- gersdorffite NiAsS, tennantite $Cu_6[Cu_4(Fe,Ag,Zn)_2]As_4S_{13}$.

Secondary minerals include [4, 5, 11]:

- annabergite $Ni_3(AsO_4)_2 \cdot 8H_2O$,
- azurite $Cu_3(CO_3)_2(OH)_2$,
- brochantite $Cu_4(SO_4)(OH)_6$,
- chalcophyllite $Cu_{18}Al_2(AsO_4)_4(SO_4)_3(OH)_{24} \cdot 36H_2O$,
- clinoclase $Cu_3(AsO_4)(OH)_3$,
- erythrite $Co_3(AsO_4)_2 \cdot 8H_2O$,
- euchroite $Cu_2(AsO_4)(OH) \cdot 3H_2O$,
- malachite $Cu_2(CO_3)(OH)_2$,
- pharmacosiderite $KFe^{3+}_4(AsO_4)_3(OH)_4 \cdot 6\text{-}7H_2O$,
- olivenite $Cu_2(AsO_4)(OH)$,
- scorodite $Fe^{3+}AsO_4 \cdot 2H_2O$,
- strashimirite $Cu_8(AsO_4)_4(OH)_4 \cdot 5H_2O$,
- tyrolite $Ca_2Cu_9(AsO_4)_4(CO_3)(OH)_8 \cdot 11H_2O$.

4. Materials and methods

4.1. Sampling in the Ľubietová-Svätodušná deposit

Samples for the study were taken from the surface and subsurface layers of the spoil heap created during the exploitation of the Ľubietová-Svätodušná deposit. The spoil heap is located in a forest at the end of the Peklo valley. It is several hundred meters long and several meters wide. The largest amount of secondary minerals is located in the lower parts of the heap and at its eastern and western ends. Samples were taken from places with the highest concentration of secondary minerals. The selection of the research material was guided by the presence of macroscopically visible (usually green) secondary minerals in the rocks.

4.2. Characteristics of natural samples

Studies were carried out in the laboratories of the Department of Mineralogy, Petrography and Geochemistry, the Department of Economic and Mining Geology (Laboratory of Ore Microscopy) and the Faculty Laboratory of the Faculty of Geology, Geophysics and Environmental Protection of AGH University of Science and Technology, as well as in the Laboratory of Scanning Microscopy of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica.

Macroscopic observations of the collected secondary minerals were performed using an Olympus SZX-9 stereoscopic microscope with an Olympus DP-12 digital camera controlled by the Analysis program. They were then separated and ground in an agate mortar and identified using X-ray diffractometry (XRD). A Philips PW 3020 X'Pert-APD diffractometer equipped with a graphite reflection monochromator was used for the study. Qualitative identification was performed using the XRAYAN computer program. The crystal morphology of natural secondary minerals from the Ľubietová-Svätodušná deposit was analyzed by scanning electron microscopy (SEM). For this purpose, a JEOL JSM 6390 LV microscope was used together with an energy dispersive spectrometer (EDS).

5. Results

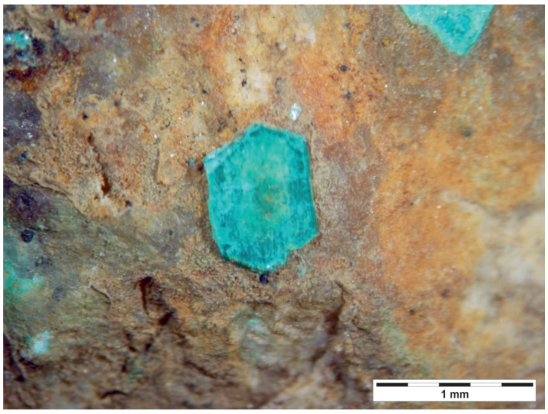
Eleven secondary mineral phases differing in color and formation were collected from the heap, including five identified as arsenates (samples LS1, LS2, LS3, LS4, LS5).

In sample LS1, the studied mineral has an emerald color and forms crystals with a tabular shape. The plates are 0.5 mm to 4 mm in size but are 2 mm on average. Some plates are hexagonal in shape. The mineral under study has a strong pearl luster, a pale green streak, and excellent, unidirectional cleavage (Fig. 3a). It is brittle and soft. The crystals occur on quartz arkose. Based on the results of XRD analysis, the emerald plates from sample LS1 were identified as chalcophyllite. The analysis did not reveal any other phases within the detection limits of the method (Fig. 3b). Observations made with a scanning electron microscope (SEM) show that chalcophyllite has a lamellar segregation (Fig. 3c). Chemical analysis of the crystals performed with an energy dispersive spectrometer (EDS, data not shown) confirmed the presence of Cu, Al, S, As, and O in their composition.

In the LS2 sample, the studied mineral has a blue-green color. It forms veins and larger aggregates. The crystal sizes range from about 0.5 mm to about 4 mm. Some reach 6 mm. The veins have an average thickness of about

1.5 mm, but there are also 3 mm thick. The mineral has a glassy luster and a pale green streak (Fig. 4a). It occurs in strongly cracked quartz-limonite breccias. Based on the results of the XRD analysis, the green crystals from the LS2 sample were identified as euchroite. The analysis did not reveal any other phases within the detection limits of the method (Fig. 4b). Observations made using SEM show that in the tested sample, the euchroite crystals are irregular and cracked, have a conchoidal fracture, and the surfaces of the crystal walls are uneven (Fig. 4c). EDS chemical analysis (data not presented) confirmed the presence of Cu, As and O in their composition.

a)



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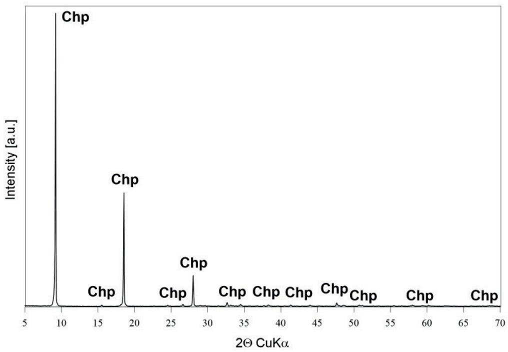

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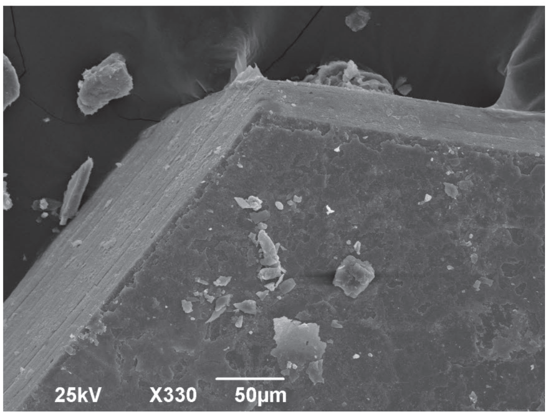
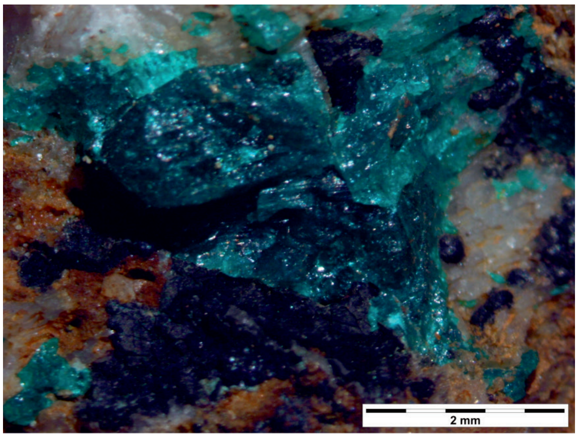


Fig. 3. Sample LS1: a) macrophotography of chalcophyllite; b) the XRD patterns of chalcophyllite (Chp); c) the SEM images of chalcophyllite

a)



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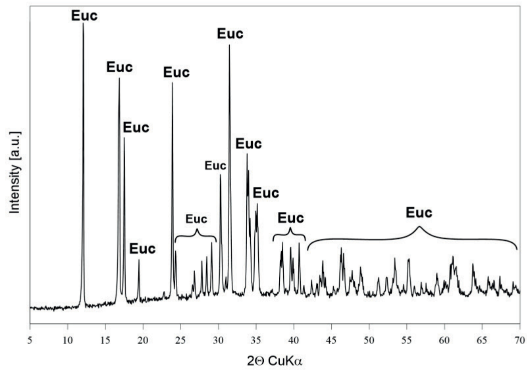

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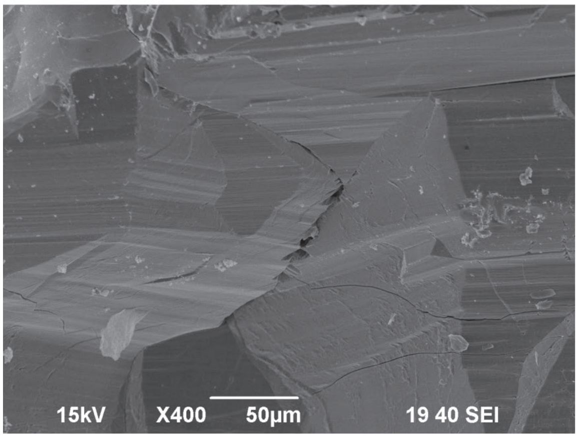
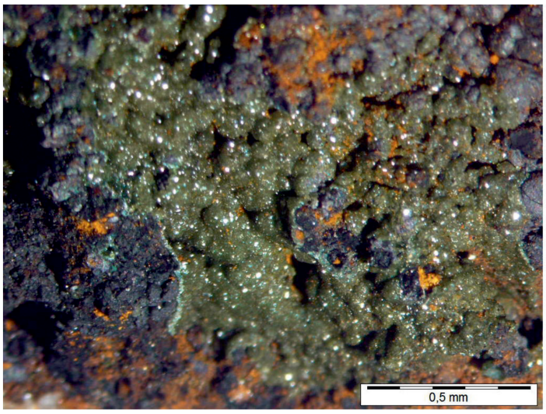


Fig. 4. Sample LS2: a) macrophotography of euchroite; b) the XRD patterns of euchroite (Euc); c) the SEM images of euchroite

In the LS3 sample, the studied mineral has an olive color. It forms very fine-crystalline clusters in druses and voids and on the surface. It has a diamond luster (Fig. 5a). Based on the XRD analysis results, very fine dark green crystals from the LS3 sample were identified as olivenite. In addition to olivenite peaks, peaks originating from minerals from the garnet group, potassium feldspars and plagioclase are also visible (Fig. 5b). Observations made using SEM show that in the tested sample, olivenite forms mostly thick-tabular or pyramidal crystals. The wall surfaces are uneven, rough (Fig 5c). EDS chemical analysis (data not presented) confirmed the presence of Cu, As and O in their composition.

a)



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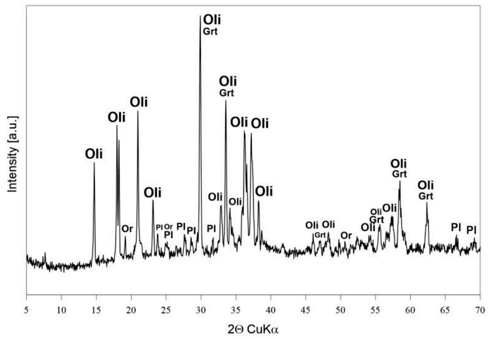

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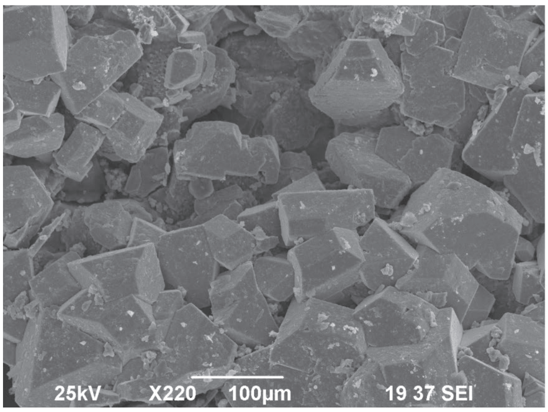
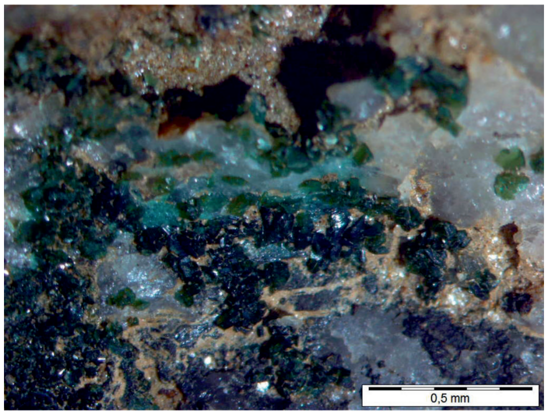


Fig. 5. Sample LS3: a) macrophotography of olivenite; b) the XRD patterns (Oli – olivenite, Grt – garnet, Or – potassium feldspar, Pl – plagioclase); c) the SEM images of olivenite

In the LS4 sample, the studied mineral has a light green color. It forms very small crystals. Their size ranges from 0.1 to 1.5 mm. Crystals of 0.5 mm and smaller predominate. The mineral has a glassy luster (Fig. 6a). It appears in the zones between quartz veins and limonite.

Based on the results of the XRD analysis, the light green crystals from the LS4 sample were identified (similarly to the LS3 sample) as olivenite. The diffraction pattern shows mostly peaks originating from olivenite. One can also observe peaks indicating the presence of mica (muscovite), quartz and a small amount of euchroite (Fig 6b). Observations made using SEM show that in the tested sample olivenite forms plates or elongated crystals. They have an uneven surface and form intergrowths (Fig 6c). EDS chemical analysis (data not presented) confirmed the presence of elements such as Cu, As and O.

a)



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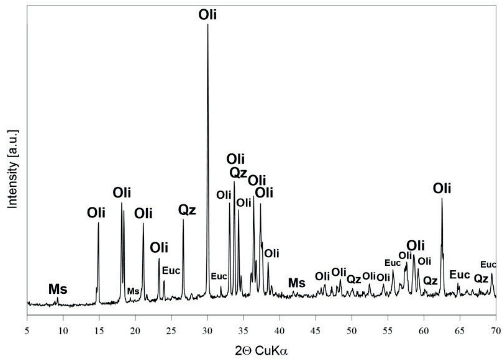

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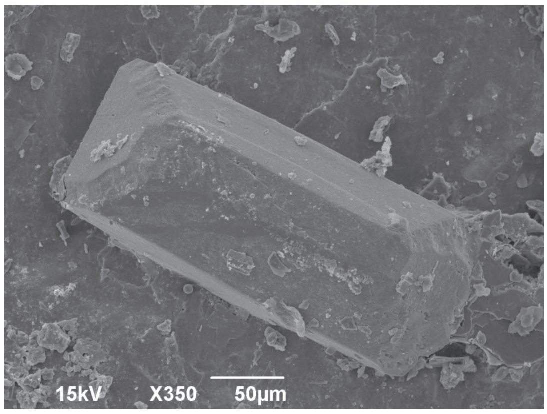

Fig. 6. Sample LS4: a) macrophotography of olivenite; b) the XRD patterns (Oli – olivenite, Ms – muscovite, Qz – quartz, Euc – euchroite); c) the SEM images of olivenite

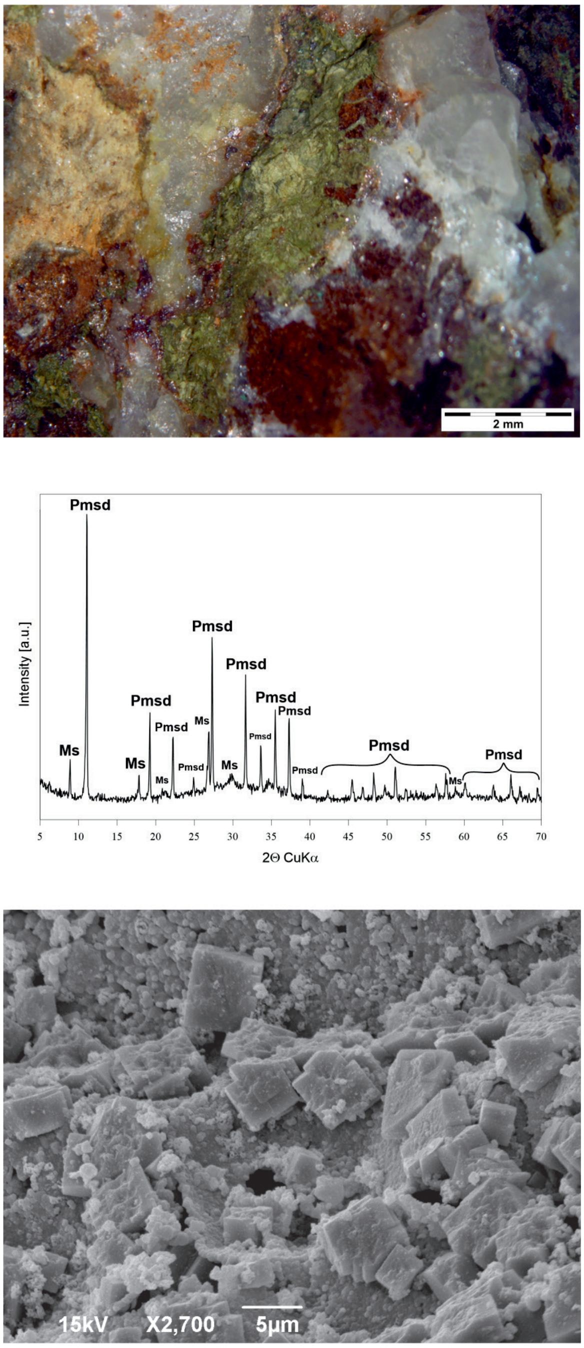

Fig. 7. Sample LS5: a) macrophotography of pharmacosiderite; b) the XRD patterns (Pmsd – pharmacosiderite, Ms – muscovite); c) the SEM images of pharmacosiderite

In the LS5 sample, the studied mineral has a light green color. It is found on limonite (more often) and quartz. It is a very loose mineral. It has a matte, dusty, and sometimes oily luster (Fig. 7a). Based on the results of the XRD analysis, the light green mineral from the LS5 sample was identified as pharmacosiderite. In addition to the pharmacosiderite peaks, the diffractogram also shows peaks indicating the presence of micas (Fig. 7b). Observations made using SEM show that in the sample under study, pharmacosiderite forms thin rhombohedral plates or oval grains (Fig. 7c). EDS chemical analysis (data not presented) confirmed the presence of elements such as As, Fe, and O, which corresponds to the chemical composition of minerals from the pharmacosiderite group.

Macroscopic observations and observations using a scanning electron microscope (SEM) of the tested arsenate samples confirm the forms of their occurrence presented in the literature [4]. Observations using SEM and chemical analysis (EDS) showed that some of the tested crystals are heterogeneous, contain various substitutions and show significant variability in the content of individual elements within single grains.

6. Conclusions

In summary, numerous secondary minerals were found in the Ľubietová-Svätodušná deposit heap, but only four of them belonged to the arsenate group. These were chalcophyllite, euchroite, pharmacosiderite and olivenite. These minerals were described and characterized in detail using XRD and SEM/EDS. It was noted that euchroite and olivenite predominate in the arsenate heap. Euchroite is emerald green in color and occurs mainly in the form of veins filling the cracks, while olivenite forms various crystals with colors from light to dark green. It appears both in the form of plates and small needles. Sometimes the needles form radial clusters. The results of SEM-EDS analyses showed that natural arsenates do not form pure phases, they contain numerous substitutions.

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Conflicts of Interest: The author of this paper declares no conflicts of interest.

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