



Hellenic Republic

**National and Kapodistrian
University of Athens**

**Faculty of Geology and Geoenvironment
Department of Mineralogy and Petrology
Professor Dr. Panagiotis Voudouris
Head of Mineralogy-Petrology Museum
University Campus-Zografou
15784, Athens, Greece
Tel.: +30-210-7274129
www.voudouris.org**

Evaluation

for the thesis of

Mr. **Sławomir Mederski**

entitled

“Characteristics of the hydrothermal base-metal mineralization of the Kizhnica ore field, Kosovo: Mineralogy, geochemistry and genesis“

Submitted for the degree of candidate of PhD in the field of science natural sciences and the scientific discipline earth and related environmental sciences

Krakow, 2023, 240 pages, 106 figures in the English-language version of thesis + 46 tables (EPMA, LA-ICP-MS data) in the Appendixes.

In the current thesis the results of an extensive geological-mineralogical-geochemical investigation of base-, critical- and precious metal mineralization in the Kizhnica-Hajvalia-Badovc ore field in central Kosovo, are compiled.

The evaluated mineralogical and geochemical data from the studied material comprises electron probe microanalyses of a huge amount of sulfides, sulfosalts, sulfoarsenides, native elements, oxides, tungstates and carbonates. In more detail in the thesis were analyzed 319 sphalerites, 132 bismuthinite derivatives, 55 cosalites, 114 pyrites, 171 tetrahedrite group minerals, 323 sulfarsenides, 71 galena, 9 native gold, 20 stibnite+berthierite, 39 Ni-Fe sulfides, 1 stannite, 6 cassiterite, 1 cinnabar, 13 realgar+duranusite, 61 kannizarites, 25 galenobismutite, 10 gustavite, 58 Pb-Sb sulfosalts, 20 wolframite, and 50 grains of various of bournonite, cupropearceite, pearceite, wittichenite, unknown AgCuBiS_3 .

It also includes 129 LA-ICP-MS analyses of sphalerite, 122 analyses of pyrite, 32 of chalcopyrite, 31 of stibnite, 20 of arsenopyrite, and 30 of tetrahedrite group minerals in order to estimate their trace element contents.

In the introduction (Chapter 1; 20 p.) a comprehensive description of the metal zonation in porphyry systems, is followed by an overview of the metallogeny of the Serbo-Macedonian metallogenic province. Chapter 1 also deals with a detailed description of the geology of Kosovo and of the studied areas at the Kizhnica-Hajvalia-Badovc ore field, as well as the styles of mineralization present. The introduction also describes the current state of knowledge on the mineralogy,

geochemistry and formation conditions in various mineralization in the Kizhnica-Hajvalia-Badovc ore field, with emphasis on previous published work of dissertation author. Objectives of the thesis, the relevance and purpose of the study, the novelty of the results, are clarified at the end of Chapter 1.

Chapter 2 (10 p.) introduces the methodology applied both on field and laboratory. The various analytical methods are discussed here in detail.

Chapter 3 (83 p.) includes results of the Mr Sławomir Mederski's thesis. This chapter present the various types of mineralization in representative hand specimens, and the mineralogy of all examined samples is documented very clearly and is supported by several reflected-light photomicrographs and back-scattered electron (BSE) images both demonstrating relationships of the minerals assemblages providing data for the paragenetic sequences. EPMA maps with the distribution of elements in the metallic minerals, and several binary and ternary plots, demonstrate compositional relationships combined with element substitutions in the structural formulas of the analyzed minerals. The detailed mineralogical and mineral-chemical characterization of the individual metallic mineral phases, ends with their classification. Analyzed phases are compared in the plots with similar phases elsewhere, and their mineral-chemistry and formation conditions are discussed in the text, in the light of the most modern literature and previously published data. Mineral stabilities in thermodynamic phase diagrams provided information on physicochemical conditions of formation for distinct mineral assemblages.

Chapter 4 (50 p.) presents an extensive geochemical comparison of minor and trace elements in main sulfides, sulfosalts and sulfarsenides (sphalerite, pyrite, chalcopyrite, stibnite, arsenopyrite, and tetrahedrite group minerals) obtained by LA-ICP, which have provided important information on the incorporation of critical and precious metals and metalloids in their structure. Using Box plots showing minor and trace element concentrations, elemental concentration scatterplots and representative time-resolved laser ablation ICP-MS depth profiles, it was possible to distinguish types of substitutions between minor and trace elements in the structure of minerals analyzed, and 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). Using the GGIMFis geothermometer based on the concentrations of Ga, Ge, with In, Fe, and Mn measured by LA-ICP-MS in sphalerites, crystallization temperatures were also estimated. This chapter is together with the previous one the highlight of Mr Sławomir Mederski's thesis.

Chapter 5 (30 p.) represent a synthesis of all data and their metallogenetic implications. The discussion is subdivided in three major parts: the first one is dealing with the proximal Bi-Cu±Au zone, by comparing its mineralogy with other mentioned Bi-Au ± Cu localities from the the Serbo-Macedonian area, but also by investigating major ore minerals as carriers of the critical metal(loid) bismuth. The second part refers to the Pb-Zn-Sb±Ni zone, and investigates the incorporation of indium, tin and nickel in the related metallic phases. Finally the thesis demonstrated how the study of As-Tl-Sb-Hg-rich pyrite can be used as a mineral with diagnostic pathfinder elements for Carlin-type gold deposits, and emphasized and presence of distal Carlin-type and sediment-hosted gold deposits systems in the Serbo-

Macedonian metallogenic province. This chapter is a top part of Mr Sławomir Mederski's thesis.

Chapter 6 (2 p.) concludes the presence of three mineralized zones in the Kizhnica-Hajvalia-Badovc ore field: a Bi–Cu±Au zone, a base-metal Pb–Zn–Sb±Ni zone, and a distal sediment-hosted Sb–As–Ti–Hg zone. Each zone has prospectivity and economic potential for distinct critical and precious metals. This metal zonation was identified for the first time in the area and is probable associated with a concealed porphyry system. The knowledge obtained from the doctoral thesis is of major importance, and shows that using modern mineralogical and geochemical methods at the microscale can be applied to the broader context and exploration. Interpretations and conclusions of the thesis testify to the author's ability to interpret the results in a scientifically plausible manner, also based on most modern literature by comparing them with previously published data, and are commendable.

As a whole, the thesis of Mr Sławomir Mederski is extensive, rich in valuable results, editorially of very good quality, and an important contribution to the knowledge of the mineralogical and mineral-chemical relationships of a large amount of sulfides, sulfosalts, sulfoarsenides, native elements, oxides, tungstates and carbonates present at Kizhnica-Hajvalia-Badovc ore field. All these results contribute to a better understanding of the mineralogy and geochemistry of base, precious and critical metals in zoned magmatic-hydrothermal systems and are valuable for exploration for similar deposits in general.

In conclusion, the candidate adequately identified and described the research problem and goal; the candidate is sufficiently acquainted with the appropriate methods and techniques of research; the candidate has sufficient acquaintance with the relevant literature; the candidate has satisfactorily understood the nature of the problem and assessed the significance of the findings; and finally the thesis satisfactorily presented the results of independent research.

Candidate thesis "Characteristics of the hydrothermal base-metal mineralization of the Kizhnica ore field, Kosovo: Mineralogy, geochemistry and genesis" completed by Mr Sławomir Mederski meets the requirements for candidates with a speciality 'Mineralogy and Economic Geology' and candidate Mr Sławomir Mederski deserves the award of the degree of candidate in the field of science natural sciences and the scientific discipline earth and related environmental sciences.

Prof. Dr. P. Voudouris

Athens, 6.9.2023

