

Assoc. prof. RNDr. Stanislav Jeleň, CSc., Department of Geography and Geology, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovak Republic

Review of submitted PhD. Thesis
Slawomir Mederski

**CHARACTERISTICS OF THE HYDROTHERMAL BASE-METAL
MINERALIZATION OF THE KIZHNICA ORE FIELD, KOSOVO: MINERALOGY,
GEOCHEMISTRY AND GENESIS**

Following the letter of the dean of the Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Krakow, prof. dr. hab. Eng. Jacek Matyszkiewicz – no. RDN-NoZIS-dz.510/8/2023, I submit this assessment of the dissertation M.Sc. Slawomir Mederski.

The presented dissertation, prepared at the Economic Geology Department, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków under the expert guidance of Associate Professor Jaroslav Pršek, presents long-term mineralogical-geochemical research of hydrothermal base-metal ores of one of the most important ore districts/fields of the Republic of Kosovo - Kizhnica - Hajvalia – Badovc (KHB). The ore field is located in the central part of Kosovo and occupies the southern part of the "Trepça Mineral Belt" (part of the Serbian-Macedonian Metallogenic Province). The assessed work provides textural-structural characteristics of various types of hydrothermal base-metal ores and detailed data on the chemical composition of the main and minor sulfides, but also rare sulfosalts filling ore bodies, variations of minor and trace elements in their chemical composition from mineralogical samples of available ore bodies, various veins, occurrences and manifestations of mineralization from different parts of the ore field. The mineralogical research was carried out with the financial support of the Society of Economic Geologists of Canada Foundation (SEGCF) Student Research Grant 2019, the Society of Economic Geologists Foundation (SEGF) Newmont Mining Corporation Student Grant 2020, and statutory funds of the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków, Poland in cooperation with the management of the relevant mining facilities in Kosovo and also with the help of company managers and local geologists.

Currently, in the European Union, a high attention is given to the so-called critical (strategic minerals, respectively). From this point of view, the topic of the dissertation is highly relevant and very necessary for the needs of obtaining detailed information on the mineralogical characteristics of complex base-metal ores, the distribution of the main, secondary and trace elements of the main sulfides, the detection of minerals - carriers of precious (Au, Ag), but also other accompanying useful metals (e.g. Bi, Sb, Co, Ni, Sn, Cd, Tl, In, Ga, Ge etc.). At the same time, an increase in the value of the exploited ores is achieved through the rational use of accompanying elements. Beside the economic aspect, work also has an environmental aspect of use. A complex mineralogical-geochemical evaluation of the distribution of elements in ores

and minerals will also provide suitable data and contribute to subsequent potential research, assessment and evaluation of the impact of historical and current mining activities, extraction and processing on the environment and landscape components in the area of the ore field - Kizhnica - Hajvalia - Badovc and possible ecological remediation of the area burdened/contaminated with heavy metals.

The PhD. thesis has 240 pages of text, including literature containing 344 cited sources. It contains 106 images presenting various geological maps, schemes, photographs of ore filling textures of exploited bodies illustrative diagrams and situation maps, BSE microphotographs of mineral aggregates and various identified sulfosalts, BSE images and EPMA analysis location, which clarify and supplement accompanying text. The work also includes 6 appendices on CD media. Appendix 1-5 contains approx. 2750 EPMA analyzes of the chemical composition of minerals together with conversion to formula coefficients of apfu from following deposits, sites and occurrences: Kizhnica andesite quarry (1), Kizhnica Bi-Au-Cu-Te hornfels (2), Janjevo Cu-Bi-Ag±W locality (3), Badovc Pb-Zn-Sb-Ni deposit (4), Janjevo As-Sb-Tl-Pb±Hg±Au locality (5). Appendix 6. brings data about 364 LA-ICP-MS analyses (sphalerite, pyrite, chalcopyrite, stibnite, arsenopyrite and minerals tetrahedrite-tennantite group) from the Kizhnica-Hajvalia-Badovc ore field. Data of sphalerite LA-ICP-MS analyses (tab. 6.1.) are used also for determining the mineral crystallization temperature using GGIMFiS geothermometry (Ga, Ge, In, Mn and Fe in sphalerite) after Frenzel et al. (2016). Calculations of appropriate analytical data (used GGIMFiS geothermometer) in sphalerite from the Bi-Cu±Au zone in the Kizhnica andesite quarry provided a temperature range of its formation of 253–267 °C, and from the Janjevo site Cu-Bi-Ag±W interval of 159–273 °C. Within the Pb-Zn-Sb±Ni zone, calculations were made from analytical measurements of sphalerite of three types of ores from the Badovc locality. Massive banded Pb-Zn-Sb ores indicated formation temperatures in the range of 248–332 °C, sphalerite from rhodochrosite-stibnite breccia a value of 208 °C, and Pb-Zn-Sb-Ni ores in listvenites, the calculated sphalerite formation temperatures ranged from 212 to 344 °C. The Sb-As-Tl-Hg zone is represented by sphalerite from the Janjevo As-Sb-Tl-Pb±Hg±Au locality, where the calculated temperatures ranged from 251 to 264 °C. An arsenopyrite geothermometer based on As content in arsenopyrite (Kretschmar and Scott, 1976; Scharp et al., 1985) was also used for determining the formation conditions. The precipitation of arsenopyrite should have occurred under the temperature of $357\text{ °C} \leq T \leq 440\text{ °C}$ and S_2 activity of $-9.1 \leq \log f(S_2) \leq -6.2$.

The main goals of the work, as stated in the introductory part of work, are: to characterize the horizontal (metallic) zonation connected with the volcanic centres in the KHB ore field and also with the types of base-metal mineralization in each zone, to describe in detail the mineralogy of the deposits and the occurrence of minerals associated with each metallic zone, to determine the minor and trace elements present in the main ore minerals at each site using the LA-ICP-MS method, explaining the mechanisms of incorporation of these minor and trace elements and specifying the possibility of major critical metals in specific metal zones as well as potential prospecting targets.

The work is clearly divided into 6 parts. In the introductory theoretical part, the author concise presents a current ideas and knowledge about the spatial distribution of metals in the vicinity

of porphyry systems, especially porphyry Cu±Mo±Au deposits. Characteristic schemes of porphyry systems are presented, and together with them various genetic types of deposits, zones of surrounding hydrothermal alterations, or possible exit paths of the fluid to the intrusion surroundings. Typical deposit examples of the mentioned systems in the world are presented (Bingham district, Utah, Mineral Park, Arizona, Sepon, Laos) and also in the Serbo-Macedonian metallogenetic province (Boranja ore field, Podrinje district, Serbia). The following text presents the latest knowledge of the metallogenesis of the Serbian-Macedonian Metallogenetic Province (SMMP) and a brief description of the geological building of Kosovo and the Kizhnica–Hajvalia–Badovc ore field. The most important Tertiary magmatic-hydrothermal deposits of the SMMP and also in the investigated area of the Kizhnica – Hajvalia – Badovc ore field are clearly located on the maps.

For his own study, the author used a set of several samples - the samples from various mineralization types collected from different parts of the ore field, during six field research trips in the years 2017-2023. Samples for mineralogical and geochemical research were taken from practically the entire Kizhnica-Hajvalia-Badovc ore field, especially from abandoned mine works, previously realized drilling works, surface outcrops, old heaps, or mineralization outlets in the alteration zones. They represent of various styles of hydrothermal mineralization: veins, contact mineralization associated with hornfels, metasomatic ore bodies, epithermal veinlets in listvenites and volcanic rocks, and disseminated mineralization. In the first period, the PhD. student focused on the mineralization occurrences bound mainly to the Bi–Cu±Au zone and mineralization in the listvenite environment. Later he studied the unique lower temperature As–Sb–Tl–Pb±Hg±Au mineralization in Janjevo. The minerals of the ores were mainly investigated using new laboratory analytical methods from the five newly discovered localities in the Kizhnica-Hajvalia-Badovc ore field: epithermal veinlets from the Kizhnica andesite quarry, Kizhnica Bi–Au–Cu–Te hornfels, Janjevo Cu–Bi–Ag±W deposit, Badovc Pb–Zn–Sb–Ni deposit, and Janjevo As–Sb–Tl–Pb±Hg±Au locality.

In addition to the classic field research and mineralogical study of polished sections and thin polished sections using optical methods, the author also used the possibilities of electron microscopes in his work to investigate the inhomogeneous structure of minerals and complex aggregates of several minerals from the group of sulfarzenides and sulfosalts. Numerous electron-probe microanalyses (EPMA) and LA ICPMS spot analyzes were used to detect variations in the chemical composition of minerals. It is especially necessary to emphasize that the author, in addition to the equipment of the domestic AGH University, also used the possibilities of some foreign laboratories (e.g. Geological Institute of the Bulgarian Academy of Sciences in Sofia, Bulgaria and Institute for Geosciences, Friedrich-Schiller-Universität Jena, Germany (JEOL Super Probe 8230), and in National Museum, Prague, Czech Republic (Cameca SX 100).

The third part presents the results of a detailed mineralogical study of the investigated selected deposits and occurrences in the subject area of the KHB ore field. The PhD. student detect and characterize in detail the entire spectrum of diverse minerals. In addition to sulfides, they are e.g. sulfosalts of the bismuthinite-aikinite series – bismuthinite, krupkaite, aikinite, also cosalite, cannizzarite, galenobismuthite, tetrahedrite group minerals – tetrahedrite-(Zn),

tennantite-(Zn), tetrahedrite-(Fe), tennantite-(Fe), gersdorffite, cobaltite, native Bi and Au, tetradymite, bournonite, gustavite, pearceite, cupropearceite, wittichenite, AgCuBiS_3 – unnamed phase, wolframite, Pb-Sb sulfosalts (boulangerite, semseyite, chovanite), jamesonite, berthierite, gersdorffite-ullmannite series, millerite, polydymite, violarite, unnamed mineral phase NiFe_2S_4 , stannite, cassiterite, magnetite, hematite, Cr-spinels (spinel, chromite, magnesiochromite), fuchsite, Pb-Sb±Tl ±As sulfosalts (parapierrotite, Tl-rich pligionite, fülöppite, chovanite, heteromorphite, Sb-rich baumhauerite, bernarlottiite, robinsonite, twinnite, zinkenite, stibnite, cinnabar, realgar, duranusite, carbonates (calcite, rhodochrosite, dolomite, siderite), quartz, baryte, fluorapatite, rutile, illite, Fe±Mn±Tl hydroxides, gypsum, valentinite, and native sulphur.

The fourth part provides an evaluation of the analytical data of LA-ICP-MS minor and trace elements in the chemical composition of the main sulfides - sphalerite, pyrite, chalcopyrite, stibnite, arsenopyrite and the tetrahedrite group minerals. The author's findings are important - sphalerite with Badovc Pb-Zn-Sb-Ni deposit shows significant concentrations of many important trace elements: indium in listvenite ores, tin in massive-banded ores, in addition gallium, germanium, and silver in sphalerite from rhodochrosite-stibnite breccia. The study of minor and trace elements in sphalerite made it possible to confirm the assumed zonation in the Kizhnica-Hajvalia-Badovc ore field: Bi-Cu±Au zone, Pb-Zn-Sb±Ni zone, and distal Sb-As-Tl-Hg zone. From point of view of minority and trace elements is the pyrite holder mainly of following elements such as Ni, Co and Cu, or Sb, Tl, Hg and Pb. Hereby, gold is not large spread in these pyrites. Pyrites from the KHB ore field are not a significant carrier for selenium and tellurium. Chalcopyrite from all studied localities within the Kizhnica-Hajvalia-Badovc ore field is a very important carrier of indium. PhD. student investigations on stibnite from the KHB ore field show that at low hydrothermal temperatures stibnite can incorporate a wide range of trace elements such as As, Pb, Hg, Tl, Ag, and Cu. Arsenopyrite from the Kizhnica Bi-Au-Cu-Te hornfels shows significant concentrations of Co and Ni, arsenopyrite from the Janjevo Cu-Bi-Ag±W site shows high concentrations of Sb, Bi, and Pb, while arsenopyrite from the Badovc listvenite Pb-Zn-Sb-Ni ores shows the incorporation of Ni, Sb, as well as Au. Arsenopyrite can be an important carrier of cobalt, bismuth and especially gold. Tetrahedrite members from the Kizhnica-Hajvalia-Badovc ore field are characterized by elevated concentrations of Ag and Cd and tennantite members show a positive correlation with Pb, Ge, or Sn.

The last section, discussion and conclusion brings important interpretations of obtained results. The PhD. student prepared a very high-quality discussion with an important comparison of his own results with the data of other renowned authors on similar objects of study. Interpretations of the mechanisms of incorporation the minor and trace elements into the structure of sulfides are especially important. A significant achievement of the PhD. student and his supervisor is the discovery of a distal sediment-hosted Sb-As-Tl-Hg zone in the Kizhnica-Hajvalia-Badovc ore field. This mineralization carries diagnostic pathfinder elements for Carlin-type gold deposits such as Sb-As-Tl-Hg-Ba. Although the studied deposit bodies associated with this mineralization do not show high gold concentrations, the doctoral research allows to classify this location as a world class thallium mineralogical locality. Localities with thallium sulfosalts are very rare, and in addition, the Janjevo As-Sb-Tl-Pb±Hg±Au locality shows a high complexity of Pb-Sb±Tl±As sulfosalts with the potential for documenting new mineral phases.

According to the results of the doctoral student's research, the Janjevo site is the best-known manifestation of crystallization of colloform pyrite rich in As, Tl, Sb, Hg under the hydrothermal conditions.

Comments and questions:

Throughout the whole text of the thesis is necessary to apply the principles of literature citation according to current standards. Rather frequently there is some discrepancy between citations in the text and in the bibliography/References. Certain citations mentioned in the bibliography/References are not in the text of work (e.g.):

p.1 – citation Sillitoe 1973 is not in References

p.4, 5 – citation Babcock et al. 1995 is not in References (Babcock et al. 1998)

p.18 – citation Kolodziejczyk et al. (2016) is not in References (Kolodziejczyk (2016)

p.43 – citation Borodaev et al. (2000) is not in References

p.107 – citation Čík et al. 2021 is not in References (Čík et al. 2020)

p.166 – citation Voudouris et al. 2019 is not in References

p.174 – citation Belkin and Luo 2008 is not in References

p.178 – citations Sillitoe and Bonham 1990, Johnson et al. 2020 are not in References

p. 72 – Fig. 43. in picture (h) is not correct abbreviations – Btr – berthierite, correct is Brt

p.79 – siderite-rodochrosite members..... correct siderite-rhodochrosite members

p.81 - millerite formula - $(\text{Ni}_{0.94-0.97}\text{Fe}_{0.03-0.06})_{\Sigma 1.00}\text{S}_{1.01-2.03}$ is not correct - $(\text{Ni}_{0.94-0.97}\text{Fe}_{0.03-0.06})_{\Sigma 1.00}\text{S}_{1.01-1.03}$

p.98 – Fig. 61. (b) ... dolomitemdolomite, (d)... demseitesemseyite

abstract - ... Pb-Sb sulfosols ... Pb-Sb sulphosalts

p. 183 – chacopyrite chalcopyrite

Some mistake is in the Excel Table 2.7. (Representative EPMA data of Pyrite ..., Appendix 2.) - apfu coefficients in the table is shifted by 1 column to the left (values 1.99, 2.01, ... are incorrectly under the column "Total", they should be under the element "S" and similarly the values 1.00, 0.99, ... are incorrectly under the element "Cu" and should be under the element "Fe")

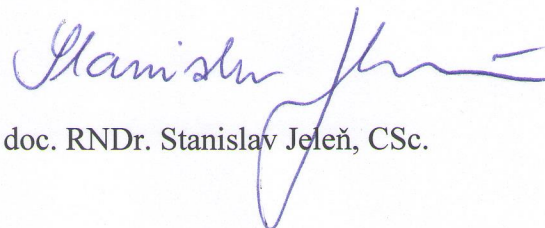
To determine the temperature conditions of ore formation, the doctorand used suitable geothermometers. In the future, the doctoral student also plans to study fluid inclusions in suitable minerals to confirm the crystallization temperature of the minerals in the ores under investigation? Possibly also an additional isotopic study with D and O isotopes, or S to supplement the genetic data on the origin of the investigated mineralization?

A detailed mineralogical-geochemical study by PhD student Slawomir Mederski demonstrated a distinct horizontal zonation in the Kizhnica-Hajvalia-Badovc ore field bound to a volcanic center (hidden porphyry system) and the author identified three zones here: Bi–Cu±Au zone; base-metal zone (Pb–Zn–Sb±Ni) and distal one Sb–As–Tl–Hg in sedimentary rocks. The dissertation describes three newly discovered types of Bi–Cu±Au mineralization: epithermal veinlets in the Kizhnica andesite quarry, Khiznica Bi–Au–Cu–Te hornfels and Janjevo Cu–Bi–Ag±W deposit. Work brings new data on the very varied and diverse mineralogy of ores consisting of sulfides (chalcopyrite and pyrite), sulfarzenides (arsenopyrite, rarely gersdorffite-cobaltite) and various groups of sulfosalts: Bi–Pb±Cu±Ag paragenesis (members of the bismuthinite-aikinite series + cosalite ± cannizzarite ± galenobismuthite ± gustavite), Cu–Bi±Ag±As paragenesis ± cupropearceite ± unnamed AgCuBiS₃ phase) and minerals of the tetrahedrite group + native Bi ± native Au.

From a professional point of view, the PhD thesis of Slawomir Mederski, M.Sc. is very well prepared and brings a large number of new knowledge and analytical data on the chemical composition of sulphides, sulfarzenides/sulfantimonides (arsenopyrite, gersdorffite, ullmannite, cobaltite) and a various groups of sulfosalts bismuthinite-aikinite series (bismuthinite, krupkaite, aikinite, cosalite, galenobismuthite, gustavite, cannizzarite), Pb-Sb sulfosalts, Pb-Sb±Tl ±As sulphosalts, that the author described for the first time from the Kizhnica-Hajvalia-Badovc ore field. Particularly valuable are the data on chemical composition of Pb-Sb±Tl±As sulphosalts and two other unknown mineral phases AgCuBiS₃ and NiFe₂S₄. In a review of studied issue, discussion and interpretation of results are included relevant literature data from foreign sources. Specifically, it is necessary to highlight the author's thorough knowledge of specialized literature and also to appreciate the high level of interpretation of analytical data and comparing them with those of other authors from the analogous objects in the world. Submitted work clearly shows that the author dedicated several years to the study of the issue and has knowledge of interpretations of used analytical methods of research. During doctoral studies received financial support from the Society of Economic Geology Foundation (2019 and 2020) by her own effort, actively participates at the international scientific forums (e.g. SGA congresses – biennial meetings in Québec City, Canada, Glasgow, UK and Rotorua, New Zealand (virtual meeting - Covid-19 pandemic), CEMC conference in Banská Štiavnica, Slovakia, Miskolc, Hungary). Furthermore, the author significantly exceeds required criteria of publishing activity established by Scientific Council of Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow. Assessed PhD thesis elaborating chosen topic fulfilled stated objectives with its content as well as scope.

Submitted PhD thesis of Slavomir Mederski, M.Sc. is written at the great professional level, bringing comprehensive factual material and convincing, scientifically supported interpretations and generalizations; and meets the requirements and criteria required (by regulation of Ministry of Education on procedure to obtain scientific-academic title) from this kind of works. Therefore, I propose to award to the Slavomir Mederski, M.Sc., after a successful defense, a scientific-academic degree „philosophiae doctor“ („PhD“).

Banská Bystrica, 30th August 2023



doc. RNDr. Stanislav Jeleň, CSc.