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General geology and economic geology
Mineralogical and geochemical characteristics of the Skouries porphyry-Cu-Au-Pd-Pt deposit (Greece): Evidence for the precious metal

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Abstract. SEM/EDS studies on drill core samples from the deeper parts of the Skouries deposit showed frequent association of magnetite and Cu-minerals (bornite and chalcopyrite) with inclusions of thorite, U-bearing thorite, hydroxylapatite and rare earth element (REE)-enriched silicates of the epidote-group (allanite), zircon and rutile, linked to pervasive potassic and propylitic alteration type, in the central parts of the deposit. Isotopic and fluid inclusion trends in the Skouries porphyry Cu deposit seem to be systematic, beginning with high $\Delta^{18}O$ and low $\delta^18O$ values for fluids in equilibrium with vein quartz representative of the main stage of Cu, Au, Pd, Pt mineralization, to low $\Delta^{18}O$ and high $\delta^18O$ values for fluids linked with the pyrite-chalcopyrite mineralization.

Mineralised porphyry from the peripheral parts of the deposit, characterized by the presence of xenoliths of mafic rock contain up to 690 ppm Cr, which is mainly hosted in disseminated fine grained-magnetite. Its Cr content ranges from 0.3 to 2.26 wt% Cr$_2$O$_3$, in contrast to the Cr-free magnetite accompanying the quartz veins of the main porphyry. Such a relatively high Cr content, despite the evolved geochemical signature, indicates that the high Pd and Pt mineralization in the porphyry deposit of the Skouries may be linked to the incorporation of PGE-enriched material either in the mantle source and/or within the crust at depth, prior to final emplacement.

Keywords: Platinum, palladium, gold, monazite, magnetite, allanite, porphyry deposits, Skouries, Greece

1 Introduction

Recently, significant palladium and platinum contents were determined in numerous porphyry-Cu deposits, including those in the Cordillera of British Columbia, the Skouries (Greece), Elatsite (Bulgaria), Santo Tomas II (Philippines) and elsewhere (Mutschler et al. 1984; Eliopoulos and Economou-Eliopoulos 1991; Eliopoulos et al. 1995; Tarkian and Koopmann 1995; Tarkian and Striby 1999; Economou-Eliopoulos and Eliopoulos 2000; Tarkian et al. 2003). Textural relations between base metal sulphides, PGM and Au–Ag tellurides support the association of precious metals with the Cu-minerals (bornite and chalcopyrite), indicating that the main Pd-bearing mineral merenskyrite, was deposited during the major stage of Cu deposition (Tarkian et al. 1991).

Furthermore investigation on porphyry samples from the deeper parts of the Skouries deposit revealed some mineralogical and geochemical characteristics. Compilations of published and these new data and their implication to the precious metal concentration are briefly discussed.

2 Geological Setting

The Skouries porphyry Cu-Au deposit, located at the Chalkidiki peninsula, northern Greece, belongs to the Serbomacedonian Massif consisting of a crystalline basement, which is comprised of two lithostratigraphic-tectonic units, the lower Kerdyla Formation and the upper Vertiskos Formation, separated by a NW-striking fault system. The Vertiskos Formation consists of old basement gneiss, amphibolite, schist and marble, Tertiary intrusions, ophiolites, subvolcanic–porphyritic stocks and volcanic complexes related to the porphyry Cu deposits of the regional area (Kockel et al. 1977; Perantonis 1982; Frei 1995; Tobey et al. 1998). Their setting is mainly controlled by deep fracture systems that facilitated the subvolcanic intrusions to reach higher levels of the crust (Kockel et al. 1977; Perantonis 1982; Frei 1995). Whole rock K-Ar and zircon U/Pb intercept isotope data (Tompouloglou 1981) indicated that subvolcanic–porphyritic stocks, such as the Skouries, are relatively younger than the intrusions of the Serbo–Macedonian massif and are 18 Ma (Miocene).

The Skouries deposit is related to pipe-like intrusions of subalkaline–alkaline composition, (Eliopoulos; Economou-Eliopoulos 1991). The defined reserves are approximately 206 Mt at 0.54 % Cu, and 0.80 ppm Au (Tobey et al. 1998). At least four monzonite porphyries have been described by Kroll et al. (2002). In decreasing age, and increasing degrees of fractionation of the parent magmas, they are: (1) pink monzonite, (2) main monzonite, (3) intra-mineral monzonite, and (4) late-stage porphyry. High-grade ore is directly associated with the main and intra-mineral monzonite phases (Kroll et al. 2002). Due to the repeated overprinting and intense silicification, with potassic being the predominant alteration type, the typical alteration types of the porphyry Cu intrusions are not well preserved in the Skouries intrusion.
Figure 1: Back scattered images from the Skouries porphyry deposit, showing textural relationships between metal minerals. Abbreviations: mt = magnetite; cp = chalcopyrite; bn = bornite; gn = Se-bearing galena; rt = rurile; zr = zircon; all = allanite.
3 Characteristic features of the mineralization

Two mineral assemblages, occurring as veinlets and disseminations can be distinguished: (a) magnetite (average 6 vol%)-bornite-chalcopyrite, linked to pervasive potassic and propylitic alteration type, in the central parts of the deposit, and (b) chalcopyrite-pyrite, dominantly at the peripheral parts of the deposit. Molybdenite occurs in small amounts, commonly in late pyrite-sericite-carbonate bearing veinlets. Chalcopyrite, and to a lesser extent bornite, contain exsolutions of galena, which commonly has significant concentrations of Se, while claustrahalite is rare. Minor ore minerals are gold-electrum, claustrahalite-galena, hessite and merenskitye-moncheite (Tarkian et al. 1991; Fig. 1). Sphalerite with a low iron (~3 wt% Fe) content is rare. Pyrite at the peripheral parts of the porphyry stock occurs as thin replacement on chalcopyrite. Chalcopyrite may be surrounded by digenite, suggesting relatively oxidized fluids with a high ratio of metal to reduced sulphur during the evolution of the mineralized ore forming system.

A salient feature of the Skouries porphyry is the high values of the ratio Ce/Lu (~225), relatively high Th and U contents (up to 63 ppm and 9 ppm, respectively), Ba (up to 2260 ppm) and Sr (up to 1230 ppm) contents, reflecting probably a strong fractionation of parental magmas (Eliopoulos and Economou-Eliopoulos 1991). Furthermore, the investigation using SEM/probe reveals the frequent association of magnetite and Cu-minerals (bornite and chalcopyrite) with inclusions of thorite, U-bearing thorite, hydroxylapatite and rare earth element (REE)-enriched silicates of the epidote-group (allanite), zircon and rutile, (Fig. 1).

More specifically, Al and Ca decrease as iron and REE (La, Ce, Nd) increase outward, attaining values up to 24.4 wt% total REE content, due probably to the substitution of Al by Fe²⁺ and Ca by La, Ce and Nd. Also, the average F content (whole rock) is 900 ppm F (Eliopoulos and Economou-Eliopoulos 1991), while mica phases contain up to 0.19 wt% Cl and 2.48 wt% F (Kroll et al. 2002).

Despite such an evolved geochemical signature of the Skouries deposit there is often a Cr- and Ni-enrichment, reaching values up to 690 ppm Cr and 560 ppm Ni (Economou-Eliopoulos et al. 2001). Furthermore, the SEM/EDS investigation indicated that Cr is mainly hosted by disseminated fine-grained magnetite within mineralised porphyry characterized by the presence of mafic fragments or xenoliths. Their Cr content ranges from 0.30 to 2.26 wt% Cr₂O₃, in contrast to the Cr-free magnetite of the main porphyry.

Table 1: Electron microprobe analyses of REE-minerals from the Skouries deposit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SOP 46</th>
<th>SOP 43</th>
<th>SOP 18</th>
<th>SOP 18</th>
<th>SOP 18</th>
<th>SOP 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral</td>
<td>Monazite</td>
<td>Thorite</td>
<td>Thorite</td>
<td>Na₄Ce₆</td>
<td>Thallite</td>
<td>Allanite</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.15</td>
<td>18.82</td>
<td>15.63</td>
<td>38.34</td>
<td>32.13</td>
<td>35.37</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>27.18</td>
<td>16.18</td>
<td>14.11</td>
</tr>
<tr>
<td>FeO</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.57</td>
<td>8.32</td>
<td>14.91</td>
<td>17.41</td>
</tr>
<tr>
<td>CaO</td>
<td>0.76</td>
<td>n.d.</td>
<td>n.d.</td>
<td>12.18</td>
<td>13.59</td>
<td>n.d.</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>30.26</td>
<td>n.d.</td>
<td>n.d.</td>
<td>17.21</td>
<td>3.89</td>
<td>n.d.</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.85</td>
<td>5.11</td>
<td>n.d.</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>17.21</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>12.54</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>31.37</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.16</td>
<td>n.d.</td>
<td>12.54</td>
</tr>
<tr>
<td>NdO₂</td>
<td>10.45</td>
<td>n.d.</td>
<td>n.d.</td>
<td>4.74</td>
<td>2.18</td>
<td>n.d.</td>
</tr>
<tr>
<td>ThO₂</td>
<td>5.06</td>
<td>79.44</td>
<td>70.68</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

99.22 98.26 98.56 99.02 99.98 99.09

4 Evolution of the mineralised system

Evidence from mineralogical and geochemical data, including stable isotopic data indicate that the high Pd and Pt mineralization in the porphyry deposit of the Skouries may be linked with the genesis of alkaline arc magmas. The incorporation of PGE-enriched material either in the mantle source and/or within crust at depth, prior to the final emplacement, exemplified by the ⁸⁷Sr/⁸⁶Sr and ²⁰⁷Pb/²⁰⁴Pb values (Jankovic 1980; Gilg 1993; Frei 1995; Kroll et al. 2002) could supply PGE to the porphyry stocks or hydrothermal systems. Additionally, isotope and fluid in-
clusions data provide evidence for the evolution of mineralising fluids in porphyry systems. Isotopic and fluid inclusion trends in the Skouries porphyry Cu deposit seem to be systematic, beginning with relatively high δ8O (8 to 12.6 per mil) and low δD (-110 to -73 per mil) values, and CO2-rich fluid/intermediate salinity for fluids in equilibrium with vein quartz linked to the main stage of Cu, Au, Pd, Pt mineralization to low δ18O and high δD values/low salinity fluids for fluids linked with the pyrite-chalcopyrite mineralization (Tompouloglou 1981; Gilg 1993; Frei 1995 present study).

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