Se- and Te-bearing sulphides in copper ore deposits of Murgul, NE Turkey

ALEXANDER WILLGALLIS¹, NEVZAT ÖZGÜR² and EVELINE SIEGMANN¹

1) Institut für Mineralogie der Freien Universität Berlin, Takustr. 6, D-1000 Berlin 33, West Germany
2) Institut für Angewandte Geologie der Freien Universität Berlin, Wichernstr. 16, D-1000 Berlin 33, West Germany

Abstract: Electron microprobe analyses of ore samples from the Murgul copper deposit (NE Turkey) serve to identify several rare and complex ore minerals with occasionally high contents of Bi, Se and Te. These are tennantite, aikinite, hessite, tetradymite, galena, and matildite. The subvolcanic hydrothermal environment of the mineral assemblages corresponds to medium temperature conditions of formation.

Key-words: Se- Te-bearing sulphides, Bi-minerals, electron microprobe analysis, Murgul copper deposit, subvolcanic, island-arc volcanism.

Introduction

The Murgul copper ore deposit (two open pits: Anayatak and Cakmakkaya) is located in the eastern part of the East Pontides (Fig. 1). It belongs to the East Pontic Metallogenetic Province which, according to plate tectonic interpretations, represents a volcanic island-arc system developed South of the Pontic microplate during the Lias through to the Miocene (Akın, 1979; Özgür & Schneider, 1988; Schneider et al., 1988).

The stratigraphy is 2,000 to 3,000 m thick and can be divided into three groups: the lowest group is of Jurassic to Upper Cretaceous age (the Lower Basic Series and Lower Dacitic Series), a second group is Maastrichtian (Upper Basic Series) and an uppermost group corresponds to Tertiary volcanic activity (Upper Dacitic Series) (Maucher, 1960; Özgür, 1985; Özgür & Schneider, 1988).

The stratigraphy is 2,000 to 3,000 m thick and can be divided into three groups: the lowest group is of Jurassic to Upper Cretaceous age (the Lower Basic Series and Lower Dacitic Series), a second group is Maastrichtian (Upper Basic Series) and an uppermost group corresponds to Tertiary volcanic activity (Upper Dacitic Series) (Maucher, 1960; Özgür, 1985; Özgür & Schneider, 1988).

The Murgul deposit is linked to the upper part of the earliest volcanic series, and is associated with a 250 m thick felsic volcanic sequence of Senonian age which consists of altered breccias and tuffs.

The deposit contains predominantly pyrite and lesser chalcopyrite as valuable ore minerals. Minor quantities of galena, sphalerite and tennantite occur locally only (Özgür, 1985; Özgür & Schneider, 1988; Schneider et al., 1988).

The Murgul copper deposit consists of (i) widespread disseminated ore with varying Cu contents ranging from 0.2 to 0.7 percent, (ii) stockwerklike ore with average Cu contents from 5.0 to 10.0 percent (Schneider et al., 1988). This geometrical classification represents also a temporal sequence. The earliest formation is of the disseminated type and the latest formation is the lode type. The high Se and Te contents are restricted to the lode type mineralization. The recoverable ore reserves of the two major ore bodies (Anayatak and Cakmakkaya) are estimated at about 40 million metric tonnes with an average content of 1.25 percent Cu, 0.1 percent Zn, 0.05 percent Pb, 25 ppm Ag, and 0.2 ppm Au.
The chemistry of the sphalerite reveals a formation temperature of between 250 and 300 °C (Özgür, 1985; Möller et al., 1983). Fluid inclusion measurements on quartz samples from this deposit establish a temperature of formation between 250 and 285 °C (5% NaCl eq. content) (Özgür, 1985).

Se contents in chalcopyrite from the two ore bodies are remarkably high (up to 500 ppm). It was desirable to identify the host mineral phases of the trace elements for both scientific and economic reasons. Microprobe analyses are used to complement the earlier work of Arman and Altun (1983) and extend the described mineral assemblages.

**Analytical methods**

Se-Te-bearing ore minerals can be recognized under the microscope, but they are too small to be identified because of their finegrained intergrowth fabrics. The size of the different μm.

Electron microprobe techniques (ARL-SEMQ with wavelength-dispersive spectrometers) were employed using the following standards: PbSe for Pb (Mα), Bi₂S₃ for Bi (Mβ), Cu (Kα), Se (Lα), Te (Lα), ZnS for Zn (Lα), S (Kα), As (Kβ).
and Ag (Lα). MAGIC 4 (Colby, 1968) was used as the data reduction program.

Prior to each quantitative analysis, a careful check was made for all elements present.

**Results**

The complexity of the intergrowth ore assemblage in Murgul is shown in Fig. 2, which illustrates a polished section from the Çakmakkaya ore body. There are five mineral phases intergrown with quartz: chalcopyrite, tennantite, aikinite, hessite and tetradymite-group. Analytical results are presented in Table 1.

Chalcopyrite has a stoichiometric composition. Only Cu, Fe, and S have been detected.

A Sb-free bismuthian tennantite forms a “border zone” surrounding the other mineral phases. In addition to the major elements, low contents (< 0.1 wt.%) of Te and Se are detected. We repeatedly examined the occurrence of these rarely observed elements (Johnson et al., 1986) and interpret them as substitutions in the terraheudrite solid solution series (Wuensch, 1964).

In the centre and left part of Fig. 2, aikinite is present. The cation proportions (Table 1) correspond sufficiently well with the formula of aikinite (PbCuBiS3) within the range of precision. Approximately 10% of the S positions are taken by Se and Te.

A telluride of the argentite group surrounds aikinite. According to the analyses (Table 1), hessite (Ag2Te) forms the basis of this mineral. The very low contents of Cu and S conform to the atomic ratio of covellite, a widespread secondary mineral in the deposit. However, if we consider the ionic size and ionic charge as well as the homogeneous distribution of the two elements, we may suppose a limited solid solution in this Ag-telluride.

An average of 3 analyzed sample sports (Table 1) in the homogeneous phase establish the mineral composition of tetradymite, in which approximately 20% of the crystal lattice positions of Te and S are taken by Se.

Taking into account the diadochic replacement of Bi, Te, and S by Pb, Cu, and Se, the stoichiometry of tetradymite (Bi2Te2S) is satisfied. Arman and Altun (1983) incorrectly assumed that mixed-crystals of tetradymite and tellurobismutite (Bi2Te3) were present.

Galena (PbS) and sphalerite (ZnS) occur only sporadically at Murgul. In our study, galena locally contains selenium (Anayatak: polished section P 28/2). Furthermore, the elements Bi, Cu, Ag, and Fe can be detected in such galenas (Table 1). The small amounts of Cu and Fe in the galena are very homogeneously distributed and are probably linked to finely disseminated mineral inclusions. The similarly dispersed Bi and Ag suggest mixing between galena and matildite (AgBiS2) (up to 1%). This assumption implies a temperature of mineral formation above 225 °C (Ramdohr, 1980).

The content of Se in some grains of galena attains 1 wt.%. This is taken to indicate a mixed-crystal formation of galena and clausthalite (PbS-PbSe). Kieft and Oen (1977) have reported an Au-Ag-Se-paragenesis on Sumatra where Se is mainly dissolved in acanthite (Ag2S), but less in galena (max. 0.3 wt.%). In any case,
### Table 1. Microprobe analyses (wt. %, n = number of analyses) of sulphides and tellurides from the Murgul deposit.

1b): spot analysis of tennantite with max. Se content. Data probably caused by inclusions are given in brackets.

<table>
<thead>
<tr>
<th>area</th>
<th>1a</th>
<th>1b</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>galena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>40.15</td>
<td>38.5</td>
<td>11.9</td>
<td>0.30</td>
<td>0.51</td>
<td>(0.3)</td>
</tr>
<tr>
<td>Ag</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>61.2</td>
<td>0</td>
<td>- 0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>8.38</td>
<td>7.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(0.2)</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>-</td>
<td>33.9</td>
<td>6</td>
<td>6.38</td>
<td>84.8</td>
</tr>
<tr>
<td>As</td>
<td>19.12</td>
<td>17.7</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bi</td>
<td>4.76</td>
<td>5.81</td>
<td>34.9</td>
<td>0</td>
<td>52.49</td>
<td>0.7</td>
</tr>
<tr>
<td>Te</td>
<td>0.67</td>
<td>0.87</td>
<td>0.65</td>
<td>0</td>
<td>31.27</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>27.15</td>
<td>26.3</td>
<td>14.9</td>
<td>0.20</td>
<td>3.10</td>
<td>12.5</td>
</tr>
<tr>
<td>Se</td>
<td>0.05</td>
<td>0.36</td>
<td>2.75</td>
<td>-</td>
<td>6.33</td>
<td>1.0</td>
</tr>
<tr>
<td>Tota l</td>
<td>100.3</td>
<td>97.7</td>
<td>99.1</td>
<td>99.6</td>
<td>100.0</td>
<td>99.8</td>
</tr>
<tr>
<td>n</td>
<td>9</td>
<td>1</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

1: tennantite:
   a) Cu$_{9.66}$Zn$_{2.02}$Fe$_{0.03}$As$_{3.90}$Bi$_{0.35}$Te$_{0.08}$S$_{12.95}$Se$_{0.01}$
   b) Cu$_{9.59}$Zn$_{1.97}$Fe$_{0.03}$As$_{3.76}$Bi$_{0.44}$Te$_{0.11}$S$_{13.03}$Se$_{0.07}$

2: aikinite:
Pb$_{0.96}$Cu$_{1.10}$Bi$_{0.98}$Se$_{0.20}$Te$_{0.03}$

3: hessite:
Ag$_{1.02}$Cu$_{0.02}$Te$_{1.94}$S$_{0.02}$

4: tetradymite:
Bi$_{1.76}$Pb$_{0.02}$Cu$_{0.06}$Te$_{1.72}$S$_{0.68}$Se$_{0.56}$

5: galena:
Pb$_{1.00}$Ag$_{0.01}$Bi$_{0.01}$S$_{0.95}$Se$_{0.03}$

The Se contents of galena determined by Arman and Altun (1983) (up to 20 wt. %) are remarkably high and, according to Ramdohr (1980), very rare, indicating a high-temperature of formation for these PbS-PbSe members.

### Summary

The high trace element contents of Se, Te, and Bi in the lode-type mineralizations are explained by the presence of the mineral phases tennantite, hessite, aikinite and tetradymite. Moreover, these minerals represent some rarely described examples of replacement of Se and Te in sulphides or tellurides.

This paragenesis is specific for the latest ore stage at Murgul with depositional temperatures around 225-300°C.

### Acknowledgements

The authors wish to thank H.-J. Schneider and B. Lehmann, Freie Universität Berlin, for various scientific discussions regarding this paper.

### References


Maucher, A. (1960): Die Kieserze von Keltas. Ein Beispiel submariner...


Received 27 March 1989
Accepted 2 November 1989