Characterization of gold grains from Bigorne deposit: search indicators to hypogene mineralization. Preliminary studies.

Sara Leal, Alexandre Lima[1,2], Fernando Noronha[1]
[1]*Institute of Earth Sciences, Polo-Porto, University of Porto, Portugal*
[2]*Department of Geosciences, Environment and Spatial Planning, University of Porto, Portugal*

Abstract. The Bigorne gold deposit (northern Portugal) located in the European Variscan belt is a system of gold-bearing quartz veins, which crosscut late-to post-D3 biotite granites. The mineralized structures correspond to sheet-veins system parallel to the late-Variscan strike-slip fault Penacova-Régua-Verín (NNE-SSW).
In Bigorne veins, it was possible to define two types of gold occurrence: I - Native gold, as free particles; II- Au-Bi minerals in association with native-Bi and Bi-Te minerals.

The gold minerals from mineralized veins and the gold grains sampled in superficial environments reveal similar chemical composition where the Au occurs in association with Ag, Cu, and Cd. This fact provides evidence of very limited transport and therefore a restricted and single local source for gold primary particles from the mineralized veins.

It is very important to improve the geological and mineralogical knowledge about gold occurrences in Portugal to improve the knowledge of the Phanerozoic gold systems.

1 Introduction

The Central Iberian Zone (CIZ) presents an exceptional geological interest for its great exploration potential for a number of critical elements (Te, Bi, and Sb) and gold.

In Northern Portugal, gold deposits are hosted in Variscan granites (e.g. Penedono, Grovelas, Jales, and Limarinho) and in Palaeozoic metasediments (e.g. Valongo, França, Gralheira, and Tresminas) (Noronha et al. 2000 and references therein; Fuertes-Fuente et al., 2016). These gold mineralizations show a strong correlation to shear zones (syn-D3) (Mateus and Noronha 2010 and references therein), however, there are other significant alignments, such as those which are subparallel to major NNE-SSW regional faults (Noronha et al. 2000; Mateus and Noronha 2010). The primary gold particles in Northern Portugal occurs more frequently as inclusions within sulfur-rich minerals, such as pyrite and arsenopyrite or in the limits of the grains of these sulfides. Gold occurs as a native metal, commonly in alloy with silver, and in some cases mercury, copper, and other elements. Gold grains liberated from the veins into superficial sediments during weathering are chemically stable and may be characterized according to morphology, alloy composition and suite of mineral inclusions. The morphology and chemistry of alluvial gold grains and their inclusions are potential indicators of characterizing the primary gold mineralization, mineralization style, and the potential host rock (e.g., Townley et al., 2003; Chapman et al. 2011).

In this paper, a detailed description of hypogene gold assemblage and of gold grains from superficial environments was made in Bigorne deposit. The main objective is a comparative study, in order to test this approach (describe for authors cited above) in Portuguese deposits. In this case, the comparison between the gold particles from mineralized veins (hypogene gold) and the gold grains from detritical deposits (alluvial and eluvial deposits).

2 Geological setting

Bigorne region is located in the CIZ (Figure 1), which corresponds to the autochthonous of the Variscan basement of the Iberian Massif (Julivert et al. 1972). The region is mainly composed of Variscan granitoids emplaced into Neoproterozoic–Early Paleozoic sedimentary sequences, which were variably affected by regional metamorphism and deformation during the Variscan orogeny (Sousa 1982; Ribeiro 1990). The CIZ tectonic-metamorphic evolution is described as the result of two main deformation phases (D1 and D2), during which the crust reached its maximum thickness, followed by a late, post-thickening, ductile-brittle tectonic event (D3) (Noronha et al. 1979; Ribeiro et al. 1990).

2.1 Lithostratigraphy

The lithostratigraphy is variably metamorphosed and comprises metapelites and metagreywackes belonging to Schist-Greywacke Complex (SGC) with lower-Cambrian age (Carrington da Costa, 1950); an Ordovician clastic succession of stable marine platform sediments; and Silurian black schist (Teixeira, 1955; Teixeira et al., 1968). The pelitic rocks, sandstones, and greywackes were transformed into slate, quartzite, phyllite, spotted schist and hornfels as a result of variable metamorphic conditions attained during Variscan times.

The emplacement of voluminous amounts of granitic magmas during and slightly after D3 (316 to 300 Ma: Costa et al. 2014) generated low-P–high-T contact aureoles in this zone.

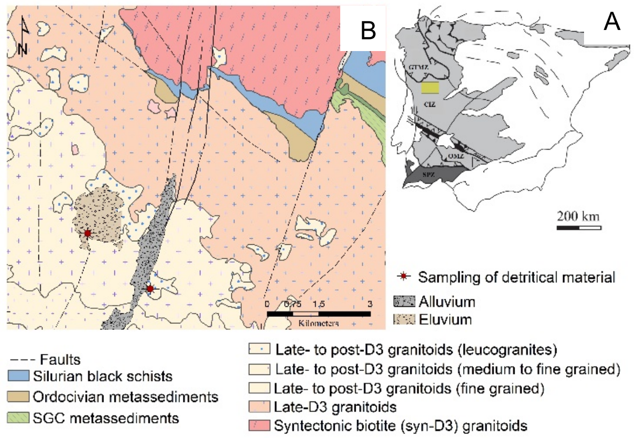

Figure 1. A - Map of Iberian Massif showing major tectonic units and main structures. B - Geological map of Bigorne area (adapted from Teixeira et al., 1968).

2.2 Granitic rocks

Variscan intrusions cover about 90% of the total exposure area. The intrusive sequence consists of (1) syn- D3 (U-Pb ages: 317Ma) biotite granites, and a volumetrically dominant (2) late and late- to post-tectonic association formed by granodiorite–monzogranite and biotite–muscovite granites (ca. 304) (Ferreira et al. 1987; Costa 2011; Costa et al. 2014). They form a large, composite batholith consisting of volumetrically dominant plutons of biotite monzogranites and two-mica granites and minor spots bodies of granodiorites. Small masses of leucogranites are also observed.

2.3 Tectonic setting

The main structures significant to gold mineralization of the region can be described to the effects of D3 phase from the Variscan Orogeny. Later ductile-brittle structures as NNE-SSW Penacova-Régua-Verín fault (PRVF) must be mentioned. The PRVF is one of the late Variscan deep crustal structure, which belongs to the NNE–SSW trending brittle system that crosscuts the whole of Northern Portugal (Pereira et al., 1993; Marques et al., 2002). The PRVF was nucleated on D3 phase and reactivated latter as a sinistral strike-slip fault with transtensional component (Pereira et al.1993). There is an important alluvial deposit (Figure 1) associated with the Balsemão River that corresponds to a NNE-SSW strike-slip fault, parallel to the main PRVF (Teixeira et al., 1968).

3 Samples and analytical techniques

Representative rock samples were collected at Bigorne outcrop. The petrographic studies were carried out using a Leica optical microscope at DGAOT-FCUP and observations were made in reflected light. Gold grains samples were collected from two detritical deposits on Balsemão River (alluvial samples) and in Lagoa S. João area (eluvial samples). In this study, gold grains were isolated by routine techniques of sluice box and panning to concentrate heavy minerals. Gold grains were hand-picked from the heavies under the binocular microscope. The grains were photographed to record their morphological characteristics prior to mounting according to size, setting in epoxy resin and polishing as described in Chapman et al. (2000). The samples were studied SEM-EDS and EPM (Cameca SX100 incorporating Secondary Electrons, Backscattered Electrons, Absorbed Detectors, and Energy Dispersive Spectrometry) at Oviedo University (Spain).

4 Bigorne gold deposit

4.1 Deposit-scale structure

The gold mineralization occurs disseminated or along a network of microfractures and quartz veins of variable length (wide from centimetric up to metric dimensions) in granitic rocks, commonly in sheeted vein array (Figure 2). The veins fill (2-10cm) extensional fractures developed during the late stages of ductile-brittle deformation.

The main vein trending observed in the outcrops is N10º-20ºE; 70ºW and N20º-40ºE; 60º-75º-80ºW. On a regional scale, gold deposits tend to occur near large transcrustal "first-order" regional faults and shear zones that functioned as major conduits for mineralizing fluids (e.g. Mateus and Noronha 2010). In this case, at deposit-scale, however, the ore shoots are frequently localizing within "second- and third-order" structures, subparallel to the main structure (PRVF).

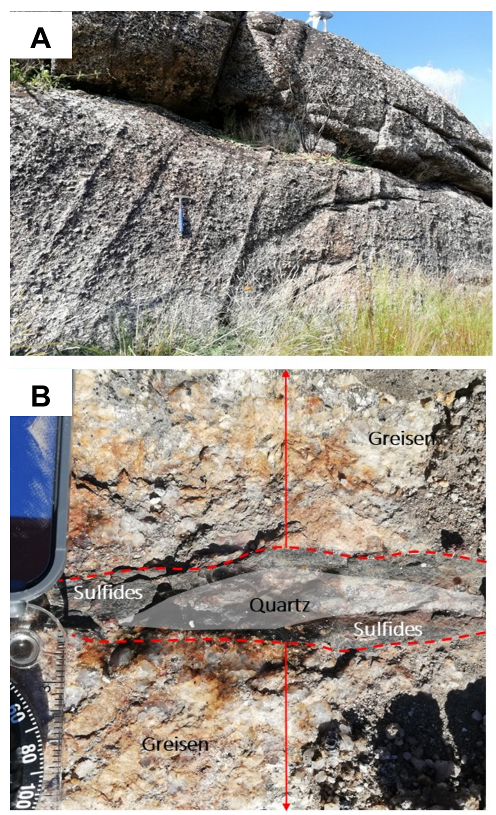

Figure 2. A – Sheeted vein array in granitic rocks; B – Quartz-sulfide vein.

4.1 Mineral assemblage from mineralized veins

Arsenopyrite is the commonest sulfide in the mineralized veins. The grains are commonly allotriomorphic to subidiomorphic, in the latter case showing well-developed faces at the border of aggregates. The arsenopyrite is optically homogeneous and in most cases, the content of Au, Ag, Te, Bi, Sb were below their respective detection limits. Most of the fractures are filled by late-developed scorodite. Other sulfides present, but in less quantity is pyrite and chalcopyrite.

Pyrite shows tiny inclusions of chalcopyrite, sphalerite and galena. Weathering processes have oxidized and the primary sulfides are altered, leading to the growth of supergene minerals, mainly scorodite ($FeAsO_4$. $2H_2O$), goethite ($FeO(OH)$) and covellite (CuS).

Gold occurs as native-Au (Figure 3-A) in a lesser amount as maldonite (Au_2Bi) (Figure 3-B) associated with native-Bi (Figure 3-D); hedleyite (Bi_7Te_3) also occurs associated with native gold. Maldonite and hedleyite appear as small irregular inclusions or cavity infillings in arsenopyrite crystals (5µm up to 30 µm). They often form composite grains or aggregates (Figure 3-C). Gold particles are irregular and appear included in arsenopyrite, pyrite and scorodite, as well as along grain boundaries. The size of gold particles varies between 5µm up to 100µm. The Ag content of native-Au is commonly low (mean 9.20 wt.%); in scorodite particles contain Ag up to 7.77 wt.%. Bismuthinite and native bismuth were observed included in arsenopyrite. However, native bismuth is also present in aggregates associated with gold, maldonite, and hedleyite.

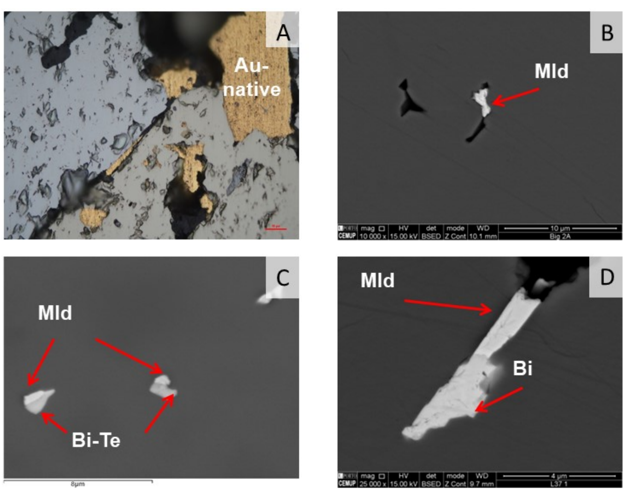

Figure 3. A – Photomicrograph of coarse native gold in pyrite and arsenopyrite. Backscattered electron images: B-C-D: B – Maldonite (Mld) in arsenopyrite; C – Maldonite in association with Bi-Te minerals (hedleyite); D - Maldonite with native bismuth.

5 Gold particles

5.1 Grain morphology and chemical composition

The gold grains were grouped according to grain morphology, chemical composition and were calculated the *fineness* for each group (100×Au/(Au+Ag); Fisher 1945). Most of the grains exhibit rounded shapes with smooth outlines. However, it is possible to distinguish two groups: (I) rounded and well-rounded particles of high fineness and homogeneous structure (Figure 4-A and 5-A); and (II) rounded to sub-rounded high fineness particles with heterogeneous inner structure (Figure 4-B and 5-B). The main gold grains from Group I are flaky and have a small size (Figure 4-A). The outline is relatively regular and surface topography tends to be smooth. The grains from Group II present a bigger size (> 250 µm) and have a more angular shape (Figure 4-B).

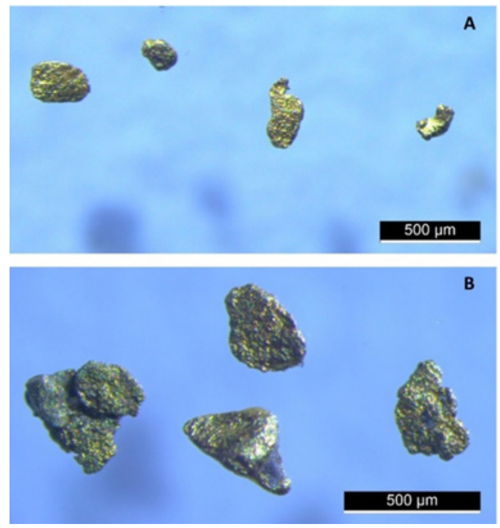

Figure 4. Examples of gold grains from detritical deposits. A – Group I. B – Group II.

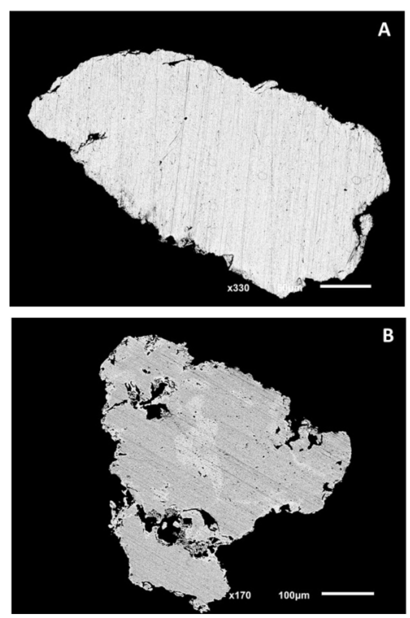

Figure 5. Back-scattered Electron (BSE) images of some gold grains. A – Example of gold grains from Group I; B - Example of gold grains from Group II. In these grains, the presence of Au- enriched rims is common.

Overall, the gold alloy composition is predominantly a binary Au-Ag alloy with a minor contribution from Cu and Cd (Table 1). In both cases, the mineral inclusions were not found in these studied grains.

Table 1. Electron microprobe analysis of gold from Bigorne area (mean values in wt.%; (n) number of gold grains studied).

Type of gold	Au	Ag	Cu	Cd	*Fineness*
Mineralized veins (n=10)	89.69	9.04	0.037	0.069	770-963
Group I (n=10)	93.47	6.29	0.10	0.05	929-942
Group II (n=12)	93.62	6.10	0.02	0.05	876-994

6 Conclusions

Regardless of the association of native-Au with maldonite and hedleyite in some aggregates minerals present in mineralized veins, this association is not founded in gold grains from superficial environments (but it is necessary to take into account that sampling is small yet). The gold particles have similar chemical composition (Au-Ag alloy). The rounded and homogeneous gold grains from Group I correspond to the alluvial sample. Sub-rounded, irregular shape and Au- enriched rims of the Group II are distinctive of an eluvial material. The flaky and the small size of the grains from the alluvial sample is easier to transport. These characteristics match with other deposits, as placers. The fact of the grains has similar characteristics from eluvial and alluvial samples provides evidence of very limited transport and therefore a restricted local source (Townley et al., 2003; Chapman et al. 2011). The same chemical compositions of the all types of gold (hypogene, alluvial and eluvial) suggest a single episode of gold deposition.

However, we must emphasize an increase of the size of gold grains from superficial environments in relation to the particles from mineralized veins. Considering that, gold grains become enlarged and the presence of Au-enriched rims in individual grains, suggest the existence of supergene regrowth (from mineralized veins to superficial environments) and supergene process such as silver leaching (from the eluvial to the alluvial gold grains). For future works, gold grain studies such as this require sufficiently large populations of grains to develop robust interpretations and the application in other Portuguese gold deposits with different characteristics.

Acknowledgments

The first author is financially supported by SFRH/BD/114693/2016 (FCT Portugal). The authors acknowledge the funding by COMPETE 2020 through the Institute of Earth Sciences project (UID / GEO /04683/2013) with POCI-01-0145 reference - FEDER007690.

References

Chapman, R.J., Leake, R.C., Moles, N.R., et al. (2000) The application of microchemical analysis of gold grains to the understanding of complex local and regional gold mineralization: A case study in Ireland and Scotland. Econ. Geol. 95:1753–1773.

Chapman, R.J., Mortensen, J.K., LeBarge, W. (2011) Styles of lode gold mineralization contributing to the placers of the Indian River and Black Hills creek, Yukon territory, Canada as deduced from microchemical characterization of placer gold grains. Mineral. Deposita 46:881–903. http://dx.doi.org/10.1007/s00126-011-0356-5

Carrington da Costa, J. (1950) Notícia sobre uma carta geológica do Buçaco, de Nery Delgado. Publicação Especial Comunicações Serviços Geológicos Portugal, 27p.

Costa, M.M.C. (2011) Geoquímica dos granitóides de Aguiar da Beira, Norte de Portugal. Universidade de Coimbra, Unpublished, p. 316.

Costa, M.M., Neiva, A.M.R., Azevedo, M.R., Corfu, F. (2014) Distinct sources for syntectonic Variscan granitoids: Insights from the Aguiar da Beira region, Central Portugal. Lithos, 196-197:83-89.

Ferreira, N., Iglesias, M., Noronha, F., Pereira, E., Ribeiro, A., Ribeiro, M.L. (1987) Granitóides da Zona Centro- Ibérica e seu Enquadramento Geodinâmico. In: Bea, F., Carnicero, A., Gonzalo, J.C., Lopéz Plaza, M-, Rodriguez Alonso, M.D., (Eds.). Geologia de los Granitoides y Rocas Asociadas del Macizo Hespérico. Libro de Homenaje a L.C. Garcia de Figuerola. Editorial Rueda, Madrid, Spain, 37-51.

Fisher, N.H., 1945. The fineness of gold with special reference to the Morobe goldfield, New Guinea Econ. Geol., 40:449-495; 537-563.

Fuertes-Fuente, M., Cepedal, A., Lima, A., Dória, A., Ribeiro, M.A., Guedes, A. (2016) The Au-bearing vein system of the Limarinho deposit (northern Portugal): Genetic constraints from Bi-chalcogenides and Bi–Pb–Ag sulfosalts, fluid inclusions and stable isotopes. Ore Geol. Rev, 72:461 213-231.

Julivert, M., Fontbote, J. M., Ribeiro, A., Conde, L. E. N. (1972) Mapa tectónico de la Peninsula Ibérica y Baleares. Inst. Geol. Min. ESpaña, escala 1:1.000.000

Marques, F.O, Mateus, A, Tassinari, C. (2002) The Late-Variscan fault network in central-northern Portugal (NW Iberia): a re-evaluation. Tectonophysics 359:255-270, doi:10.1016/S0040-1951(02)00514-0.

Mateus, A, and Noronha, F. (2010) Sistemas mineralizantes epigenéticos na zona Centro-Ibérico; Expressão da estruturação orogénica Meso- a Tardi-Varisca. In: Cotelo Neiva, J.M., Ribeiro, A., Mendes Victor, L., Noronha, F., Magalhães Ramalho, M., (Eds). Ciências geológicas: Ensino, investigação e a sua história. Associação Portuguesa de Geólogos, Vol II Geologia Aplicada, 47-61.

Noronha, F., Ramos, J.M.F., Rebelo, J.A., Ribeiro, A., Ribeiro, M.L. (1979) Essai de corrélation des phases de déformation hercynienne dans le Nord-Ouest Péninsulaire. Boletim Sociedade Geológica Portugal 21 (2/3):227-237.

Noronha, F., Cathelineau, M., Boiron, M.-C., Banks, D.A., Dória, A., Ribeiro, M.A., Nogueira, P., Guedes, A. (2000) - A three stage fluid model for Variscan gold metallogenesis in northern Portugal. J Geochem Explor., 71:209-224.

Pereira, E., Ribeiro, A., Meireles, C. (1993) Cisalhamentos hercínios e controlo das mineralizações de Sn–W, Au e U na Zona Centro-Ibérica, em Portugal. Cuad. Lab. Xeol. Laxe 18:89–119.

Ribeiro, A., Pereira, E. & Dias, R. (1990) Central-Iberian Zone. Allochthonous Sequences. Structure in the Northwest of the Iberian Peninsula. In: Dallmeyer, R. D. & Martínez García, E. (eds) Pre-Mesozoic Geology of Iberia. Springer, Berlin, 220–236.

Sousa, M.B. (1982) Litoestratigrafia e estrutura do "Complexo Xisto-Grauváquico" Ante-Ordovícico- Grupo do Douro (NE de Portugal). Ph.D. thesis, Univeristy of Coimbra.

Teixeira, C., Medeiros, A. C., Fernandes, A.P. (1968) Folha 14-A Lamego da Carta Geológica de Portugal, escala 1:50.000. Direção Geral de Minas e Serviços Geológicos, Lisboa.

Teixeira, C. (1955) – Notas sobre a Geologia de Portugal: o Complexo Xisto-Grauváquico ante-Ordoviciano. Empresa Literária Fluminense, Lisboa, 50 p.

Townley, B.K., Herail, G., Maksaev, V., Palacios, C., de Parseval, P., Sepuldeva, F., Orellana, R., Rivas, P., Ulloa, C. (2003) Gold grainmorphology and composition as an exploration tool: application to gold exploration in covered areas. Geochem. Explor. Environ. Anal. 3:29–38.

Pb-Zn-Sb-Ni-Au mineralization from the Kizhnica area, central Kosovo: new data on the listwaenite type mineralization

Sławomir Mederski, Jaroslav Pršek, Katarzyna Hincyngier
AGH University of Science and Technology, Kraków

Abstract. Polymetallic and listwaenite-type mineralization from the areas adjacent to the abandoned Kizhnica mine in Kosovo has been investigated. Presence of sphalerite, galena, chalcopyrite, pyrite, stibnite, Pb-Sb sulfosalts (boulangerite, semseyite, chovanite and jamesonite), berthierite, Fe-Mn carbonates and quartz were identified in massive - vein - banded ore. Galena, sphalerite, boulangerite, pyrite, gersdorffite, ullmannite, arsenopyrite, tetrahedrite, pyrrhotite and native Au were confirmed in listwaenite-type of mineralization. The chemical composition of major ore minerals is presented in this paper.

1 Introduction

Kosovo is characterized by presence of numerous Pb-Zn deposits, which belong to the Trepça Mineral Belt (TMB). These deposits are located in the Vardar Zone, belt extending from Bosnia through Kosovo, Macedonia and Greece to Turkey (Hyseni et al. 2010). Vardar Zone in Kosovo is characterized by Paleozoic (Veles Series) and Mesozoic rocks, Jurassic ophiolites (serpentinites, peridotite), Cretaceous and younger igneous rocks, Oligocene-Miocene volcanic rocks (e.g. andesites, trachytes and dacites) and pyroclastic volcanic rocks (tuffs) (Hyseni et al. 2010). The Oligocene-Miocene ore mineralization in Kosovo is related to the post-collisional magmatic activity. Three regional NNW-trending mineralization zones within the Belt are present: (1) Batiava – Artana Zone; (2) Belo Brdo – Stan Terg – Hajvalia Zone; (3) – Crnac Zone. Base metal mineralization in Kosovo occurs as skarn, carbonate replacement and vein deposits. Among the main Pb-Zn orebodies occur listwaenites, which are host rocks for the dispersed Ni mineralization. In Kosovo, listwaenite mineralization was recognized in the Crnac deposit in Rogozna Mountains (Radosavljevic et al. 2015) and in the Stan Terg area (Bal et al. unpublished). In Crnac deposit millerite, bravoite, niccolite and members of the gersdorffite-ullmannite series occur in paragenesis with base metal minerals. Cu mineralization occurrence in serpentinites from the Kizhnica area was noted by Werner (2017), but typical listwaenite-type mineralization rich in nickel and gold hasn't been described yet.

2 Geology

In the Hajvali-Kizhnica-Badovc region 3 structural zones (Fig. 1), which control Pb-Zn mineralization, are present: Hajvali-Badovc; Kizhnica; Okosnica (Durmishaj et al. 2015).

The area consists of Paleozoic and Mesozoic magmatic, metamorphic (serpentinites, gneisses) and sedimentary rocks (flysch), Neogene volcanic rocks (andesites) and Pliocene sediments (Fig. 1). The polymetallic mineralization in Kizhnica Pb-Zn-Ag deposit occurs as lenses, irregular veins, and stockwork-impregnations at the contact between the Jurassic serpentinites and the Cretaceous flysch series, usually close to the andesite intrusions (1.6 x 0.3 km wide zone) (Kołodziejczyk et al. 2016b).

Besides the main ore bodies exploited during the 20th century as an open pit, there are numerous polymetallic occurrences in the Kizhnica area. Preliminary studies indicate that the large scale mineral zonation in the whole massif can be inferred. Moreover, alteration typical for porphyry-epithermal systems has been observed in the hills.

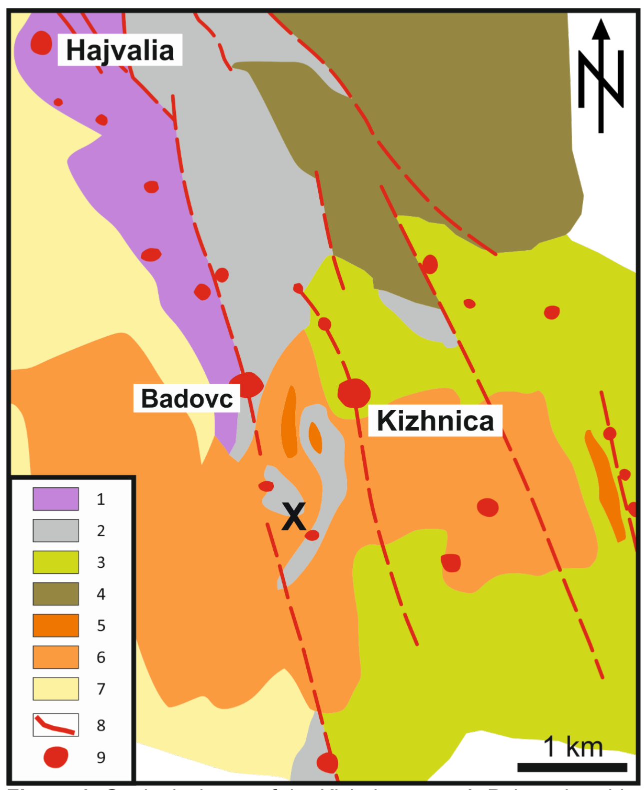

Figure 1. Geological map of the Kizhnica area. **1.** Paleozoic schist & marble. **2.** Serpentinite. **3.** Flysch series. 4. Diabase. **5.** Dyke. **6.** Tertiary volcanics: andesite & dacite. **7.** Neogene sediments. **8.** Faults. **9.** Polymetallic mineralization occurrences. **X.** Sampling locality.