A new natural occurrence of Co$_8$S$_8$ in pyrrhotite ore from the ophiolite complex of Pindos, Greece

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With 1 figure and 2 tables in the text


Abstract: A new natural occurrence of Co-pentlandite is found in pyrrhotite ore bodies within the gabbros of the complete ophiolite complex of Pindos (N. W. Greece), near its contact with serpentinites. The associated minerals except the pyrrhotite are chalcopyrite, pyrite, troilite, mackinawite, magnetite, malachite and azurite. The grains of the mineral show a light yellowish colour and their microhardness is 390 kg/mm$^2$. The chemical composition of the Co-pentlandite corresponds to the formula Co$_{0.85}$Fe$_{0.55}$S$_8$ whereas the Ni and Cu contents are lower than 0.1 wt%.

Key words: Cobalt pentlandite, colour, microprobe data, microhardness, mineral association, pyrrhotite, gabbro, ophiolite; Pindos mountains (Perivoli).

Introduction

The name cobalt pentlandite, as it is proposed by Moh (1976), is inconsequent since it suggests a mineral with some cobalt, though the cobalt pentlandite actually contains only cobalt instead of nearly 1:1 contents of Fe and Ni of the real pentlandite.

This name has essentially been used in literature for synthetic phases of the Ni$_{1-x}$Fe$_x$S$_8$–Co$_8$S$_8$ series and also for natural pentlandite occurrences with significant Co-content. Stumpfl & Clark (1964) described the first natural occurrence of pure Co$_8$S$_8$ with oriented intergrowths of Cu-rich linnaeite in the copper ore from Vauze Mine, Quebec. In this area pipe-like and stratiform chalcopyrite-rich ore-bodies, accompanied by considerable amounts of sphalerite and pyrrhotite, are found in Precambrian andesites. In fact, this paper is referred to a new occurrence of the mineral Co$_8$S$_8$ identified in pyrrhotite-rich orebodies found in the gabbros of an Alpine-type ophiolite complex, an entirely different petrological environment from the previously mentioned occurrence. However, the name cobalt pentlandite for the mineral phase Co$_8$S$_8$ seems now more inconsequent than in the past and it is suggested that the mineral must be referred under a special name.
Geological environment

The geology of the Pindos mountains has been studied and discussed by many authors (BRUNN, 1956; PARROT, 1966; PARASKEVOPoulos, 1977). It is accepted that the Smolica ultrabasic and basic rocks belong to the Pindos ophiolite complex which includes large and extended masses or smaller bodies found as klippen lying tectonically on the Pindos sediments. It is also suggested that those ophiolites are related to the evolution of an ocean in the concept of the plate tectonic theory.

The ultramafic-mafic sequence includes, from the bottom to the top, serpentinites, peridotites, gabbros cumulated or not, diabases and spilitized pillow lavas under a cover of late Mesozoic sediments. Sulfide ores are found in various localities around the small village Perivoli as massive veins and disseminated ores (SKOUNAKIS, Economou & Sideris, 1980).

In the Tsouma hill, 500 m NW of the Perivoli, a sulfide ore of lens-like form with some apophyses, consisting mainly of pyrrhotite, is found in gabbros, not far from its contact with serpentinites.

Physical and chemical characters of the mineral phase Co₃S₈

The Co-bearing mineral is found in the form of flames within the pyrrhotite grains. The associated minerals, found in small quantities, are chalcopyrite, pyrite, troilite, mackinawite, magnetite, malachite and azurite. The crystals of the Co-bearing mineral are ca. 70 μ thick (Fig. 1). In reflected light the grains are isotropic with a light yellowish colour.

![Image](image_url)

Fig. 1. Exsolution of Co-pentlandite (white) in pyrrhotite (gray), ppL, oil.
Electron probe distribution of elements in the minerals and quantitative analyses were carried out with the Cambridge Instruments Microscan 5 of the Institute of Ore Deposits, Univ. of Athens. Pure metal standards for Co and Ni and natural minerals for the other elements are used. The chemical composition of the Co-bearing mineral corresponds to the formula Co$_{8.67}$Fe$_{6.38}$S$_8$ (Table 1) whereas the Ni and Cu contents are lower than 0.1 wt%. The mineral grains are generally homogeneous (Fig. 1) but sometimes a compositional variation is observed across them.

Vickers microhardness of cobalt pentlandite from Perivoli is 390 kg/mm$^2$ (using 25 g load) and found to be higher than of the specimens from Varislahti and Outukumpu, referred by Stumpfl & Clark (1964) (Table 2).

Chemical tests on cobalt pentlandite show that a preferable way of distinguishing it from minerals similar in appearance e.g. pyrite, in a solution of nitric acid (HNO$_3$ 1 : 1). The application of a film of the acid solution results in the appearance of a bluish-green colour after one minute. In fact, in a few seconds the original light yellowish colour of the cobalt pentlandite changes through strong yellow, brown, and bluish to bluish-green. This tarnish is not always rubbed off. The previously mentioned test gives always positive results. A good etching substance is not known until now and the action of HCl, HClO$_3$, H$_2$SO$_4$, KOH and NaOH is negative.

X-ray powder diffraction patterns of the cubic mineral is in agreement with that of synthetic Co$_8$S$_8$. The crystal structure of the synthetic Co$_8$S$_8$

### Table 1. Microprobe analysis of Co-pentlandite from Pindos.

<table>
<thead>
<tr>
<th></th>
<th>Wt %</th>
<th>basis of 8 (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>63.50</td>
<td>8.57</td>
</tr>
<tr>
<td>Fe</td>
<td>4.14</td>
<td>0.59</td>
</tr>
<tr>
<td>Ni</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>S</td>
<td>32.24</td>
<td>100.03</td>
</tr>
</tbody>
</table>

### Table 2. Microhardness of some cobalt pentlandites.

<table>
<thead>
<tr>
<th></th>
<th>% Co</th>
<th>% Ni</th>
<th>% Fe</th>
<th>% S</th>
<th>MH (kg/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perivoli, Pindos</td>
<td>63.50</td>
<td>0.10</td>
<td>4.14</td>
<td>32.24</td>
<td>390</td>
</tr>
<tr>
<td>Varislahti</td>
<td>49.33</td>
<td>9.06</td>
<td>10.32</td>
<td>31.29</td>
<td>310</td>
</tr>
<tr>
<td>Outukumpu</td>
<td>30.94</td>
<td>21.10</td>
<td>15.62</td>
<td>32.34</td>
<td>280</td>
</tr>
</tbody>
</table>
is well known (Lindqvist et al., 1936; Lindqvist & Westgreen, 1938; Gellers, 1962; Rajamani & Prewitt, 1975). Pearson & Biener (1956) and Knop & Ibrahim (1961) confirmed the same structure for pentlandite (Ni,Fe)₉S₈ which has been refined by Rajamani & Prewitt (1973).

It should be noticed that X-ray powder diffraction patterns for the associated pyrrhotite show a hexagonal structure. Its chemical composition is free of Ni, Co and Cu, being close to Ni₉Fe₈=0.99.

Discussion

For the previously mentioned pure cobalt pentlandite from Vauze copper mine Stumpel & Clark found the following values: Co 66.6 %, Ni 0.1 %, Fe 1.3 %, Cu 0.3 % and S 31.7 %. Other localities with natural phases of cobalt pentlandite rich in Co but containing more than 9 % Ni and 10 % Fe (Stumpel & Clark, 1964) are described by Kuovo et al. (1959) from a number of Finnish localities including Outukumpu. Thus only the natural occurrence of pure cobalt pentlandite from the Vauze mine is the most similar to that one from the Perivoli area, which is free of Ni but has an Fe-content to about 5 %.

The occurrence of pentlandite, which is a common mineral in both massive and disseminated sulfides associated with basic rocks in the form of flames within pyrrhotite grains is considered to be an exsolution phenomenon. In the case of Perivoli area the microscopic research shows similar relationship between the pyrrhotite and the cobalt pentlandite, but not confirmed extrapolations of the known special characters and behaviour of the common pentlandite (sensus stricto) perhaps should lead to erroneous results.

However, the pentlandites in general are stable and exhibit a considerable compositional range depending upon the coexisting phases (Misra & Fleet, 1973). These compositional limits are marked by the absence of natural iron or nickel end-members whereas the compositions along the Co₉S₈–Ni₄,5Fe₄,5S₈ join are more common.

As far as the thermal behaviour of the pentlandites is concerned Vaasjoki et al. (1974) have shown that its thermal stability rises with the increasing presence of the Co. Leegard & Rosenqvist (1964) found that confining pressure reduces is thermal stability to 425 °C at 25 kbar, Morimoto & Kullerud (1965) found that pentlandite has an unusual large coefficient of thermal expansion, which result was reconfirmed by Rajamani & Prewitt (1974). Therefore, the thermal stability of cobalt pentlandite remains in doubt and any consideration on the origin for a certain case should be questionable.
The sulfide mineralization of Perivoli consisting mainly of pyrrhotite with exsolution of cobalt pentlandite and small amounts of chalcopyrite may be classified with similar mineralization found in the ophiolite complexes (Jancovic, 1977). The ophiolite sequence of Perivoli, in addition to the researched sulfide mineralization, includes disseminated and stockwork sulfides within the upper gabbros or microgabbros and massive sulfides in the spilitized rocks under the pillow lavas (Scounakis et al., 1980). The presence of the previously mentioned sulfide ores within the layered sequence suggests that the original magma was probably saturated in sulfur. The uncommon formation of the sulfide mineralization in Tsouma hill within the deep level of the gabbro close to its contact with serpentinized peridotite may be due to a local supersaturation of the surrounding magma in sulfur under the conditions described by Buchanan & Nolan (1979).

References

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