A new occurrence of argentian pentlandite from the Koronuda ore mineralization, Macedonia, Greece

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With 4 figures and 2 tables in the text


Abstract: Argentian pentlandite from Koronuda (Macedonia, Greece), occurs as small patches in chalcopyrite. The mineral is reddish-brown, isotropic in reflected light and contains 12.54 to 14.01 wt.% Ag. It has a mean composition (Fe,Co,Cu)$_{9}$(Ni$_{2.88}$Ag$_{1.01}$)S$_{8}$. The chemical composition is consistent with the observation by Hall & Stewart (1973) that Ag replaces Ni and Fe only in the octahedrally coordinated 4b site of the pentlandite type structure.

The chalcopyrite enclosing argentian pentlandite shows inversion twins, establishing the minimum temperature of chalcopyrite formation to be approximately 540 °C (Yund & Kullerud 1966). The inversion twins in chalcopyrite and the maximum stability temperature of 455 °C for argentian pentlandite (Mandziuk & Scott 1977) confirm the textural relations that the Koronuda argentian pentlandite is an exsolution product from chalcopyrite.

Key words: Argentian pentlandite, patches, chalcopyrite, inversion twins, sulfide paragenesis, alteration, exsolution, microprobe analyses, polished section; Greek Macedonia (Koronuda).

Introduction

The chalcopyrite from the Au–Ag–Cu–Co–Ni–As–S mineralization in the muscovite–chlorite gneisses near the village of Koronuda (Macedonia, Greece) encloses argentian pentlandite. This is a newly documented occurrence in Europe.

Argentian pentlandite was first described by Shishkin et al. (1971) from U.S.S.R. and by Vuorelainen et al. (1972) from Finland and subsequently reported by Scott & Gasparrini (1973), Karpenkov et al. (1973), Mariko et al. (1973) and Groves & Hall (1978). In these deposits argentian pentlandite is commonly found in chalcopyrite as small blebs or exsolution bodies with or without normal pentlandite. The crystal structure of argentian pentlandite was determined by Hall & Steward (1973) and the stability and phase relations were described by Mandziuk & Scott (1977).
Geological setting of the occurrence

The argentian pentlandite-bearing ore body occurs eastern of the village Koronuda (long. 32°0' E, lat. 40°59' N) in the metamorphosed Vertiscos series of the Serbomacedonian massif. The metamorphic rocks in the area include predominantly muscovite gneisses with interstratified garnet-two mica schists and amphibolites. These rocks have undergone a medium-grade Pre-Alpine metamorphism (lower amphibolite facies according to KOCKEL et al. 1971).

The ore mineralization occurs in a lenticular body, which is mainly pegmatitic near the wall-rocks with plagioclase, clinohlore and quartz and quartzose in the inner part. The lenticular axis of the ore body intersects obliquely the schistosity of the wall-rocks.

The field investigation has not found any evidence of post-metamorphic magmatic activity. The ore mineralization has been probably formed by element mobilization during the metamorphic event (MPOSkos 1976).

Sulfide paragenesis

The sulfide aggregates consist of complex intergrowths of the following minerals in approximate order of abundance: chalcopyrite, pyrrhotite, pyrite, marcasite, cobaltite-gersdorffite-arsenopyrite solid solutions, sphalerite, galena, silver- and bismuth tellurides and argentiferous gold with 32 % silver. In contrast to the other described argentian pentlandite occurr-

Fig. 1. Inversion-twin lamellae developed in chalcopyrite. Polished section, crossed nicols.
rences, normal pentlandite has not been observed in the Koronuda ore mineralization.

Microscopic studies suggest that the sulfide minerals have been crystallized in the following order: galena, cobaltite-gersdorffite-arsenopyrite solid solutions, chalcopyrite, sphalerite, argentian pentlandite, pyrrhotite, pyrite. Pyrrhotite commonly replaces chalcopyrite and in turn is replaced by pyrite, marcasite, magnetite, goethite and siderite.

The chalcopyrite crystals are coarse granular having twin lamellae (Fig. 1) indicating the cubic-tetragonal inversion. Oriented exsolutions of pyrrhotite in chalcopyrite occur as tiny worms or strings. The total amount of the exsolved pyrrhotite is a fraction of one per cent of the amount of chalcopyrite. Exsolutions of sphalerite in chalcopyrite occur as tiny worms and oriented lenticular crystals, and sphalerite “stars” are observed in chalcopyrite suggesting symplectic intergrowths. The sphalerite of the Koronuda ore mineralization is characterized by a high Cd content; 4.32 to 5.02 wt.% and 2.04 to 3.81 wt.% in the sphalerite “stars”.

The argentian pentlandite occurs commonly as small patches up to 100 μm across within the chalcopyrite. It is reddish-brown, isotropic and without visible cleavage, as described by most authors. Most grains are anhedral, but crystal faces are developed in some cases (Fig. 2). Fig. 3 shows an oriented intergrowth between exsolved pyrrhotite and argentian pentlandite with the (111) face of argentian pentlandite being parallel to the (001) face of pyrrhotite. In places small grains of argentian pentlandite

Fig. 2. Argentian pentlandite crystals (dark gray) lie oriented within chalcopyrite (light gray). Polished section, one nicol.
Fig. 3. Regular intergrowth of argentian pentlandite (dark gray) and pyrrhotite (medium gray) enclosed in chalcopyrite (light gray). Polished section, one nicol.

have a common orientation within chalcopyrite, suggesting that some of it may have exsolved from chalcopyrite. Such features confirm previous suggestions (Shishkin et al. 1971; Vuorelainen et al. 1972; Scott & Gasparrini 1973; Mandziuk & Scott 1977; Groves & Hall 1978) that argentian pentlandite may exsolve either from chalcopyrite (see also discussion in this paper) or from an Ag-bearing Cu–Fe–S intermediate solid solution.

Compositional data

Argentian pentlandite grains from Koronuda were large enough to obtain reliable electron microprobe analyses. The analyses were performed at the National Technical University of Athens using a wavelength dispersive spectrometer attached to a Cambridge stereoscan S 600. The following standards were used: pyrite for Fe and S and Co, Ni, Cu and Ag metals. Raw data were reduced using the delta correction method of Hirata & Okumura (1978). The analyses are presented in Table 1. The formula is calculated on the basis of eight sulfur atoms.

The Fe/Ni atomic ratio ranges from 1.540 to 2.046, with a mean value 1.779. These values lie within the range (1.34 to 2.57) of the previous analysed natural argentian pentlandites. The mean Fe/Ni atomic ratio is 0.113 higher than the value representing stoichiometric argentian pentlandite (Fe/Ni 1.666), when there is one Ag atom per unit formula. The metal/
sulfur atomic ratio ranges from 1.10 to 1.142 with a mean value 1.118 and lies also within the range given for the previous analysed natural argentian pentlandites (1.096 to 1.173). The mean M/S atomic ratio is 0.007, lower than the ideal M₈S₈ stoichiometric ratio of 1.125 for pentlandite.

The Cu and Co content ranges from 0.31 to 0.82 wt.% and from 0.08 to 0.27 wt.% respectively. These represent the highest so far determined values of Cu and Co in argentian pentlandite.

The analyses 1 to 5 and 6 to 10 of Table 1 show an obvious difference in the Fe and Ni atoms per unit formula. The first group of analyses (1 to 5) gives a mean value for Fe atoms of 4.92 and for Ni atoms of 3.03; whereas the second group (6 to 10) gives 5.28 and 2.65 atoms, respectively.

Table 1. Microprobe analyses of argentian pentlandite from Koronuda (Macedonia, Greece).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Ag</th>
<th>S</th>
<th>Total</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Ag</th>
<th>S</th>
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<th>M/S</th>
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<td>1</td>
<td>32.62</td>
<td>21.26</td>
<td>0.12</td>
<td>0.48</td>
<td>13.82</td>
<td>31.20</td>
<td>99.52</td>
<td>4.80</td>
<td>2.98</td>
<td>0.01</td>
<td>0.06</td>
<td>1.05</td>
<td>8.00</td>
<td>1.610</td>
<td>1.112</td>
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<tr>
<td>2</td>
<td>32.03</td>
<td>21.84</td>
<td>0.20</td>
<td>0.62</td>
<td>14.01</td>
<td>31.10</td>
<td>98.80</td>
<td>4.73</td>
<td>3.07</td>
<td>0.03</td>
<td>0.07</td>
<td>1.07</td>
<td>8.00</td>
<td>1.540</td>
<td>1.121</td>
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<td>3</td>
<td>33.07</td>
<td>22.51</td>
<td>0.08</td>
<td>0.32</td>
<td>13.19</td>
<td>31.20</td>
<td>100.37</td>
<td>4.87</td>
<td>3.15</td>
<td>0.01</td>
<td>0.04</td>
<td>1.00</td>
<td>8.00</td>
<td>1.546</td>
<td>1.133</td>
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<td>4</td>
<td>33.90</td>
<td>21.43</td>
<td>0.17</td>
<td>0.31</td>
<td>13.26</td>
<td>31.36</td>
<td>100.43</td>
<td>4.96</td>
<td>2.98</td>
<td>0.02</td>
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<td>1.00</td>
<td>8.00</td>
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<td>100.44</td>
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<tr>
<td>6</td>
<td>33.58</td>
<td>20.02</td>
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<td>0.51</td>
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<td>31.98</td>
<td>101.65</td>
<td>5.27</td>
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<td>0.02</td>
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<td>9</td>
<td>35.60</td>
<td>18.90</td>
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<td>0.66</td>
<td>12.54</td>
<td>31.43</td>
<td>99.37</td>
<td>5.20</td>
<td>2.63</td>
<td>0.03</td>
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<td>0.10</td>
<td>0.42</td>
<td>13.41</td>
<td>31.23</td>
<td>99.53</td>
<td>5.28</td>
<td>2.58</td>
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<td>0.05</td>
<td>1.02</td>
<td>8.00</td>
<td>2.046</td>
<td>1.117</td>
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</tbody>
</table>

Table 2. Calculated compositions of argentian pentlandites from Koronuda and other occurrences.

1* (Fe₄Co₃Cu)_1.92Ni₃.03Ag₁.03S₈ Koronuda, Macedonia, Greece
2* (Fe₄Co₃Cu)_5.28Ni₄.63Ag₁.00S₈ Koronuda, Macedonia, Greece
3 Fe₅.16Ni₂.79Ag₁.00S₈ Windarra (GROVES & HALL 1978)
4 Fe₅.24Ni₂.81Ag₁.01S₈ Windarra (GROVES & HALL 1978)
5 Fe₄.85Ni₃.17Ag₀.99S₈ Bird River, Man. (HALL & STEWART 1973)
6* Fe₄.93Ni₂.28Ag₁.03S₈ Bird River, Man. (SCOTT & GASPARINNI 1973)
7* Fe₅.62Ni₂.62Ag₁.03S₈ Sudbury (KARFENKOV et al. 1973)
8* Fe₄.41Ni₂.82Ag₀.81S₈ Finnish deposits (VUORELAINEN et al. 1972)
9* Fe₅.5S₂Ni₂.57Ag₁.10S₈ Talnakh (SHISHKIN et al. 1971)
10 Fe₄.51Ni₃.37Ag₁.09S₈ Khovuksa (SHISHKIN et al. 1971)

* Indicates mean compositions
1 mean composition of analyses 1 to 5 of Table 1
2 mean composition of analyses 6 to 10 of Table 1
The mean composition of the analysed argentian pentlandites are compared to other argentian pentlandites in Table 2. The composition of the Koronuda material approaches to the ideal formula $(\text{Fe, Ni})_8\text{AgS}_8$ and this compares well with the data of Groves & Hall (1978) and Hall & Stewart (1973), see Table 2. As in most previously analysed argentian pentlandites, where there is approximately one silver atom per formula, the Ag in this sample apparently occupies only the 4b octahedral sites in the crystal structure.

Hardness data

The Vickers micro-indentation hardness measured on a Leitz Durimet with a 25 g load, ranges from 171 to 193 kg/mm² for six indentations with a mean of 184 kg/mm². This is 24 kg/mm² higher than the mean value given by Shiskin et al. (1971), Scott & Gasparrini (1973) and Groves & Hall (1978) and approaches the lower value (192 kg/mm²) given by Mariko et al. (1973) for an argentian pentlandite from the Kamaichi mine, Japan.

Alteration

In supergene environments argentian pentlandite alters into a white coloured isotropic mineral. The initial stages of alteration develop along fractures and grain boundaries. The X-ray element scanning images (Fig. 4), and the electron microprobe profiles across the alteration products, suggest that in the process silver and iron are depleted from argentian pentlandite. Nickel remains in situ and produces a cubic nickel sulfide. Iron is in part enriched in the boundary zones between unaltered argentian pentlandite and the alteration products. Most of the silver migrates out of the system. Similar alteration was described by Vuorelainen et al. (1972) for the Finnish samples.

Discussion

Argentian pentlandite has been found as a minor constituent in the Koronuda ore body occurring within chalcopyrite. It is one of the main sources of silver in the investigated ore body. Its optical properties agree with those described by most previous authors. Its Vickers hardness approaches the values of Mariko et al. (1973), but are higher than the values given by other authors. The metal : S ratio is approximately 9 : 8 and the Ag : S ratio 1 : 8, which confirms previous suggestions that Ag occupies only the octahedral sites. The mean composition is close to Fe$_8$Ni$_8$AgS$_8$ in agreement with most other reliable microprobe analyses, and this agrees with Scott & Gasparrini (1973) who reported that argentian pentlandite
Fig. 4. a: Argentian pentlandite (ap) enclosed in chalcopyrite (cp) is partially altered into a nickel sulfide (ns), (bz) are iron-rich alteration zones, without nickel and silver. After a SEM photograph. – b: X-ray image of AgKα, c: of NiKα, and d: of FeKα.

is not a member of an isomorphous solid-solution series with normal pentlandite, but a distinct mineral species.

Argentian pentlandite is a stable phase below 455 °C. At about 455 °C it breaks down to Ag + monosulfide solid solution + pentlandite (MANDZIUK & SCOTT 1977). In the Koronuda ore body argentian pentlandite occurs only within chalcopyrite. The latter shows inversion twins. The inversion twins establish the minimum temperature of chalcopyrite formation to be approximately 540 °C (YUND & KULLERUD 1966). These temperature data are only consistent with an exsolution origin – the argentian pentlandite formed < 455 °C and chalcopyrite formed > 540 °C. However, argentian pentlandite could have been formed by any process < 455 °C, but textural evidences indicate exsolution.
References


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