

MINERAL COMPOSITION OF SULPHIDE-OXIDE PB - ZN ORE FROM RUDNIK MINE

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Abstract: Explorations of the ore bodies Prlovi 1, Prlovi 2 and Z of the mined ore deposit Prlovi have included ore microscopy of mineral samples from many boreholes. The orebody Prlovi 2 is prospective for the lead (4%) and zinc (3%) concentrations of which 1.89% Pb and 1.58% Zn occur in sulphides and 2.17% and 1.44% in oxides. The purpose of the ore microscopy was to recommend, based on mineral composition and texture, how to enrich the complex sulphide-oxide mineral. The paper describes the composition of the intergrown minerals and suggests the method of the mineral product recovery. Illustrations in the paper are good representative microphotographs of the identified and characteristic structural features.

Key words: oxide-sulphide mineralization, Pb-Zn minerals, low-grade ore, texture, mineral recovery predicted, processing

1. INTRODUCTION

The depletion of rich portions of the Pb-Zn mineral ore deposit Rudnik induced the Mine geologists to explore new and the abandoned non-economical orebodies or parts of the mineral deposit (Lazić et al. 2005a). In addition to the copper-rich portions of the orebodies, the exploration was extended to include minerals with elevated lead and zinc, as well as high arsenic or complex texture (Lazić et al. 2005a, 2007, 2004). The 1967 exploration in Prlovi 2 was not satisfactory and therefore discontinued. The Prlovi deposit is now being opened on the surface. The upper most layers of rocks are much altered and sulphide minerals transformed through the long process of oxidation and alteration of adjacent rocks into the strings of hypogene oxide or sulphate or even silicate minerals (Lazić et al. 2005b; Tomanec 2011).

Years of investigation on Rudnik Mountain were carried out largely in a part of the Prlovi deposit and deep in the orebody Z. An opencut was started by removing two layers of overburden and test drilling from the two pit benches; removed waste was transported to the mineral processing works (Lazić et al. 2005b; Tomanec 2011). More than sixty polished sections were prepared from cores of the boreholes (numbered 134, 139, 143, 145 and 147) for this study. Core fragments from the orebody Z also were used for interpretation of the mineral derivation (Tomanec, 2011). The mineral composition data were used to delineate the oxidation and the primary sulphide mineralization zones

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2. SAMPLING AND PREPARATION

Materials for ore microscopy were collected from the 'metal-low oxide ore' in the new Prlovi opencast. Samples also were taken of weakly cemented drill-cores from cataclased rocks strongly affected by oxidation of the almost completely transformed and leached primary minerals (Lazić et al. 2005b). Representative samples of mineral fragments were hand-picked for ore microscopy. Friable, mainly clayey material was used to prepare specimens suitable for polished thin sections. Selection was made among different structural or textural features and among different colours as well. A task of the study was to identify the intensity of oxidation and the level of primary sulphide leaching and replacement by stable hypergene minerals, mainly sulphates, carbonates, more rarely or rarely by alkaline lead and zinc oxides (Lazić et al. 2005b; Tomanec 2011). Concentration of Pb-Zn sulphide and oxide minerals from the sampled materials of the Rudnik Mine was also intended.

3. COMPOSITION AND TEXTURE

Prlovi 2 Ore body area is built of weakly cemented material of cataclased rocks strongly affected by oxidation processes that removed almost completely the primary Pb-Zn sulphide minerals (except in borehole 143/09 and the bottom of borehole through the Orebody Z).

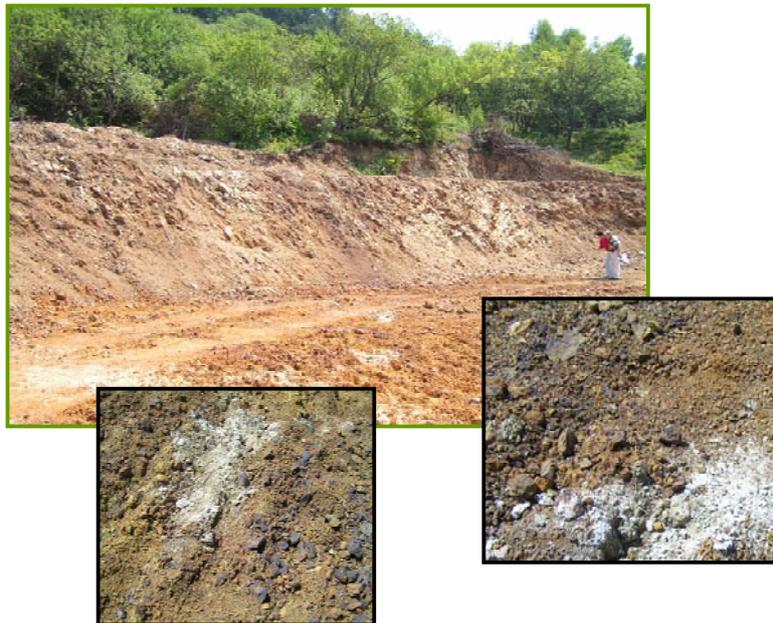


Figure 1 - Opencast second bench where samples were collected from boreholes and exposures (magnified, aggregate of hypergene minerals in the rock)

Leached rocks are coated mainly by iron oxides (characteristically brown-yellow, ochre-yellow or dark-brown in colour), sporadically in elevated concentrations (masses, fibrous aggregates) of limonite-goethite minerals (brown-yellow, terra-cotta or ochre-yellow in colour), or oxide mineral in greenish shade (tinged by copper mineral oxidation), and very low yellowish-reddish tinted by hypergene lead mineral (Figure 1).

Minerals identified so far in the genetic and paragenetic mineral associations of the area are: galena (PbS), anglesite (PbSO₄), cerussite (PbCO₃), scrutinyite (PbO₂), minium (Pb₃O₄, Pb₂PbO₄), marmatite (Zn,Fe)S, sphalerite (ZnS), smithsonite (ZnCO₃), monheimite (smithsonite with Fe) (Zn,Fe)[CO₃], willemite (Zn₂SiO₄), hemimorphite (calamine, galmei), Zn₄Si₂O₇(OH)₂·H₂O, hydrozincite Zn₅[(OH)₃CO₃]₂ or Zn₅(CO₃)₂(OH)₆, limonite, goethite, lepidocrocite, pyrite, pyrrhotite, marcasite, arsenopyrite, malachite, cuprite, opal, scheelite, etc (Lazić et al. 2006; Tomanec 2011). Some of the mentioned mineral species are barely occurrences of only mineralogical or genetic significance for interpretation without economic value.

The presented research data include mineral compositions for the whole investigated area. Microphotographs are depicting characteristic spots of the identified minerals and their texture that may suggest the complexity of mineral recovery by grinding and the difficulty of predicting the concentrate quality (Tomanec, 2011).

Borehole – 134/09

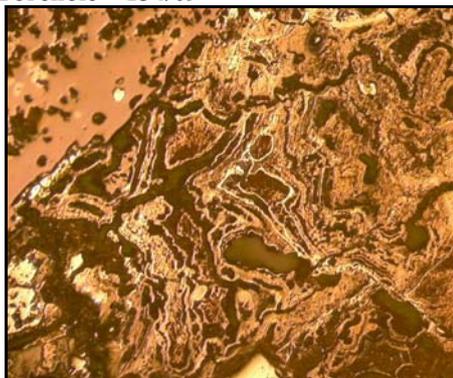


Figure 2 - Typical reticular and collomorphic textures of sulphide-replaced limonite, or goethite. Sulphide relics (1-2 µm) and alternating iron oxides and bands of sulphate minerals are few micrometers apart

Borehole – 134/09



Figure 3 - Common texture samples from the zone of oxidation; mineral association (mixture of limonite, goethite, anglesite, cerussite, galena)

Galena occurs rarely (except borehole 143/09) in complex structural features or in very small aggregates of relic crystals strongly affected by oxidation, or corrosion. It also occurs in micron inclusions, grains trapped in cerussite (isolated microcrystals that ceased being corroded). The first mentioned type of galena occurs in the form of intergranular, latest sulphide minerals; filling voids around the rounded

silicate grains galena forms aureoles, narrow veinlets, cements remnants of the primary sulphide minerals completely transformed by oxidation and replaced by hypogene minerals (Figure 6, 7, 8, 10). These structural features are unfavourable for recovery of galena, both new galena from aureoles and relict galena. Fine grinding (crumbling, attrition) of intergrown grains, such as galena-silicate (hard-soft mineral) will produce even finer galena, but the intergrowths will survive (Lazić et al. 2007). The second type of galena are relict grains of the corroding mineral, which may occur in the form of large serrate grains, always coated by oxidation products – anglesite+cerussite frequently in a mixture with iron oxides and hydroxides (Figure 4, 8, 10). Individual extraction of minerals from this kind of ore is also complicated and the recovery rate will be low or impossible to separate sulphides from the "accessory non-sulphide minerals" (Figure 4, 5, 6).

Borehole – 134/09

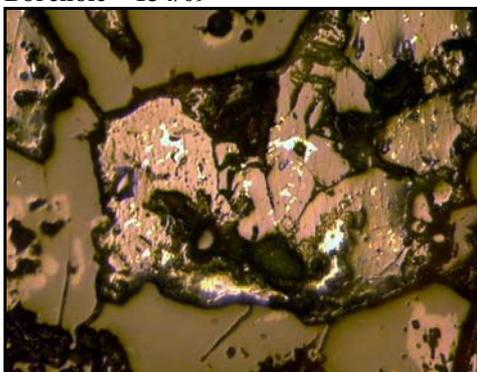


Figure 4 - Relict galena grains replaced by anglesite or cerussite

Borehole – 139/09

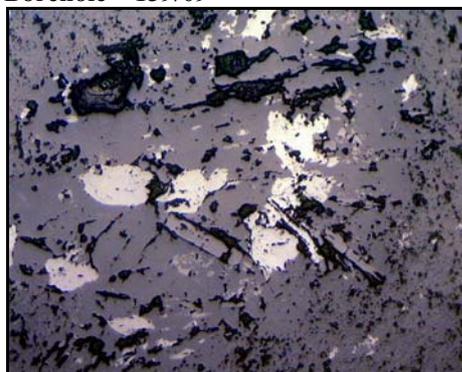


Figure 5 - Cerussite with micrometric relics of galena

Note that there are many intergrowths (only the mineral found in borehole 143/09) with the latest formed arsenopyrite, which is dominantly coarse-grained and comparatively easy to recover.

Marmatite occurs in several grades and different features. Marmatite of interest is young (mineralized together with galena) in interstices of silicate minerals, enveloping and including gangue grains, which makes it difficult for recovery. Unlike the first generation marmatite, new marmatite (even sphalerite) contains few or are without chalcopyrite and pyrrhotite secretion droplets. Marmatite of the primary sulphide mineralization occurs in specific structural features, mainly in cavernous structures, in voids left by the oxidation process, filled at present by hypogene minerals – mixed iron and zinc oxides. This fill is weakly cementing the mineral so that it is easily crushed and washed. The mixture in the mineral may be expected to behave likewise in the process of concentration (Lazić et al. 2007; Tomanec 2011).

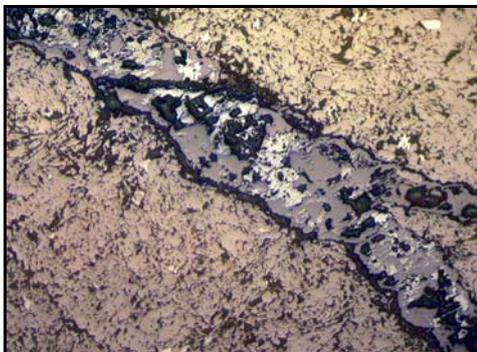
Borehole – 139/09

Figure 6 - Veinlets primary mineralized by galena sulphides, marmatite replaced by iron oxide minerals, banded collomorphic textures, with relics of corroded galena, pyrite substituted by limonite, anglesite, cerussite

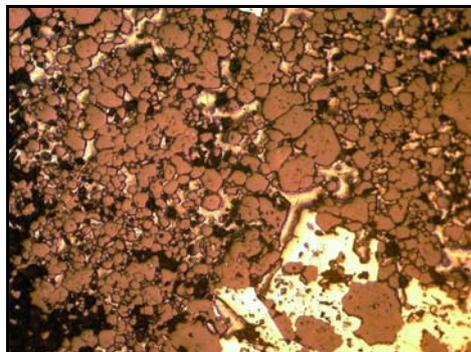
Borehole – 143

Figure 7 - Intergranular mineralization by new fine-grained galena. Galena replaced by new marmatite filling voids in silicate matrix. Impregnations. The figure low right shows coarse galena and newest arsenopyrite grains

Arsenopyrite occurs in the latest grade of the Pb-Zn mineralization. Arsenopyrite crystal aggregates are quite large, mostly medium monocrystals intermingled with galena and marmatite.

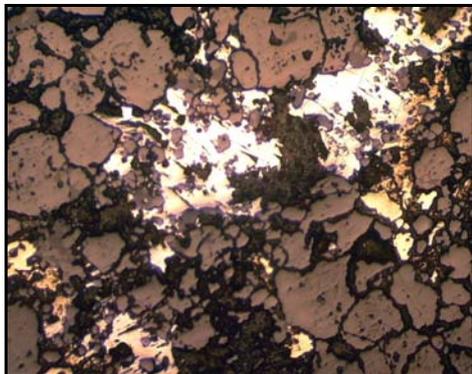
Borehole – 143

Figure 8 - Corrosion relics of galena replaced by unstable anglesite, and marginally cerussite

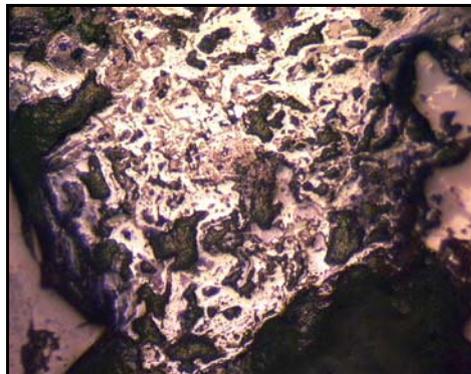
Borehole – 145

Figure 9 - Reticular, collomorphic texture of the final sulphide oxidation products – limonite, goethite; interstitial fill of cerussite+anglesite mixture

Goethite, Limonite are the commonest minerals besides lepidocrocite and often iron hydroxides found in cracks and veinlets as earthy masses mixed with clay minerals, or in a variety of specific colloform, banded textures. This paragenetic association includes: relics of corroded, serrate galena, always coated by anglesite

and/or cerussite and some other hypogene minerals of the same association (Figure 2, 3, 9). There are also brecciate structures with relict, cataclased pyrite in the above described goethite-limonite cement, and rarely marcasite as a typical product of pyrrhotite disintegration.

Characteristic are reticulate, banded and collomorphic textures of sulphides replaced by limonite and subordinately goethite. These textures enclose relict sulphides (corroded pyrrhotite replaced by marcasite, or limonite minerals) 1-2 μm in size; iron oxides (sulphides replaced by limonite, less by goethite and opal), and sulphate mineral and carbonate bands a few micrometers apart (Tomanec, 2011).

Cerussite, of particular interest for mineral concentration, generally occurs in two forms. One form of occurrence is isolated, comparatively large grains surrounded by gangue minerals and often micrometric crystals of relict galena, which is almost impossible to liberate, recover (Lazić et al. 2007, 2004; Tomanec 2011) (Figure 4, 5, 10). The other form of the occurrence is commoner, but in small masses, interstitial between silicate grains as a mixture with anglesite and limonite-goethite, and occasionally lepidocrocite. Leached zones of the banded-collomorphic texture include remnant galena grains almost completely replaced by the mixture anglesite-cerussite-limonite.

Borehole – 147/09

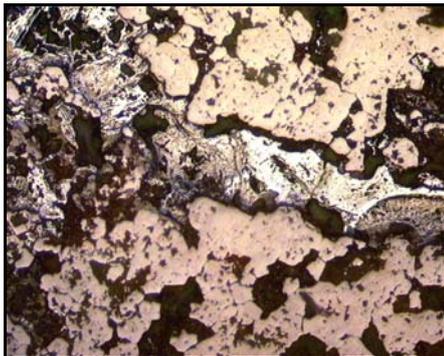


Figure 10 - Disintegrating galena (relict corroded grains) in veinlets and microfissures replaced by cerussite, anglesite and mixture of iron oxides

Ore body Z

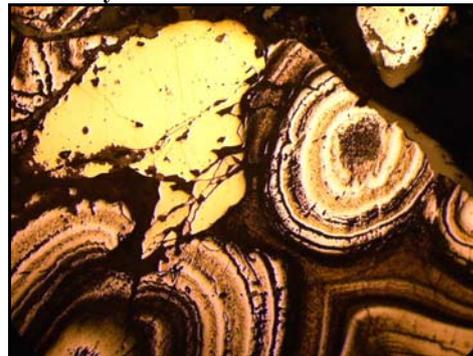


Figure 11 - Polyphase reworked oolites and new mineralization by the high-temperature chalcopyrite (with cubanite and sphalerite globes). Reniform features of limonite/ goethite layers leached and precipitated lead as sulphates and/or carbonate

Anglesite commonly occurs in isolated zones of highly oxidized leached rock. It always occurs in a mixture with iron oxides – limonite, goethite and clay minerals, or cerussite microcrystals (Figure 8, 9). The mineralized zones of hypogene minerals are 'soft' and friable, which suggests their easy grinding and transformation into slurry and elimination of 'non-oxide', sulphide, carbonate lead (and some other) gangue.

Willemite is a rare mineral of the association that recurs isolated, mainly associated with 'hard' material examined. It is medium- to fine-grained, in contact with calamine.

Ore body Z sampled for microscopic examination is a massive ore of megascopic sulphide minerals, with specific oölitic to partly pisolitic texture. Visible, quite large oololiths of different concentric layers are built dominantly of pyrite (primarily gel and later crystals), melnikovite pyrite, limonite and negligible manganese oxides (Tomanec, 2011). Pyrite, solidified gel, possessing oolitic texture of concentric zonation and reniform crystal aggregates, is characterized by radial contraction fissures from gel solidification and a silica-rich layer (Figure 11, 13, 14). Opal fills are also common. Large chalcopyrite crystal aggregates abounding in globular concentrations of sphalerite are also identified; marmatite very rich in copper (emulsion chalcopyrite) is contained in orientation directions in the form of solid solution decomposition texture (Figure 11, 12, 13). Characteristically, coarse-grained chalcopyrite is abundantly enclosing pyrrhotite, whose large crystal aggregates were seen in thin sections. Large galena aggregates deformed and cataclased have cracks filled with carbonates and sulphates.

Ore body Z

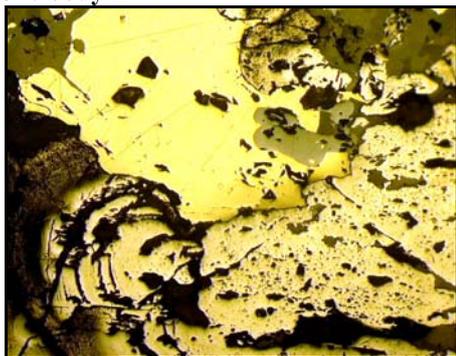


Figure 12 - New sulphide minerals – chalcopyrite, marmatite, pyrite, carbonates and cemented oololith fragments. CuFeS_2 shows sphalerite globes

Ore body Z

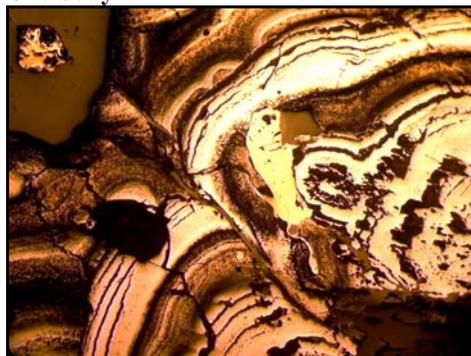


Figure 13 - Cataclased oololith relics with new chalcopyrite. Fissures filled with iron oxides, cerussite, anglesite and relict pyrite

First transformation products were oololiths with the nuclei of (not always) mineralized bacteria, and successive concentric layers of pyrite, limonite, melnikovite pyrite and rarely goethite (Figure 13, 15). Gel oololiths (pisolitic in size) acquired contraction cracks of solidification (Tomanec, 2011). Crystal oololiths were shortly worked, partly cataclased on the way to the similar geological environment where they are found as broken relics or as nuclei in another stage of the process of oolitisation. Later, with the supply of new material, the accretionary bodies of the oololith fragments were cemented into new aggregates of much more complex texture (Figure 11, 14). The following stage consisted of the introduction of sulphide mineralization and formation of large crystals of pyrrhotite, then chalcopyrite and copper-rich sphalerite (Figure 11, 12, 13).

Ore body Z

Figure 14 - Oolite fragment with concentric layers of solidified gel pyrite, limonite, goethite, manganese oxides. Oolitic and reniform features and contraction fissures in the gel pyrite indicate polyphase formation and crystallisation, and supply of new materials

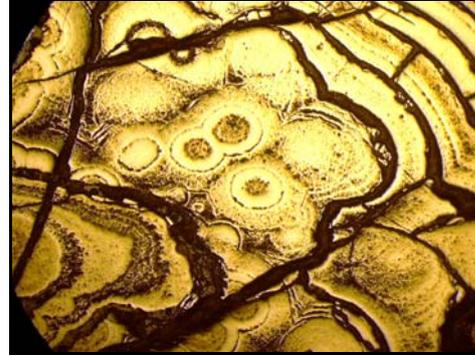
Ore body Z

Figure 15 - Mineralised bacteria as an oolite nucleus

Note that cracks of the oolite grains are filled with a mixture of limonite mineral and certain silicates, and with fine grains of gold (leached from pyrite or other sulphides in the course of decomposition).

4. CONCLUSION

The low-grade oxide ore at the surface of Prlova 2, based on the megascopic description of samples and the microscopy of polished sections, is an intensively oxidized ore mineral of lead and zinc, with most of sulphides replaced by hypergene minerals. Parts of the orebody were previously estimated as non-economical low-grade mineral reserve (Tomanec, 2011). Fine relict sulphide minerals are contained in very small amounts (galena, pyrite, pyrrhotite – in this order) or are a transitional mineral such as marcasite; covellite with chalcocine is rare. The final products of decomposition are mainly iron oxides: limonite, goethite and less frequently lepidococite, then somewhat more abundant cerussite closely associated with anglesite (negligible amounts) or coating galena or filling veinlets and fissures in rocks. A specific feature of the ore is the infrequent occurrence of marmatite and chalcopyrite oxidation products, which may be explained by the comparatively short transition of these minerals into soluble sulphates that are leached from the system and consequent lead-enrichment of oxide minerals. In addition to the migratory nature of the minerals, very small amounts of malachite and of cuprite were identified as rare skeleton structures of arsenopyrite corroded and replaced by magnetite (Tomanec, 2011).

Concerning the preparation of mineral, note that the relict, small grains of galena have an unfavourable feature – coating of cerussite (mainly anglesite), or

limonite, iron hydroxide. Microscopy detected also malachite in fine-grained silicified matrix, with associated cuprite.

The prospected and sampled Rudnik minerals of the Orebody Z include minerals which resembled and previously were interpreted as 'fluorescent scheelite'. Examined under X-ray, these minerals, in addition to scheelite contain hemimorphite [$\text{Zn}_4(\text{OH})_2(\text{Si}_2\text{O}_7) \cdot \text{H}_2\text{O}$], wulfenite [$\text{Pb}(\text{MoO}_4)$], and subordinately anglesite (PbSO_4), calcite (CaCO_3), and opal.

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