Hydrothermal zonality in porphyry-copper deposits (PCD) of the Panagyurishte ore region, Bulgaria

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Introduction
The Upper Cretaceous (92–86 Ma; von Quadt et al., 2005) porphyry-Cu±Mo±Au intrusion-centered deposits (Elatsite, Medet, Assarel, Tsar Assen, Vlaykov Vruh) in the Panagyurishte ore district (Fig. 1) are one of the most studied and well understood ore systems in Bulgaria. We have to note the benchmark works of Bogdanov (1987), Strashimirov et al. (2002), Tarkian et al. (2003), Kouzmanov et al. (2009), Popov et al. (2012) that are amongst the most cited PCD references in the Bulgarian ore geology literature. The Cu-porphyry hydrothermal zoning types are complicated and commonly masked due to overlapping of alteration and ore assemblages, still not well understood and subject of extensive studies. In this contribution we review the hydrothermal zonality in Cu-porphyry systems from the Panagyurishte ore district (Elatsite, Medet, Assarel and Vlaykov Vruh). We also note trace-elements variations in the ore associated pyrite with distance from porphyry-copper centers as possible porphyry trace-elements indicators.

PCD hydrothermal zonality types

Host-rocks alteration and ore mineral assemblages zonality
Host-rocks alteration and ore mineral assemblages zoning commonly is defined by lateral changes from the porphyry center of “A” and “M” veins (Early Q-KFs-Bt with Bn-Mt±Au, Ag, PGM, Te) to “B” veins (Cp-Py±Au, Moly) and “D” (late Q-Py) veins (Fig. 1) Cu-poor veins associated with phyllitic (Q-Ser) alterations. The “D” type pyrite often overprints and is closely associated with the Cp, Au and Moly-rich “B” veins and that is why could be attached to ore pyrite. Further the PCD core with potassic alteration grades outward into propylitic alteration zones (Fig. 1). At these more distal veins Qz-Gn-Sf-Cp±Ag, Sb and As sulphosalts and Q-Carb±Flu, Zeol “C” veins occur in association with chlorite, locally epidote, albite or adularia (Sillitoe, 2010; Popov et al., 2012). The early “A” veins (Fig. 1) sometimes display “wormy” structure indicating their formation was before the parent intrusion solidification and commonly are overprinted by Cp-rich “B” veins that in some parts of Elatsite, Medet, Assarel and VI. Vruh PCD associate with Moly veins.

Temperature and fluid salinity zonality
Temperature gradients of highly saline fluids (40–65% NaCl eqv.) from about 750 °C at the mineralization center to approximately 150 °C and drop of fluid salinity (5–15 NaCl eqv.) are considered to be a general feature for PCD and in particular for the studied deposits (Tarkian et al., 2003; Kehayov et al., 2003) and good explanation for the lateral zoning. The bornite rich core in association with sylvanite (AuAgTe₂), hessite (Ag₂Te) and merenskyte (PdTe₂) indicate that the telluride minerals deposition most commonly occurs at temperatures below 354 °C (Petrunov, Dragov, 1993; Bogdanov et al., 2005) that is also gold ore enrichment pathfinder for PCD.
**Trace-element zoning in pyrite**

The concept of PIM (porphyry indicator minerals) has been developed during the last decade worldwide PCD study supported by the large exploration and mining companies (Florian, 2013; Cooke et al., 2017) that could provide a key tool to the increase of exploration targeting success.

Trace-elements in ore associated (“B” and “D”-type) pyrite from Elatsite, Medet, and Vlaykov Vruh PCD have been studied based on selected 46 LA-ICP-MS analyses (Perkin-Elmer ELAN DRC spectrometer with New Wave UP193FX LA device at the Geol. Institute, BAS) to test possible porphyry trace-elements indicators. Trace elements of interest as PIM in the ore pyrite are: W, Ti, V, Sn, Co, Ni, Au, Ag, Cu, Pb, Zn, As, Sb, Bi, Ge and Se (Table 1).

The most typical PCD trace-elements indicators values (Table 1), some of them highly variable in the ore associated pyrite (in ppm) are: W (0.2–0.3) Ela, (0.5–8) Med, (0.4–13) VV; Ti (13–81) Ela, (9–78) Med, (26–7014) VV; V (0.5–1) Ela, (9–744) VV and Se (332–882) Ela, (149–246) Med, (55–570) VV (Fig. 1). The most commonly detected values for Sn (0.7–10), Au (0.08–0.6), Ag (0.08–0.7), Cu (2–69), Pb (0.1–43), Zn (5–38), As (2–12), Sb (0.3–1), Ge (3–28) and Bi (0.1–17) ppm in the ore-related pyrite are low variable (Table 1). The high Ti values are due to fine inclusions of rutile, while the high Co values in Elatsite (1070 ppm) and Medet (7061 ppm) are due to inclusions of carrolite.

**Conclusions**

Our preliminary results of PCD zonality and trace elements indicators study (Fig. 1) of the ore associated pyrite could be summarized as follows:

- **Sn (˃3ppm)**, **W (˃6ppm)**, **Co (˃6ppm)**, **Bi (˃5ppm)** and **Te (˃3ppm)** are important trace elements indicators in pyrite for central proximity to Cu and Au rich ore mineralization closely associated with K-silicate host rocks alterations.
- **Se (˃50ppm)**, **Ge (˃20ppm)**, **Pb and Zn (˃0.2ppm)** and **Ag (˃0.5ppm)** indicate more...
distal zones with “D” and “C” veins and Cu poor mineralization.

- The actinolite commonly is closely associated with bornite and chalcopyrite mineralization and is good proximity indicator for “A” and “B” type veins.

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References


Table 1. Typical pathfinder values in PCD pyrites from Panagyurishte ore district (in ppm)

<table>
<thead>
<tr>
<th></th>
<th>W</th>
<th>Ti</th>
<th>V</th>
<th>Sn</th>
<th>Co</th>
<th>Ni</th>
<th>Au</th>
<th>Ag</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
<th>Ge</th>
<th>Se</th>
</tr>
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<tr>
<td>El</td>
<td>0.2–0.3</td>
<td>13–81</td>
<td>0.5–1</td>
<td>0.7–0.9</td>
<td>5–1070</td>
<td>1–194</td>
<td>0.08–0.1</td>
<td>0.08–0.1</td>
<td>2–15</td>
<td>0.1–0.3</td>
<td>5–6</td>
<td>2–11</td>
<td>0.3–0.5</td>
<td>0.1–0.2</td>
<td>4–14</td>
<td>332–882</td>
</tr>
<tr>
<td>Med</td>
<td>0.5–8</td>
<td>9–78</td>
<td>1–8</td>
<td>3–10</td>
<td>12–7061</td>
<td>5–28</td>
<td>0.1–0.5</td>
<td>0.1–0.6</td>
<td>21–61</td>
<td>0.1–0.3</td>
<td>6–23</td>
<td>2–12</td>
<td>0.3–1</td>
<td>0.1–5</td>
<td>5–6</td>
<td>149–246</td>
</tr>
<tr>
<td>VV</td>
<td>0.4–13</td>
<td>26–7014</td>
<td>1–744</td>
<td>1–3</td>
<td>2–34</td>
<td>4–335</td>
<td>0.1–0.6</td>
<td>0.2–0.7</td>
<td>14–69</td>
<td>8–43</td>
<td>11–38</td>
<td>3–8</td>
<td>0.4–1</td>
<td>1–17</td>
<td>3–28</td>
<td>55–570</td>
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