DISCLAIMER
This book contains abstracts and complete papers approved by the Conference Review Committee. Authors are responsible for the content and accuracy.

Opinions expressed may not necessarily reflect the position of the International Scientific Council of SGEM.

Information in the SGEM 2015 Conference Proceedings is subject to change without notice. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, for any purpose, without the express written permission of the International Scientific Council of SGEM.

Copyright © SGEM2015
All Rights Reserved by the International Multidisciplinary Scientific GeoConferences SGEM Published by STEF92 Technology Ltd., 51 “Alexander Malinov” Blvd., 1712 Sofia, Bulgaria
Total print: 5000

ISSN 1314-2704
DOI: 10.5593/sgem2015B11

INTERNATIONAL MULTIDISCIPLINARY SCIENTIFIC GEOCONFERENCE SGEM
Secretariat Bureau
Phone: +359 2 4051 841
Fax: +359 2 4051 865
E-mails: sgem@sgem.org | sgem@stef92.com
URL: www.sgem.org
ORGANIZERS

- BULGARIAN ACADEMY OF SCIENCES
- ACADEMY OF SCIENCES OF THE CZECH REPUBLIC
- LATVIAN ACADEMY OF SCIENCES
- POLISH ACADEMY OF SCIENCES
- RUSSIAN ACADEMY OF SCIENCES
- SERBIAN ACADEMY OF SCIENCES AND ARTS
- SLOVAK ACADEMY OF SCIENCES
- NATIONAL ACADEMY OF SCIENCES OF UKRAINE
- INSTITUTE OF WATER PROBLEM AND HYDROPOWER OF NAS KR
- NATIONAL ACADEMY OF SCIENCES OF ARMENIA
- SCIENCE COUNCIL OF JAPAN
- THE WORLD ACADEMY OF SCIENCES (TWAS)
- EUROPEAN ACADEMY OF SCIENCES, ARTS AND LETTERS
- ACADEMY OF SCIENCES OF MOLDOVA
- MONTENEGRIN ACADEMY OF SCIENCES AND ARTS
- CROATIAN ACADEMY OF SCIENCES AND ARTS, CROATIA
- GEORGIAN NATIONAL ACADEMY OF SCIENCES
- ACADEMY OF FINE ARTS AND DESIGN IN BRATISLAVA
- TURKISH ACADEMY OF SCIENCES
- BULGARIAN INDUSTRIAL ASSOCIATION
- BULGARIAN MINISTRY OF ENVIRONMENT AND WATER

HONORED ORGANIZER

BULGARIAN ACADEMY OF SCIENCES

EXCLUSIVE SUPPORTING PARTNER

INTERNATIONAL SCIENTIFIC COMMITTEE
Science and Technologies in Geology, Exploration and Mining

- PROF. JEAN-PIERRE BURG, SWITZERLAND
- ACAD. DMITRY Y. PUSCHCHAROVSKY, RUSSIA
- PROF. YEYGENY KONTAR, USA
- PROF. HELMUT WEISSELT, SWITZERLAND
- PROF. KOEN BINNEMANS, BELGIUM
- PROF. PROSUN BHATTACHARYA FIL. DR., SWEDEN
- PROF. DR UNSURL YALCIN, GERMANY
- PROF. VLADICA CVETKOVIĆ, SERBIA
- PROF. NIKOLAY I. LEONYUK, RUSSIA
- PROF. DR RADOVLAV NAKOV, BULGARIA
- PROF. DR ZDENĚK KALAB, CZECH REPUBLIC
- PROF. DSC JORDAN MARINSKI, BULGARIA
- PROF. VÍCTOR ARAD, ROMANIA
- PROF. YURY STEPIN, RUSSIA
- PROF. DR SNEZANA KOMATINA PETROVIC, SERBIA
- PROF. KUVVET ATAKAN, NORWAY
- PROF. K.N. MILOVIDOV, RUSSIA
- ASSOC. PROF. GERARDO BRANCUCCI, ITALY
- ASSOC. PROF. MARIAN MARŠALKO, CZECH REPUBLIC
- ING. SLAVOMÍR HREDZAK, PHD, SLOVAKIA
- DR. DIEGO PERUGINI, ITALY
POLYMETALLIC ORE PARAGENESIS IN THE PLAVICA ORE DEPOSIT, 
EASTERN MACEDONIA

Full Prof. Dr. Todor Serafimovski¹
Goce Zlatkov²
Doc. Dr. Goran Tasev¹
Igor Ivanovski²

¹ Faculty of Natural and Technical Sciences, University “Goce Delčev”-Štip, R. Macedonia
² Genesis Resources International Ltd, DOOEL Skopje, R. Macedonia

ABSTRACT
Within this paper we are going to present results of our study of the Plavica deposit, Eastern Macedonia, epithermal gold and associated mineral phases that have been identified in silicified tuff, secondary quartzite, quartz-pyrite-enargite veins and mainly disseminated within an altered, but mostly silicified volcanic setting. Also, there we have determined the presence of contaminated pyrite, zinc-tetrahedrite, enargite, and certainly seligmanite regularly and commonly present copper association led by chalcopyrite, followed by bornite, chalcocite, covellite, as well as as slightly higher temperature associations of arsenopyrite and molybdenite. For illustration we want to emphasize that in pyrite we found increased concentrations of copper and zinc and less silver, then enargite with increased zinc concentrations (0.24-7.56 Zn), antimony (0.46-1.33% Sb) and silver (0.09-0.54% Ag), as well as tennantite with increased iron (0.21-1.55% Fe), zinc (6.24-9.06% Zn) and silver (0.08-0.87% Ag), while within the molybdenite elevated concentrations were detected for sulfur and iron.

Keywords: Plavica deposit, mineralogy, high-sulphidation, epithermal, gold.

INTRODUCTION

Based on the geological setting, mineralogy, alteration, stable isotopes and fluid inclusions, the Plavica deposit appears to represent an example of a high sulphidation, volcanic-hosted, epithermal deposit [1], [2], [3]. The Plavica deposit is well known to the local and regional community. Its exploration and exploitation history reaches back to Roman times (large-scale mining and processing of copper from pyrite-enargite veins), limited mining during the so called ‘Turkish’ era (15th–17th centuries) when gold was extracted for production of coins. In the 20th century, initial exploration have been started by the Selection Mines Ltd an UK based company (1934-1936, more than 2800 m of underground exploration workings). Several years later, after the end of the World War II, an intense programme of exploration and drilling was undertaken by the Zletovo Mine and the Geological Survey (1945-1952; 1961-1962 and 1963-1974). Also, an extensive programme was prepared by the Geological Survey and RIK “Sileks” and realized in the period 1976-1986 (with respectable 30 325 m of exploration drilling). From the late 1980s, there have been several, further, exploration programmes for Cu and Au by foreign mining companies (e.g. Cominco, Cyprus Amax, Minorco,
Goldfields, Rio Tinto, European Minerals) with the emphasis more on Au associated with the peripheral silica bodies. The latest exploration in the Plavica concession area was performed during the period 2011-2014 by the Australian company Genesis Resources International Ltd.

Preliminary publications and explorations that have contributed to creation of intensive professional and scientific database related to the Plavica deposit are numerous, but however we would like to point out here several the most important such are [4], [5], [6], [7] and [8].

METHODOLOGY

Mineral samples were collected during the continuous exploration programme during 2011, 2012 an 2013, mostly from drillhole cores and were observed under state of the art polarized optical microscope, and the electron microprobe. The morphology and composition of gold and associated minerals were studied on a JEOL SEM JSM-6010PLUS InTouchScope at the Faculty of Geology and Geography, Sofia University, Bulgaria with the following features: Resolution in High Vacuum mode of 4nm (20kV), 8nm (3kV), 15nm (1kV) and Low Vacuum mode of 5nm (20kV) BSE, Accelerating voltage of 500V to 20kV, Magnification from x5 to x300,000. LV detector with Multi-segment BSED (as a standard) and optionally equipped with LV-SED (pressures 10-100 Pa). The standard EDS system (silicon drift detector technology), included possibilities for spectral mapping, multi-point analysis, automatic drift compensation. The JEOL was equiped with 3D Three Dimensional Image Software MP - 45030TDI, also.

GEOLOGICAL FEATURES

The Kratovo–Zletovo ore region is spatially combined with a volcanic area of the same name (1200 km²) at the boundary between the Serbian–Macedonian and Vardar ophiolite terrains [2] and is distinct due to the zonal occurrence of different polymetallic and precious metal mineralization [3]. The volcanic area is composed of the products of calc–alkaline magmatism with dominant Oligocene–Miocene andesites, dacites, and tuffs intruded by Pliocene basaltic dikes. The Plavica high-sulphidation epithermal deposit is situated in the aforementioned Kratovo-Zletovo ore region in terms of metallogeny it belongs to the Lece-Chalkidiki metallogenic zone [9], [10]. The deposit itself is located in eastern central Macedonia, 7 km north-western of the Probistip city and 5 km southern of the Kratovo city. The central part of the area is made up of several volcanic structures, hosting the large volumes of the products of advanced argillic alteration. Significant Au–Ag–Cu mineralization is related to the quartz–alunite rocks.

The widest fields of hydrothermally altered rocks were found in the central parts of the Plavica deposit and Crn Vrv (0.2 and 0.4 km² of rocks affected by argillic alteration and 8.0 and 10.0 km² of altered rocks, respectively) near the town of Kratovo. Tourmaline, pyrophyllite, diasporere, and adularia occur locally. The Plavica deposit is controlled by a large Neogene volcanic center, complicating the structure of the paleo-caldera 6.5 km² in area.

Based on study of geological structure, ore mineralogy, wall-rock alteration, and fluid inclusions, the Plavica deposit is referred to high sulfidation epithermal deposits [1], [2], [3].
ORE MINERALIZATIONS

Mineralogical–geochemical studies have shown that gold from the Plavica high sulphidation epithermal deposit (Republic of Macedonia) contains an admixture of Fe and Cu, that the morphology of gold indicates the proximity of the primary source, and that the chemical composition of gold is independent of its morphology. The composition of gold and its morphology are the direct searching criteria, indicating the genetic type of mineralization. The mineralisation occurs in four distinct settings: (i) stockwork and disseminated Cu–Au (+Mo, Ag) mineralisation occurs in the central and deepest part of the system. It is present over an area of 6 km² and was still reported at depth in the deepest drill hole (950 m below surface); (ii) veins of quartz, pyrite, sphalerite and enargite (± gold) occur at intermediate levels and appear to be superimposed on the stockwork. Old workings in the area followed these enargite veins for distances up to 200 m and show that they had a thickness from 0.7 to 5 m and a content of Cu around 2% and Au at 1 ppm. They seem to occur where the NW–SE structures intersect E–W veins, mostly in the northern part of the deposit (Figure 1); (iii) silica bodies occur peripheral to the central zone (ore bodies consist of quartz plus some opal and are sub-vertical in orientation); (iv) around the margins of the caldera, there are small veins with enrichments in Pb and Zn (up to 1% combined Pb-Zn).

There are also some U-rich veins, although their exact relationship with the Plavica system is unclear. Detailed exploration performed by the Genesis Resources International DOOEL Skopje (mostly in the northeastern part of the Plavica deposit) defined one new Cu-Au mineralization type where dominate epithermal gold of high sulfidation with representative elongated lens-like ore bodies, which follows the structural controlling forms (Figure 1).

![Fig. 1. Geological cross section through the Plavica deposit, Eastern Macedonia with a display of morphological form of particular gold ore bodies [8]](image-url)
In regards to mineralization the following minerals have been confirmed there: pyrite, pyrrhotite, chalcopyrite, magnetite, rutile, scheelite, hematite, molybdenite, galena, sphalerite, bornite, enargite, native gold, tetrahedrite, tennantite, chalcostite, digenite, covellite, proustite, native copper, malachite, azurite, while lately were confirmed seligmannite, luzonite, famatinite, petzite, bogdanovite, bezsmertnovite, sylvanite, pearceite, bilibinskite etc.

RESULTS AND DISCUSSIONS

In regards to the mineralization specifics in this part of the studied Plavica deposit of special curiosity is a gold-bearing mineralization that occurs in a variety of morphological forms and spatial presence of native gold and Au-Ag-tellurides. Sometimes native gold can be found along quartz veins of peripheral parts where present are Fe-hydroxides, also. In oxidized parties with dominant Fe-oxide and hydroxide parageneses besides frontal silification often appear later quartz-limonite veins within oxidized breccias, and for transformed Fe-hydroxide aggregates in such a manner (magnetite-hematite-martite-limonite) are related interesting flake-like gold aggregates (Figure 2). Also, gold occur as flake-like to worm-like aggregates within the limonite-goethite matrix and as a disseminated native gold within regular quartz crystal while within the brecciated and silicified rocks, can be observed later quartz cavities filled with gold and electrum of micron size (Figure 3). In some intensely silicified parts where relic pyrites occur were determined telluride of gold and silver, which themselves contain elevated concentrations of arsenic, that causes their polyhedron appearance. In similar areas, but this time directly in aggressively silicified parts was determined presences of individual grains of native gold in the half-moon like form. Also, in such silicified parties sometimes appear typical gold-bearing forms with representative yellow color, which are usually followed by scattered individual micron size grains. A special curiosity in regards to gold were determined late idiomorphic quartz crystals that enclosed usually several gold grains (Figure 3), where gold is diverse in size and form (droplet-like, irregular worm-like up to gold druses).

![Fig. 2. Microphotograph of single horseshoe-like native gold grain within quartz cavity, enclosed within quartz-Fe hydroxide vein. Plane polarized light, Magnif. x 400 II.](image)

![Fig. 3. Microphotograph of well developed native gold druse and individual gold grain in later quartz crystal. Plane polarized light, Magnif. x 630 II.](image)

Also, individual grains of native gold occur in quartz veins or quartz caverns or their marginal sections (Figure 3). Here it is worthwhile to mention that there can be seen micron size grains of native gold occurring in typical teardrop shapes representative for higher levels of the epithermal ore-bearing system. At some places in
relic grains of idiomorphic pyrite idiomorphic is found some native gold in it. Few times we noticed presence of native gold in representative two-phase and multifaceted idiomorphic aggregates and forms. This kind of native gold is characteristic of certain polymetallic stages with high presence of arsenic generated low temperature epithermal zones related to predominantly intensive silification of volcanic rock or characteristic secondary quartzite.

**Composition of some other mineral phases**

Also, we made efforts to confirm analytically some of the minerals present within the Plavica deposit ore mineral association. Our preliminary results have confirmed enargite, tennantite and molybdenite compositions.

**Enargite and tennantite**

Determined enargite and tennantite mineral grains under the polarized optical microscope have been analyzed under the microprobe (Figure 4 and Figure 5, points 1-4; Figure 6 and Figure 7, points 6, 7, 8, 9; respectively).

![Fig. 4](image1.png) **Fig. 4.** Microphotograph of complex, externally and internally corroded quartz-pyrite-enargite-famatinite aggregate, enclosing chalcopyrite and sphalerite and latter chalcocite and covellite. *Plane polarized light, Magnif. x 200 II.*

![Fig. 5](image2.png) **Fig. 5.** SEM microphotograph of Zn-enargite (points 1 and 2) and enargite (points 3 and 4) mineral grains. *Backscattered electrons (BSE), Magnif. x 1600.*

![Fig. 6](image3.png) **Fig. 6.** Microphotograph of colloformly corroded tennantite within quartz-limonite matrix. *Plane polarized light, Magnif. x 200 II.*

![Fig. 7](image4.png) **Fig. 7.** SEM microphotograph of tennantite from the Plavica deposit (points 1, 2, 3, 4). *Backscattered electrons (BSE), Magnif. x 1900.*

The chemical composition of enargite, as it is shown in Table 1, have shown slight discrepancies from the stoichiometric enargite composition (Cu$_3$AsS$_4$) in standards.
Table 1. Chemical composition of Zn-enargite (points 1 and 2), enargite (points 3, 4, 5) and tennantite (analyses 6, 7, 8, 9) from the Plavica deposit

<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical analysis (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>40.90</td>
<td>46.54</td>
<td>46.48</td>
<td>48.69</td>
<td>41.04</td>
<td>39.67</td>
<td>40.58</td>
<td>40.76</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.12</td>
<td>0.24</td>
<td>0.15</td>
<td>1.37</td>
<td>0.86</td>
<td>1.55</td>
<td>0.21</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>6.00</td>
<td>7.56</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>7.56</td>
<td>8.99</td>
<td>9.06</td>
<td>6.24</td>
</tr>
<tr>
<td>Ag</td>
<td>0.46</td>
<td>0.54</td>
<td>0.09</td>
<td>0.13</td>
<td>-</td>
<td>0.47</td>
<td>0.08</td>
<td>0.87</td>
<td>0.47</td>
</tr>
<tr>
<td>As</td>
<td>19.55</td>
<td>19.86</td>
<td>17.77</td>
<td>17.21</td>
<td>16.81</td>
<td>19.72</td>
<td>15.51</td>
<td>20.30</td>
<td>19.96</td>
</tr>
<tr>
<td>Sb</td>
<td>0.55</td>
<td>0.46</td>
<td>1.08</td>
<td>1.33</td>
<td>-</td>
<td>0.55</td>
<td>5.43</td>
<td>0.88</td>
<td>0.39</td>
</tr>
<tr>
<td>S</td>
<td>29.60</td>
<td>29.51</td>
<td>34.14</td>
<td>34.60</td>
<td>33.09</td>
<td>29.76</td>
<td>28.73</td>
<td>29.01</td>
<td>29.62</td>
</tr>
<tr>
<td>Σ</td>
<td>98.18</td>
<td>99.60</td>
<td>100.10</td>
<td>99.90</td>
<td>99.96</td>
<td>99.96</td>
<td>99.96</td>
<td>100.91</td>
<td>97.98</td>
</tr>
</tbody>
</table>

Note: Enargite (1-5): 1. (Cu₁₂[Zn₁₋₃Fe₁₋₃]S₃₋₄As₁₋₄Sb₁₋₂S₂; 2. (Cu₁₂[Zn₁₋₃Fe₁₋₃]S₃₋₄As₁₋₄Sb₁₋₂; 3. Cu₁₀As₅₁S₄; 4. Cu₁₀As₅₁S₄; 5. (Cu₂₄Fe₁₀)_10As₁₅S₄₁₇; Tennantite (6-9): 6. (Cu₄₋₈Fe₂₋₄Zn₁₋₃As₁₋₄Sb₁₋₂S₂; 7. (Cu₃₋₈Fe₁₀[Zn₅₋₈]_1₋₃As₁₋₄Sb₁₋₂S₂; 8. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂; 9. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂; 9. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂; 9. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂; 9. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂; 9. (Cu₄₋₈Zn₂₋₃Fe₁₀[Zn₅₋₈]₃₋₄Sb₁₋₂S₂)

Namely, in points 1 and 2, close vicinity of sphalerite and chalcopyrite, to analyzed enargite grains caused certain impurities in form of Zn and Fe to occur in its composition, substituting part of copper positions. Although the analysis of point 3 was quite close to the standard ones, the point 4 indicated slightly increased presence of antimony. Although relatively scarce, tennantite was determined in several samples during the optical microscope study (Figure 6) and electron microprobe analysis (Figure 7). Microscopic observations in regards to occurrence of tennantite in samples from the Plavica deposit in the best manner were confirmed by electron microprobe analyses (Table 1, analyses 6-9). As may be seen from the Table 1 above, tennantite composition is not quite stoichiometrically ideal due to decreased copper, iron and arsenic values at the expense of increased concentration of zinc. Here we would like to give an accent to the fact that the presence of tennantite within this part of the Plavica deposit, beside its importance in regards to mineralogical diversity, stress out that there were two metal stages, an early Cu-rich, Au-poor stage, dominated by enargite-luzonite, and a late Au-rich, Cu-poor stage, associated with intermediate-sulfidation-state sulfides such as tennantite-tetrahedrite and chalcopyrite, and telurides as it was confirmed for genetically similar deposits elsewhere (e.g., El Indio, Lepanto; [11]). The transition from quartz-alumite-pyrite alteration to enargite-pyrite and finally to tennantite-tetrahedrite, indicates that the fluid progressively became more reduced and less acid.

Chalcocite and covellite

Chalcocite and covellite the most commonly were determined with and around the enargite, and this is true for bornite, too. Chalcocite is very common and usually associates with covellite, pyrhotite, chalcopyrite, enargite, mainly within complex and sort of corroded and relic aggregates, while sometimes occur as individual grain aggregates followed by covellite. The corrosion and corrosion structures exist, but here the main attraction are representative so-called kant or rim structures formed by frontal edge corrosion of pyrite by chalcocite (different levels of corossion). Pair pyrite-chalcocite is represented by numerous rim structural phases originating from different pyrite relics in the middle of chalcocite grain, to real polyhedral pyrite aggregates encircled by chalcocite (Figure 8). Only at several places exist coarse pyrites, which are
not in contact with chalcocite. On the other hand there are pure chalcocite granular aggregates, partly corroded but not in contact with pyrite. Often the overall activity took place between pyrite on the one side and covellite and chalcocite on the other one. However, here cataclastic processes were major cause for covellite (or chalcocite) enclosure in stockworks within pyrite (Figure 9). At several locations already formed chalcocite veinlets within pyrite were protruded by later vein quartz, so we have a situation where quartz vein occur within quartz vein.

![Fig. 8. Microphotograph of massive pyrite grains encircled by rims of chalcocite. Plane polarized light, Magnif. x 200 II;](image1)

![Fig. 9. Microphotograph of well developed chalcocite veinlets/stockworks within cataclastic and relic pyrites. Plane polarized light, Magnif. x 200 II;](image2)

**Molybdenite**

Although hard to find, luckily we managed to find molybdenite in few of the studied samples from the Plavica deposit (Figure 10 and Figure 11).

![Fig. 10. Microphotograph of rod-like aggregates of molybdenite in quartz matrix. Plane polarized light, Magnif. x 400 II](image3)

![Fig. 11. SEM microphotograph of rod-like aggregates of molybdenite and position of analysis. Backscattered electrons (BSE), Magnif. x 1900](image4)

Analyzed composition of this molybdenite shows slight discrepancy from the stoichiometric values (Frondel and Wickman, 1970) due to small increase of sulfur and iron and decrease of molybdenum (45.52% S, 0.62% Fe, 56.86% Mo).

The presence of molybdenite points out that this sample came from the high-temperature zones within the Plavica mineralized system, which roots can be traced down to the certain intrusion as mentioned for similar deposits elsewhere (Arribas, 1995).
CONCLUSION
The latest study of ore minerals enriched the knowledge of the mineral association within the Plavica deposit, especially in the epithermal part of high sulphidation where special contribution was given in definition of morphological features of epithermal gold. The latest findings during the electron microprobe analysis gave the compositions of several representative mineral phases, regular associates of epithermal gold with their specifics. Enargite have shown increased values of zinc (0.24-7.56 Zn), antimony (0.46-1.33% Sb), silver (0.09-0.54% Ag) and iron (0.15-1.37% Fe). Also, tennantite has been characterized by certain impurities of iron (0.21-1.55% Fe), zinc (6.24-9.06% Zn) and silver (0.08-0.87% Ag). Discrepancies from the ideal composition have shown pyrite corroded, encircled and stockworked by chalcocite and covellite. Although at lower intensity, the molybdenum stoichiometry was disrupted to by very slightly increased sulfur and iron, resulting in decrease of molybdenum.

REFERENCES