Au-Ag-Te-Se minerals in the Elatsite porphyry-copper deposit, Bulgaria

Kamen Bogdanov, Alexander Filipov, Radoslav Kehayov

Sofia University “St. Kl. Ohridski”, Department of Mineralogy, Petrology and Economic Geology, Tsar Osvoboditel Bd., 1504 Sofia, Bulgaria; E-mail: kamen@gea.uni-sofia.bg

Abstract. Elatsite is one of the largest operating porphyry-copper deposits in Eastern Europe, and is also enriched in Au-Ag-Te-Se and PGE. The magnetite-bornite-chalcopyrite ore assemblage, preserved mainly in the central K-alteration core, has been examined by means of electron microprobe and SEM. Au-Ag-Te-Se minerals are abundant, and include macroscopic gold with high fineness. The ores are also enriched in hessite, stützite, sylvanite, merenskyite, empressite, wittichenite and clausthalite, found as exsolutions in bornite and chalcopyrite. Paragenetic relations display initial saturation of native Te with sylvanite (AuAgTe₂), followed by increasing Me/Te ratio from 1:1 to 2:1 in hessite (Ag₂Te). Tellurides within bornite with early macroscopic (>100 µm) gold with high fineness (>900) took place at high fTe₂ (-4; -8) and fO₂ conditions near to the magnetite-hematite buffer. The hessite-clausthalite association in chalcopyrite and the formation of stephanite, together with the drop in fineness of the late microscopic (<100 µm) gold (<650), indicate decrease of fTe₂ (-18; -19) and fS₂ (-13; -14) and temperatures <200°C in the late Te-, Se- and Au-bearing associations.

Key words: gold, tellurium, sylvanite, hessite, Elatsite porphyry-copper deposit, thermodynamic constraints

Introduction

Au-Ag-Te-Se minerals commonly occur in volumetrically amounts in the early bornite and chalcopyrite rich ores in porphyry-copper deposits, resulting in assemblages that are not only of economic interest, but also genetically significant as an important indicator for gold and PGE ore enrichment (Afifi et al., 1988; Cook et al., 2002a; Ciobanu et al., 2002, 2003; Tarkian et al., 2003; Bogdanov et al., 2004).

Geological setting

Elatsite is one of the largest operating porphyry-copper deposits in Eastern Europe and one of the richest in PGE (Pd). The Cu-Au-PGE mineralization is hosted in Late Cretaceous subvolcanic quartz-monzonitic to granodioritic intrusions (U/Pb age 91.5-92 Ma), but also well developed in Paleozoic granodiorites (U/Pb age 314 Ma) and partly in Paleozoic greenschists (Bogdanov, 1987; Petrunov et al., 1992; Popov and Kovachev, 1996; Popov et al., 2000; Bogdanov et al., 2000; Von Quadt et al., 2002; Tarkian et al., 2003; Strashimirov et al., 2003).

The porphyry Cu-Au-PGE mineralization is controlled by NW- and NE-trending faults, and covers an area of about 1 km². It can be traced to a depth of about 800 m.

Ore reserves of the deposit are estimated to 185 Mt, with 0.38% Cu, 0.21 g/t Au, 0.07 g/t Pd and 0.02 g/t Pt (Tarkian and Stribrny, 1999; Strashimirov et al., 2002, 2003; Tarkian et al., 2003).
**Au-Ag-Te-Se minerals**

Native gold is commonly observed as microscopic (1-50 µm) blebs to macroscopic (100-500 µm) irregular grains in bornite and chalcopyrite, either with or following the deposition of tellurides (Figs. 1 and 2).

Se, Te, Bi, Pd (up to 1.35%) and Pt (up to 0.21%) are characteristic trace elements within the gold. Macroscopic (>100 µm) gold with high fineness of 903-994 (Fig. 1) and telluride minerals are most abundant in the magnetite-bornite-chalcopyrite (Mt-Bn-Cp) ore assemblage preserved mainly in the central K-alteration (Q-K-Fsp-Bt) core of the deposit, testifying to the role of high-temperature bornite as a gold and Te carrier.

The quartz-chalcopyrite-pyrite (Q-Cp-Py) assemblage outside of the bornite core where microscopic (1-50 µm) gold has a fineness of 753-853 is more common and is the main gold carrier in Elatsite. In addition, the assemblage tetradymite-aikinite ± hessite is a stable association in chalcopyrite (Ciobanu et al., 2003; Bogdanov et al., 2003).

Quartz-pyrite (Q-Py) and quartz-galena-sphalerite (Q-Gl-Sp) assemblages are not abundant in gold, but more closely associated with propylitic and the phyllic-argillic alterations build up the upper and marginal parts of the ore shell. The fineness of the late gold (Fig. 2) in the latter two assemblages decreases progressively from 838-753 to 682-594, respectively (Kehayov and Bogdanov, 2005).

Telluride and selenide minerals in Elatsite were first described by Petrunov et al. (1992) and Dragov and Petrunov (1996).

Paragenetic relations of the Mt-Bn-Cp assemblage display initial saturation of native Te with merenskyite (PdTe₂) and sylvanite (AuAgTe₂), followed by increasing Me/Te ratio from 1:2 to 1:1 and 2:1 in hessite (Ag₃Te).

**Merenskyite**, with the composition Pd₀.₈₃₋₁.₀₅P₀.₀₃₋₀.₂₅Ag₀.₀₉₋₀.₁₅Te₁.₉₇₋₁.₉₉ was identified as euhedral inclusions and columnar crystals, 5-30µm in size, exsolved in bornite and chalcopyrite, and commonly rimmed by hessite.

The present natural telluride phase relations (Fig. 3) coupled with fluid inclusions studies (Tarkian et al., 2003; Kehayov et al., 2003) indicate that telluride deposition took
place at temperatures below 354°C (the melting point of sylvanite).

**Hessite, stützite, sylvanite and empressite** occur as fine (1-30 µm) inclusions, or as exolusions in bornite (Fig. 3, Table 1) and chalcopyrite, or at their grain boundaries, associated with native gold, native Te, merenskyite, or clausthalite.

The composition of hessite is universally stoichiometric (Table 1) and it is the most commonly observed telluride in the bornite core, not only in Elatsite, but also in other porphyry-copper deposits such as Assarel (Bulgaria), Majdanpek (Serbia), Santo Tomas II (Philippines), Panguna (Papua New Guinea). (Petrunov et al., 1992; Tarkian and Koopmann, 1995; Tarkian and Sterbrny, 1999; Cook et al., 2002a, b; Ciobanu et al., 2002, 2003; Tarkian et al., 2003; Bogdanov et al., 2004). Hessite in Elatsite is closely associated with gold and more rarely with clausthalite (Fig. 3) and merenskyite.

**Empressite** is an apparently scarce mineral in telluride associations of Elatsite, a fact that could be explained by the observed assemblage of native Te with stützite (Fig. 3) as a result of the decomposition of empressite (Afifi et al., 1988): 5AgTe → Ag_{5-x}Te_{3} + 2Te (T ~ 170-210°C), where AgTe is empressite and Ag_{5-x}Te_{3} (x = 0.24-0.36) is stützite.

The **Sylvanite-tellurium** assemblage (Fig. 3d) implies that the sylvanite is stable to the condensation of native Te (Afifi et al., 1988). According to the Ag content that is over 0.6 atoms p.f.u. (Table 1), the examined sylvanite can be regarded as Ag-rich, i.e., similar to that described from Sacaramb, Romania (Ciobanu et al., 2004).

The observed assemblage of *native tellurium+stützite+sylvanite* (Fig. 3d) is stable up to 330°C (Cabri, 1965; Afifi et al., 1988) and could be part of the original equilibrium assemblage as a result of exsolution from bornite, a feature also confirmed by the fluid inclusion studies (Kehayov et al., 2003).

**Rare individual inclusions of wittichenite**, 5-10 µm in size, give a general formula in the range Cu_{2.80-3.01}Ag_{0.01}Bi_{0.86-1.01}S_{2.93-3.03}Se_{0.01}. The mineral occurs within bornite, or at the grain boundary with K-Fsp.

Fine lamellar inclusions of *clausthalite*, ranging in size from 2-3 to 30-40 µm, are documented in both bornite and chalcopyrite, or at the grain boundary with stützite (Fig. 3e, Table 1). Compositions are in the range Pb_{0.9-1.12}Ag_{0.01-0.05}Bi_{0.05-0.06}Se_{0.95-0.97}.

**Bohdanowiczite**, Ag_{0.97}Bi_{0.72}Se_{2.1}, has been documented as rare 1-10 µm inclusions in bornite in a similar assemblage with hessite. The mineral has also described in the Assarel porphyry-copper deposit (Bogdanov et al., 2004).
Table 1. Compositional data for Te and Se minerals from Elatsite porphyry-copper deposit: 1-3 - hessite; 4-6 - stützite; 7-8 - empressite; 9-11 - sylvanite; 12 - bohdanowiczite; 13-14 - native Te; 15-16 - clausthalite; 17 - naumannite (in addition naumannite contains 0.53 wt.% Fe and 0.08 wt.% Cu)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ag</th>
<th>Au</th>
<th>Pb</th>
<th>Bi</th>
<th>Se</th>
<th>Te</th>
<th>Total</th>
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<td>Ag$<em>{4.70}$Te$</em>{5.30}$</td>
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<tr>
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<td>9.36</td>
<td>26.03</td>
<td>0.31</td>
<td></td>
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<td>101.00</td>
<td>(Au$<em>{0.10}$Ag$</em>{0.64}$)$<em>{1.2}$Te$</em>{1.11}$Se$_{0.03}$</td>
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<td>10</td>
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<td>98.22</td>
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<td></td>
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<td>(Te$<em>{1.0}$Ag$</em>{0.01}$)$_{1.01}$</td>
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<tr>
<td>15</td>
<td>1.93</td>
<td>74.34</td>
<td>24.11</td>
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<td>98.22</td>
<td>0.16</td>
<td>(Pb$<em>{1.00}$Ag$</em>{0.02}$)$<em>{1.00}$Se$</em>{0.91}$Te$_{0.04}$</td>
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<tr>
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<td>24.60</td>
<td></td>
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<td>98.22</td>
<td>0.16</td>
<td>(Pb$<em>{1.06}$Ag$</em>{0.04}$)$<em>{1.00}$Se$</em>{0.90}$</td>
</tr>
<tr>
<td>17</td>
<td>72.90</td>
<td>26.53</td>
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<td></td>
<td></td>
<td>99.96</td>
<td>0.00</td>
<td>(Ag$<em>{1.92}$Fe$</em>{1.02}$)$<em>{1.05}$S$</em>{0.95}$</td>
</tr>
</tbody>
</table>

*Stephanite*, with the composition $(\text{Ag}_{4.29} \text{Cu}_{0.57} \text{Sb}_{0.70} \text{As}_{0.30})_{1.09} \text{S}_{3.3}$ is stable up to 197°C (Ushko-Zaharova et al., 1986), and has been identified in association with argentite, freibergite and sphalerite in the late Q-Gl- Sp assemblage.

**Thermodynamic constrains**

The fugacities of sulphur, tellurium and oxygen as a function of temperature are important variables for the formation of the observed tellurides have been calculated for the Mt-Bn-Cp assemblage (Fig. 4) placing the $f_{O_2}$ conditions near to the Mt-Ht buffer.

Fugacity-fugacity diagrams have been used to estimate the limits of $f_{Te}/f_{S_2}$ ranges as function of the gold fineness at 350 and 200 °C (Figs. 5 and 6). The $f_{Te}$ and $f_{S_2}$ diagrams have been constructed employing data of Barton and Skinner (1979), Simon and Essene (1996) and Afifi et al. (1988) based on the regular solution model of White et al. (1957). Thermodynamic constraints...
Fig. 5. $f_{Te_2}$ and $f_{S_2}$ diagram at 350°C with isopleths calculated for electrum in equilibrium with hessite and argentite.

Fig. 6. $f_{Te_2}$ and $f_{S_2}$ diagram at 200°C with isopleths calculated for electrum in equilibrium with hessite and argentite.

Fig. 7. $f_{Te_2}$-temperature diagram showing the calculated isopleths of $X_{Ag_{el}}^*$ in electrum in equilibrium with hessite as a function of temperature.

Fig. 8. $f_{Te_2}$-temperature diagram showing the calculated isopleths of $X_{Ag_{el}}^*$ in electrum (dotted lines) and the isopleths of $X_{Fe_Sph}$ (solid lines) as a function of temperature.

Data for the pure elements, sulphides and tellurides have been taken from Afifi et al. (1988), Robie and Hemingway (1995), Barton and Skinner (1979) and Sack (2000). We have further attempted to include the data from fluid inclusion studies (Strashimirov et al., 2002, 2003; Tarkian et al., 2003; Kehayov et al., 2003), as well as the estimated gold fineness for electrum in assemblages where it coexists with hessite and argentite (Fig. 7). We have also employed the estimated Fe content in sphalerite in the late Gl-Sp-Cp assemblage and the data of Balabin and Sack (2000) for constructing the $f_{S_2}$-T diagram (Fig. 8).
Discussion and conclusions

Almost each of the observed telluride patches contains hessite, either with, or following the deposition of gold, underlining the role of hessite as an important indicator for gold enrichment.

However, it seems that the formation of tellurides in bornite, with early macroscopic (>100 µm) gold with high fineness >900 took place at high $f_{\text{Te}_2}$ (-4; -8) and $f_{\text{O}_2}$ conditions near to the Mt-Ht buffer. Temperature of about 300°C could be estimated based on observed stützite-tellurium-sylvanite association.

The hessite-clausthalite association in chalcopyrite and the formation of stephanite, together with the decrease in fineness (<650) of the late microscopic (<100 µm) gold, as well as the low Fe content (<1 mol%) in sphalerite indicate decreasing of $f_{\text{Te}_2}$ (-18;-19) and $f_{\text{S}_2}$ (-13;-14) temperatures <200°C in the late Te, Se and Au-bearing associations.

References


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