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

Review of submitted PhD Thesis
Joanna Kolodziejczyk, M.Sc.

MINERALOGICAL AND GEOCHEMICAL DIVERSITY WITHIN THE STAN TERG DEPOSIT KOSOVO

Following the letter of the Dean Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow, prof. DR. hab. Eng. Jacek Matyszkiewicz - WGGiOŚ / 533/2016, of 28/11/2016, I present this Review of PhD Thesis of Joanna Kolodziejczyk, M.Sc.

Submitted PhD Thesis carried out at Economic Geology Department, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow under supervision of associate professor Jaroslav Pršek, presents author's several years' mineralogical - geochemical research of metasomatic-hydrothermal skarn polymetallic ores of one of the most important deposits in Republic of Kosovo - Stan Terg (Trepča). Assessed thesis brings textural - structural characteristics of different types of skarn polymetallic ores and detailed information on chemical composition of the main and minor sulfides, as well as rare sulphosalts of ore bodies' filling, variations of minor and trace elements in their chemical composition from mineralogical samples of available ore bodies from different parts of the deposit. Mineralogical research was conducted in several geological projects of Economic Geology Department, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow in cooperation with leadership of Trepča mine in Kosovo as well as with the aid of company managers and local geologists.

High attention is currently devoted to critical or strategic raw materials in European Union. Therefore the theme of PhD Thesis is highly topical and is very necessary to obtain detailed information on mineralogical characteristics of polymetallic ores, distribution of main, minor and trace elements of main sulfides, mineral findings – carriers of precious (Au, Ag), as well as other accompanying industrial-use metals with (e.g. Bi, Sb, Sn, Cd, Tl, In, Ga, Ge a.o.). To obtain detailed mineralogical – geochemical characteristics of mined ores from deposit (determination of detailed chemical composition of minerals-carriers of industrial-use metals in polymetallic ores, their shaped and particle size distribution) is important also to assemble an optimal scheme of technological treatment of polymetallic ores and innovation of technological processes of extraction of precious and accompanying metals/elements to selective concentrates of Stan Terg deposit. With the optimization of scheme of technological treatment of deposit ores with the possibility of rational use of complemental elements will be also increased the values of exploited ores. Besides to the economic aspect of utilization, the thesis has an environmental one as well. Comprehensive mineralogical and geochemical assessment of the distribution of elements in ores and minerals will also provide appropriate documentation and will contribute to subsequent potential research, evaluation and assessment of the impact of mining activities on the environment and landscape components in deposit Stan Terg and potential ecological remediation of the area contaminated with heavy metals.

Opposed thesis has 219 pages including literature containing 255 cited sources. It encloses 106 figures, presenting different geological maps, photographs of textures of ore filling of exploited bodies, illustrative diagrams and situation maps, BSE microphotographs of mineral aggregates and different identified sulphosalts, BSE images and EPMA analysis location, which clarify and supplement accompanying text. The thesis also has 4 annexes on CD. Appendix A represents a mineralogical characteristic of examined samples and brief description of polished sections. At the end of annex is also a mining map of the X^{th} horizon (75 m) at the Stan Terg deposit, and numbers of the orebodies (Trepça mine, internal documents). In appendix B 21 tables are documenting the chemical composition approximately 4073 electron microanalysis (EPMA) of studied minerals. In appendix – C 7 tables are documenting trace and minor elements in sulphides (galena, sphalerite, arsenopyrite, chalcopyrite, pyrite, pyrrhotite) and tetrahedrite (about 884 LA ICPMS analyses). In Appendix D is a comparison of MASS-1 and NIST 610 concentration from Bulgaria and Australia LA-ICPMS laboratories with data from GEOREM database.

The main objectives of this work, as presented in the introduction, are: mineralogical and geochemical reexamination of Pb-Zn ores from the Stan Terg deposit using modern analytical techniques, EPMA and LA-ICPMS, determining where the minor and trace elements reside in the deposit, and determining the distribution of minor and trace elements within the main ore minerals.

The work is well-arranged into 5 parts. In the introductory theoretical part, the author brings in concentrated form contemporary ideas and knowledge about the genesis of Pb-Zn metasomatic-hydrothermal deposits, their short characteristics and general model. Moreover mentions typical examples of metasomatic-hydrothermal Pb-Zn deposits connected with volcanic-magmatic system in North and South America and Europa. The following text provides an overview of the most important minor and trace elements extending in Pb-Zn deposits (Fe, Cu, Sb, As, Bi, Ag, Sn, Mn, Te, Co, Ni, Cd, Hg, Au, In, Th, Ga, Ge), and a commentary on forms of appearance of these elements of interest in sulphides, both in the isomorphous, or as separate mineral phases closed in the sulphides. In a review of examined issue the author submits the latest knowledge and brief characteristic of Pb-Zn metasomatic-hydrothermal deposits in the Balkans and in Vardar zone. She dedicates in a greater detail to a geological – structural and a mineralogical – geochemical characteristics of the actual Stan Terg deposit within three mineralized zones Trepča mineral belt in Kosovo. For author's own study she used a set of several samples from various mineralization types collected from different parts of ore bodies of the deposit from IV to XI horizon, which represents a vertical interval approx. 420 m (about 40 samples from Southern part of the deposit, about 60 samples from Central part of the deposit and about 70 samples from Northern part of the deposit) and approx. 170 polished sections made from examined ores. To meet the set objectives the PhD student used a whole complex of the most advanced analytical techniques. Besides the classical field research and mineralogical study of polished sections through optical methods the author in her thesis took also advantage of the possibilities of electron microscopes in the investigation of inhomogeneous structures of minerals as well as complex aggregates of several minerals from the group of sulphotelurides and sulphosalts. Numerous electron microanalysis (EPMA) with calculation into empirical formulas, in some cases of analyzed sulphosalts are calculated also the numbers of homologues (kobellite homologous series), eventually in lillianite homologous series also substitution parameter and a molar % of Ag-Bi end member, and LA ICPMS spot analyses were used to detect variations of chemical composition of minerals. Particularly it should be emphasized that the author in addition to instrumentation of home AGH University made use of possibilities of certain foreign laboratories (e.g. Geological Institute of the Bulgarian and Slovak Academy of Sciences in Sofia, Bulgaria, Banská Bystrica, Slovakia and University of Adelaide, Australia). A substantial part of the work (about 85%) consists of her own results and their interpretation. In the introduction the author distinguish and summarize the following styles of mineralization in this deposit: skarn related mineralization, primary replacement ore, rhodochrosite banded and oligonite ore, breccia-style ore mineralization, nests and veinlets. The hydrothermal stage autor was divided into four sub-stages: "Pb-Zn" (mostly precipitated galena and sphalerite), "C" (chalcopyrite, bournonite, tetrahedrite, stannite), "Ag" (Ag-bearing galena, polybasite, pyrostilpnite, pyrargyrite, stephanite, freieslebenite, Ag-rich tetrahedrite, freibergite, Pb-Sb sulphosalts) and "Sb" (boulangerite, heteromorphite). The last section discussion and conclusion brings important interpretations of obtained results. Author concluded that galena is the main carrier of Bi, Ag, Au, Sb, Sn and Tl, sphalerite hosts Sn, In, Ga, Cd and Hg, pyrite host Co and Ni, arsenopyrite Ge, Au and Co, chalcopyrite Ag, Ge, Cd, Sn, Ni, and tetrahedrite Ag and Hg. By a detailed mineralogical-geochemical research were identified dominant mineralogical forms of occurrence of gold and silver as well as Bi, Te, Se, Sb, Sn. The author specified the temperature conditions of formation of association of Bi sulfosalts with native gold that crystallize at higher temperature (350 – 400 °C), generally near the volcanic conduit. Precipitation of an association of Ag minerals with electrum takes place at temperature approx. 200 °C in peripheral parts of the deposit in both south and north areas. Application of Stannite-sphalerite geothermometry pointed out at temperature of formation of base metal ore of Stan Terg deposit at interval 240 – 390 °C. In the conclusion, the author presents her own succession scheme of the hydrothermal Pb-Zn mineralization in the deposit Stan Terg.

Comments and questions:

PhD Thesis has a high level of graphic layout. Picture annexes, in particular the photographs are of high quality as well as precise computerized charts, dependency graphs. In the work appears of errors in text – minor errors, typing errors, that does not diminish its professional level. These are marked directly in the text.

- p. 57 - When examining the changes in the chemical composition of sphalerite did the author observed eventual zoning of grain – e.g. change the content of Fe – in the core vs. on the periphery, and related change of morphology of crystals of sphalerite – tetrahedral, cubooktahedral, rhombododekahedral habitus … depending on temperature, fugacity S, Eh … (e.g. Minčeva – Stefanova 1980) ?

- on Fig. 30 (p.66 – 68) it would be appropriate to show the correlation of Fe vs. Mn, resp. Fe vs. Cd. Did the author observed an increase the content of Cd in sphalerite in relation to the degree of distancing from hypothetical supply channels (e.g. volcanic dykes) ore-creating solutions? Higher Cd content of sphalerite indicates lower temperature conditions of formation of mineralization, resp. younger generation Sphalerite.

- p. 100 – Table 5. In connection with the content of Au up to 48,80 g/t in arsenopyrite – if relatively high contents of Au do not correlate with the content of Ag which form of occurrence does presume the author ("metallic" or "invisible – refractory gold", whether in the past was confirmed also the presence of invisible gold in arsenopyrite – whether someone from the previous authors of the research attempted to use Mösbauer spectroscopy to detect the forms of occurrence ^{197} of Au bound in the arsenopyrite)

- p.127 – The introductory statement is not entirely correct and contradicts the facts and correlation Ag vs. Bi in diagram fig.21 I – (p. 53) and Table 11 (Ag/Bi – 0.36/0.74, 0.48/0.89, 0.67/1.31, 0.61/1.33 respectively). Correlation of the content of Bi and Ag – suggests the possibility of the presence of the galena solid solution PbS_{ss} – matildite solid solutions – $AgBiS_2$ (Table. 11)

- The galena solid solution (PbS_{ss}) containing more than 0.5 wt.% of total metals other than lead (Foord & Shawe 1989); Silver and bismuth contents attain 0.67 and 1.33 wt.% respectively in the studied grains of galena solid solution. The ratio Ag (Cu): Bi is approximately equal 1:2 (wt.%), or 1:1 (at.%), what is in accord with the "gustavite" type of substitution: $2Pb^{2+} = Bi^{3+} + Ag+$ in PbS_{ss} typical for both the lillianite – gustavite ($Pb_3Bi_2S_6$ - $AgPbBi_3Se_6$) series and heyrovskýite ($Pb_{12}Bi_4S_{18}$ - $Ag_5Pb_2Bi_9S_{18}$) series (Makovický & Karup-Møller 1977 a,b; Chang et al. 1988).

In deep-seated parts of the Stan Terg deposit will be present in mineral aggregates PbSss in association with Bi sulphosalts, although the presence of matildite, resp. matildite solid solution has not been confirmed so far (see e.g. deposit Banská Štiavnica, Kovalenker et al. 1993)

- p. 121 – Differentiation of polymorph modification of Ag_3SbS_3 – pyrargyrite from pyrostilpnite based on color shades of internal reflexes is rather subjective. More appropriate would be to confirm the presence of rarer pyrostilpnite also by X-ray structural analysis.

- p. 124, figure 64 – theoretical formula of the stephanite is not Ag_5SbS_3, correctly is Ag_5SbS_4

- p. 125, Table 8. Notes – chemical formula based on 4 cations for freieslebenite is not correctly, but 3 cations

- p. 150 – table 19 – the content of Bi in galenite (anal 7) does not correspond to coefficient of the formula (apfu)

- Paragenetic sequences (Figure 106, p.193) – hasn't the author consider to complement the succession scheme with secondary minerals (e.g. mentioned sulphates, p. 194) - possible including Supergene (Weathering) stage directly to paragenetic sequence?

Throughout the whole text of the thesis is necessary to apply the principles of literature citation according to current standards. Rather frequently there is a discrepancy between citations in the text and in the References:

p. 1, 3 - Mainert 1992 (in References is Meinert L.D. 1992)

p. 5 – Scott and Barens, 1971 – correctly is "Scott and Barnes, 1971" *p. 7 – citation Oen, 1980* is not in References, resp. is not correctly cited (in References is Oen I.S. 1970, resp. Oen I.S., Kager P., Kieft C. 1980).

p. 8 – citations Gadd et al., 2016, Berthke and Barton 1971, Radosavljević et al. 2006 are not in References

p. 8 – Cook et al. (2007) – it is not clear, which from 3 citations of Cook et al. 2007a, b, c) is cited

p. 13 – citation Ciobanu et al. 2000 is not in References (Ciobanu and Cook 2000), and *Marhev et al. 2005,* is not in References (Marchev et al. 2005)

p. 14, 18, 31, 127, 184 – is not citation Forgan (1948), resp. is not correctly cited and is not in References (Forgan C. B. 1950)

p. 29 – citation Paton et al. 2010 is not in References

p. 20 – citation Palinkaš et al. (2013) is not in References (Strmić Palinkaš et al. 2013)

p. 121 – citation Uytenbogaardt and Burke (1985) is not in References (Uytenbogaardt and Burke 1971)

p. 127 - Kolodziejczyk et al. (2012) – it is not clear, which from 2 citations of Kolodziejczyk et al. (2012 a, b) is cited

p. 161 – citation *Féraud and Deschamps (2007)* is not in References (Féraud and Deschamps 2009)

p. 162 – citation Këpuska (1988) is not in References (Këpuska 1998)

p. 168 – citation Frenzel et al. (2013) is not in References

p. 173 – Nekrasov et al. (1975) is not in References - Nekrasov et al. (1976)

p. 177 – Evrard et al. 2011 is not in References

p. 192 – Tmava et al. 2003 is not in References (Tmava and Koliqi 2003), *Titcom et al. (1936)* is not in References (Titcomb et al. 1936)

Certain citations mentioned in the References are not in the text of work.

Nomenclature of minerals: Malcolm E Back; Joseph A Mandarino; Michael Fleischer: Fleischer's glossary of mineral species 2008. Tucson, Arizona, The Mineralogical Record, 2008, 346 p.

p.5 – falcmanite, correctly - falkmanite = boulangerite

p. 9 – picopaulite, correctly – picotpaulite, *rienierite*, correctly - renierite

p.172 – casiterite, correctly - cassiterite,

p. 115 – tetraherites, correctly - tetrahedrite

p. 98, 128 – prsenopyrite, aresnopyrite, aresenopyrites, ... correctly arsenopyrite

p. 135, figure 71 – Ouravite, correctly Ourayite *p. 142 – kobelliete*, correctly kobellite

p. 155 – cournonite – bournonite

p. 170 – spahelrite - sphalerite

PhD thesis of Joanna Kolodziejczyk, M.Sc. brings a large number of new analytical data on the chemical composition of native elements, sulphides, sulphotelurides (ikunolite, babkinite, joséite-A, joséite-B) and a wide range of complex bismuth sulphosalts lillianite and kobellite homologous series (lillianite, heyrovskýite, izoklakeite-giessenite, kobellite-tintinaite, cannizzarite), that the author described for the first time from the Stan Terg deposit. Particularly valuable are the data on chemical composition of Bi-tellurides and two other unknown phases (phase-A $(Bi,Pb)_2(TeS)_2$ and phase-B $(Bi,Pb)_{2,5}Te_{1,5}S_{1,5}$). These data are also important for topographical mineralogy of Kosovo. In a review of studied issue, discussion and interpretation of results are included relevant literature data from numerous 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 Kosovo, in the Balkans and 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 (2014 and 2015) by her own effort, actively participates at the international scientific forums (e.g. SGA congresses – biennial meetings in Uppsala and Nancy, conference in Tirana). 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 Joanna Kolodziejczyk, M.Sc. is written at the appropriate professional level, bringing comprehensive factual material and convincing, scientifically supported interpretations and generalizations; and meets the requirements and criteria required from this kind of works. Therefore, I propose to grant Joanna Kolodziejczyk, M.Sc., after a successful defense, a scientific-academic degree „philosophiae doctor" („PhD") and to award adequately the work for achieved results.

Banská Bystrica, 4th February 2017

Stanislav [signature]

Assoc. prof. Dr. Stanislav Jeleň, CSc.