THE ORE MICROSCOPIC INVESTIGATION OF THE BAKACAK
(ORDU) Pb-ZN-CU-ORE DEPOSIT

ŞÜKRÜ KOÇ

Geological Eng. Dept., University of Ankara, TURKEY

ABSTRACT

The Bakacak ore consist of Pb-Zn and Pb-Zn-Cu veins. These veins represent essentially kata and meso-thermal zones and in some cases reach to the hottest parts of the epi-thermal zone. In the paragenesis enargite and uraninite are present which represent typical minerals of the hydrothermal origin. The uraninite is reported for the first time in the Bakacak ore deposit during this research. Quartz, amethyst and calcite are the major gangue minerals. The hydrothermal solutions which lead to the formation of ore veins also cause intensive alteration of the wall rock.

INTRODUCTION

The study area lies 20 km. south of the Ordu province. It is located on Gresun. G-39–b3 sheet of the topographic map of Turkey at the scale of 1:25000 (Fig. 1). The geology, petrography mineralization of the close vicinity of the Bakacak ore deposit have been investigated (Koç, 1984) and the details of mineral paragenesis, mineral textures and mineral structures are examined. Trace element analyses (Au, Ag, Cd) are done by X.R.F. analysis technique. Although the study area is located in one of the potentially important Pb+Zn+Cu belt (Eastern Black Sea Region) the mineralization in the Bakacak area is economically significant (Aynsakan, 1961; Turkish-Yugoslavian Team, 1968), The purpose of this article is to present mineralogic characteristics and paragenetic sequence of the mineralization by making use of ore microscopic observations. The general objective is to establish the physico-chemical conditions of the ore deposition.
GEOLOGY

The major rock units of the study area are volcanics; dacitic tuffs, andesites, andesitic tuffs, basaltic andesites and trachyandesites (Fig. 1), which are especially altered in the form of silicification (Koç. 1984).

Figure 1. Geological map of the Bakacak region.
ORE MICROSCOPY

Mineralogic composition of the Bakacak ore veins and the conditions of occurrence of these minerals are shown in Fig. 2. The distribution of the ore and gangue minerals in kata-meso-and epi-thermal zones is schematically shown in Fig. 3. The primary ore mineral succession of the ore deposit is determined (From oldest to youngest) as pyrite I, sphalerite I, chalcopyrite I, sphalerite II, chalcopyrite II, pyrite II and galena.

Pyrite (FeS₂)

Pyrite I: Pyrite I occurs as bipentagonal dodecahedral crystals which are impregnated throughout the wall rock and suffered from cataclasm (Plate I.1). Cataclastic texture is commonly seen in samples, collected from the fault zones. The (110) cleavage direction is distinct in some of the pyrite I.

Pyrite II: Pyrite II occurs in the from of aggregates in some veins (Plate I.2). Although the occurrence of pyrite II can be explained in relation to kata-thermal solutions it can also be explained by semi-plastic conditions and plastic deformation at elevated temperatures. Small bead-like pyrite crystals may have been aligned before the complete solidification of the wall rock. These crystals are later replaced by chalcopyrite and sphalerite (Plate I,3). This phenomena may also have occurred by plastic deformation of the ore veins during tectonic movements and displacement of very small grains.

Sphalerite (ZnS)

Sphalerite is generally coarse - grained and shows a semiidiomorphic or xenomorphic and cataclastic structure (Plate, I,4). Under the microscope, its color is gray with moderate reflection. In some sphalericites, internal reflection ranges in color from light yellow to greenish yellow in oil immersion. This indicates low iron content in sphalerite.

Sphalerite I contains chalcopyrite “entmischung” inclusions partly aligned along certain crystallographic directions (Plate I,5) and partly concentrated in the inner parts of the crystals. It also contains pyrite aligned as chains. In some samples partial “entmischung” structure is seen. Differant sphalerite grains indicated by different reflection colors,
PLATE I

Figure 1. Cataclastic idiomorphic pyrite (Grey and fractured).
Figure 2. Aggregates of pyrite.
Figure 3. Pyrite (pale grey) chains lineated within sphalerite (Grey).
Figure 4. Cataclastic textures in sphalerite (Grey)
Figure 5. The unmixed inclusions of chalcopyrite (white) oriented in the crystallographic direction of sphalerite (Grey).
Figure 6. Sphalerite I and II.
are observed in the form of stain-like patches and solid solutions. Such structural properties have been observed (Ramdohr, 1960) in some ore deposits suggest formation at elevated temperatures. In sphalerite unidentifiable flaky and submicroscopic inclusions occurring along the crystallographic directions have also been observed.

Sphalerite II is the variety that does not (or only little) contain any inclusions. In plate I.6 engulfing of sphalerite I by sphalerite II is observed. Here chalcopyrite inclusions are concentrated at the peripheral parts of the sphalerite I. Growt twins (Plate II.1) are determined in the sphalerite grains as a result of surface etching by HNO₃ and KMnO₄ + H₂SO₄ solutions.

Replacement is effective mostly along the cataclastic fractures in some cases, sphalerite replaces chalcopyrite and in other cases chalcopyrite replaces sphalerite. Galena minerals of tetrahedrite-tennantite and secondary covellite and chalcocite also replace the sphalerite. Locally, galena wedges in to the fractures of sphalerite. This appearance is not the result of replacement. It is due to the inner structure of galena which is more convenient for translation.

The grains in homogeneous aggregates are round and polygonal, and their sizes reach up to 10–20 microns. In some samples, sphalerites with finer grain sizes are also observed. Fine-grained sphalerites represent the samples taken from the marginal zones where the temperature of the hydrothermal solution decreases much faster. Trace element analysis of sphalerite indicates the presence of very little amount of silver and cadmium.

The following is deduced from the ore microscopic study on sphalerite:

— The presence of zoning in sphalerite and the alignment of pyrite in sphalerite grains, rich in excess amounts of chalcopyrite inclusions, indicate the presence of a tectonically unstable environment. Such inclusions that are seen at elevated temperatures can be explained by mechanical movements.

— The sphalerites that contain only very little amount of chalcopyrite inclusions are free of their chalcopyrite inclusions probably as a result of excess pressure. These inclusions have filled the boundaries of sphalerite grains as thin films.
PLATE II

Figure 1. Growth twins in a sphalerite grain which were etched by $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ solution.
Figure 2. Chalcopyrite I (KI), chalcopyrite II (KII), galena (G) and sphalerite (C).
Figure 3. Cataelastic texture in chalcopyrite (white)
Figure 4. The boundary as a straight line between chalcopyrite (whitish grey) and sphalerite grains.
Figure 5. Triangular cleavage cavities in galena.
Figure 6. Galena (white) as veinlets and cavity fillings.
Chalcopyrite (CuFeS$_2$)

Two generations of chalcopyrite are identified according to the difference in their reflectivities.

Chalcopyrite I which is crystallized in the tetragonal system is easily identified by its dark yellow reflection color, slight pleochroism and distinct anisotropy under the microscope.

Chalcopyrite II is distinguished from chalcopyrite I by its lesser anisotropy (or its absence). This phenomena is typical of those crystallized in the cubic system and indicates crystallization at elevated temperatures. Chalcopyrite II shows a lighter yellow-colored reflection.

Samples are seen where the two types have been observed in contact to each other (Plate II.2).

Locally, cataclastic structures are observed in semi-idiomorphic and xenomorphic chalcopyrites (Plate II.3). The boundary between chalcopyrite and sphalerite is usually a sharp line (Plate II.4). In some parts sphalerite replaces the chalcopyrite whereas in other places cahl-copyrite replaces the sphalerite. Some chalcopyrite replaces pyrite. Chalcopyrite, is being replaced by idaite, tetrahedrite, and occasionally by bornite.

In all polished sections, the amount of chalcopyrite is less than the amount of sphalerite and galena. Locally, chalcopyrite contains sphalerite inclusions which are the remnants of the replacement.

In the oxidation zone, covellite and limonite are produced secondarily under the action of atmospheric agents Malachite and azurite are formed where calcite is present as a gangue mineral.

Negative results are obtained from the etching tests using KOH and KMnO$_4$.

Galena (PbS)

Galena is isotropic with strong white-gray reflectivity. It is easily identified by its coarse grains and clevage gaps between (100) faces (Plate II.5).

Tectonically reworked samples produce finer cube-like crystals of galena whereas disintegration of sphalerite and chalcopyrite birngs
aut angular fragments. Moreover, galena wedges into the fractures of other minerals. Due to its plasticity very fine grained gold inclusions encountered in galena.

Galena which can be formed at a wide range of temperature, indicates various replacement structures. It is younger than pyrite, sphalerite, chalcopyrite, enargite and tetrahedrite, and contains inclusions of these minerals. In some sections this veinlets of galena cut across the other minerals (Plate II.6).

Analysis of samples taken from a galena-rich ore vein by X.R.F. method indicated the presence of silver and cadmium. The cadmium content is probably related with sphalerite. The silver content of galena is measured as 153.6 ppm and 0.001 ppm gold is detected.

Native Gold (Au)

Native gold is recognized by its strong yellow reflection. It occurs as very fine grains (2–3 microns) in various minerals and also as disseminations in the gangue material.

As gold can be formed within a wide temperature range it is assumed that the gold grains of the Bakacak area are formed at meso-thermal to kata-thermal zones. Small amounts of gold are found in association. With the secondary minerals in the oxidation zone.

Enargite (Cu₃AsS₄)

Enargite is observed in small amounts between chalcopyrite and tetrahedrite-tennantite and shows a light pinkish gray reflection color. It is anisotropic. Inner reflection is not observable. Reflection pleochroism is observed when investigation is carried out with oil immersion. The "stains" of enargite in tetrahedrite are named as "mottled enargite" by Graton and Murdoch (1913). The exsolution structure among tennantite and enargite has also been reported by Göymen (1982) from (hydrothermal). Peronit Deposit, Northeast Black Sea region.

Mutual presence of enargite and tennantite indicates a genetic relationship among the two and supports the idea that enargite is formed from tennantite as an exsolution.
Tetrahedrite Group Minerals (Cu₂, As₂, Ag, Fe, Zn, Hg) (Sb, As, Bi)₂S₆

Under the tetrahedrite group minerals, tetrahedrite and tennantite are classified. These minerals are isotropic and have reflection colors ranging from olive green to grayish white. They occur next to galena, chalcopyrite and sphalerite in small quantities (Plate III.1).

Enargite contains tennantite. Tetrahedrite is associated with galena, chalcopyrite and sphalerite. It locally replaces the chalcopyrite.

The tetrahedrite group minerals are formed at a wide range of temperatures and have a hydrothermal origin.

Part of the Silver, detected by X.R.F. method, may be associated with these minerals. This is evidenced by their strong reflection.

Uraninite (UO₂)

Uraninite occurs at the (100) faces of idiomorphic galena crystals partly as spherical grains and partly as spherical aggregates (Plate III.2.3).

Under the microscope, unaninite has a weak brownish gray reflection color. When the same sample is studied under oil immersed objective the color is slightly dark brown. Its hardness, spherical shape and reaction rims around the spherical grains are the other characteristics. Uraninite occurs only at a limited extent which indicates its instability. Uraninite appears to be last in strongly cataclastic zones and by atmospheric agents.

Radioactivity of the uraninite leaves a black impression around the periphery of the grains on a photographic paper (Plate III.2). This reaction zone is seen much better in the colored film (Plate III.3).

Uraninite is a characteristic mineral of hydrothermal origin.

Bothrooidal, grape-like and spherical occurrences indicate a hydrothermal origin (Rhamdohr, 1960).

Bornite (Cu₃FeS₄)

Primary and secondary types of bornite are distinguished. Primary bornite paragenetically associates with tetrahedrite-tennantite, galena and chalcopyrite. Its reflection color is pinkish brown and slightly
PLATE III

Figure 1. Primary bornit (B), chalcopyrite (K), galena (G) and tetrahedrite (F).
Figure 2. Spherical and reniform uraninite minerals (grey) and coarse-grained galena (white).
Figure 3. Spherical uraninite minerals and characteristic fission reaction zones. Galena is white.
Figure 4. Idaita (dark grey) in chalcopyrite (Pall grey).
Figure 5. Chalcopyrite (K), galena (G) surrounded with covellit (Kv), sphalerite (ζ), pyrite (P) and chalcocite (Kk).
darker than that of enargite. Under oil immersed objective the color becomes orange and its intensity increases.

Bulletin of Chamber of Geological Engineers (Bull. No. 24) used this picture in its cover page as it can be used as a method of identification of radioactive minerals. Although bornite is isotropic, due to its idiaite content some of the Bakacak bornite is slightly anisotropic. Bornite forms et elevated temperatures (300 °C) and it is a solid solution crystal with a composition of Cu₃ FeS₆–Cu₂FeS₆ (Ramdohr, 1960), As the solid solution crystals generally split into their pure phases, cleavages parallel to (100) face indicate a zoned appearance. Bornite usually occurs between tetrahedrite-tennantite and chalcopyrite or chalcopiritne and galene. The boundary between chalcopiritne and bornit is clear and sharp.

Bornit is directly formed after chalcopyrite in the cementation zones and a cage structure is developed between these two minerals.

Idiaite (Cu₅ FeS₆)

Idiaite which has a reflexion color similar to that of bornite is characterized by its strong reflexion, pleachroism and anisotropy (Plate III.4) it is not clearly understood whether idiaite is a hydro-thermal product or formed by atmospheric agents. As the ore veins under the investigation strongly suffered from tectonic activity, the depth of oxidation is deepened.

As a decomposition product of bornite idiaite crystals are formed together with chalcopyrite lamellae. Typical polygonal fractures develop in bornites from which idiaite is formed.

Idiaite is also locally altered to covellite.

Covellite (CuS)

Under the microscope covellite is dark blue and whitish gray and shows a characteristic reflection pleachroism. Orange pinkish blue anisotropy is typical under crossed nicol. Such covellite is called "blue covellite" (Plate III.5). Covellite is seen as an oxidation zone mineral after chalcopyrite, bornite, tetrahedrite-tennantite and enargite and also in the fractures of sphalerite that contains excess amounts of chalcopyrite exsolution inclusions.
Subordinate amounts of primary covellite is observed locally in the ore veins. The covellite is seen in places other than the oxidation zone and can probably be classified as primary.

Chalcocit (Cu₂S)

Primary and secondary types of chalcocite are distinguished. The primary chalcocite is seen only in accessory amounts and it is isotropic under the crossed nicol. This is blue, isotropic neodigenite variety of chalcocite which crystallizes in the cubic system. Neodigenite (Cu₉Si₃) is a solid solution of Cu₂S and CuS and forms at a temperature higher than 103 °C.

RESULTS AND INTERPRETATIONS

Estimation of physico-chemical conditions of formation of Bakacak ore and its paragenesis are possible by synthesizing the observations made on mineralogic association, structure composition and microstructure during ore microscopic investigations.

The mineral paragenesis and conditions of ore formation are shown in Figure 2 and the distribution of elements of the ore and the gangue minerals in the kata-meso-epi-thermal zones are given in Figure 3. This data indicates the occurrence of ore under-kata-meso-thermal (and probably in small part in epi-thermal) conditions in a deep-seated environment.

In the mineralogic association of the ore veins metalloids are absent. Moreover, such an association involves only a few minerals. Occurrence of impregnation of very fine grains of gold anduraninite in these veins together with the above observations indicate a kata-thermal origin.

Cu, Pb, Zn minerals represent the meso-thermal minerals. Copper minerals are chalcopyrite, bornite and enargite. Tetrahedrite-tennantite occur in small quantities in association with chalcopyrite and bornite. Zinc minerals (sphalerite) mostly contains inclusions of chalcopyrite exsolution Lead mineral is galena and contains silver.

The least represented epi-thermal zone contains galena and chalcopyrite. Although these minerals form much finer grained aggregates, compared with the same minerals that occur in mesothermal, no gel
<table>
<thead>
<tr>
<th>MINERALS</th>
<th>HYDROTHERMAL ZONES</th>
<th>SECONDARY ZONE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Katathermal 400°-300°C</td>
<td>Mesothermal 300°-200°C</td>
</tr>
<tr>
<td>Sphalerite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native Gold</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uraninite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bornite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bornite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enargite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcolite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcolite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Covellite I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Covellite II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idiote</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sericite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malachite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azurite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pirite III</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. The genetic conditions mineral formation and paragenetic sequence of the Bakaceak Area.

structure is observed. This indicates deposition of these minerals at the temperatures of the transition zone of meso-to epi-thermal. Absence of gel structures even in the fractures where meteoric water comes into contact with epi-thermal minerals must be noted.
The main gangue minerals of Bakacak ore are quartz, amethyst and calcite. Subordinate amounts of dolomite and accessory amounts of barite are also seen. Grangue minerals also do not show gel structure.

<table>
<thead>
<tr>
<th>Hydrothermal Zones</th>
<th>Ore Minerals</th>
<th>Gangue Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Element</td>
<td>Minerals</td>
</tr>
<tr>
<td>Epithermal</td>
<td>Sb</td>
<td>in tetrahedrite</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>in tetrahedrite and galena</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Solid Solution in Sphalerite</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>Galena</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>Pyrite II</td>
</tr>
<tr>
<td>Meso thermal</td>
<td>Cu</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>Sphalerite</td>
</tr>
<tr>
<td></td>
<td>U</td>
<td>Uraninite</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>Pyrite I</td>
</tr>
<tr>
<td>Katabatic</td>
<td>As</td>
<td>Tennantite</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>Native</td>
</tr>
</tbody>
</table>

Figure 3. Schematic explanation of how ore and gangue minerals are related to elements found in Bakacak ore veins and their distribution in the kata - meso - epi thermal areas.
CONCLUSION

This investigation establishes that the Bakacak ore has a hydrothermal origin where deep-seated, meso-kata-thermal (and to a small extent epi-thermal) zones of magmatism are involved.

Previously, Bakacak mineralization was described by Aslaner (1977) as an ore genetically associated with volcanic and subvolcanic rocks and defined as a hydrothermal type that occurs in the from of veins or veinlets of stockwerk in geosynclinal deposits of pyropylitized rhyodasitic-dasitic-andesitic lavas and pyroclastics. Gümüş (1979) classified such ores of Eastern Black Sea zone as “deposits related to volcanism and subvolcanism” according to the Scheme of Lindgren’s classification. In this study a hydrothermal origin related to shallow volcanism is rejected. This is evidenced by means of the following criteria:

1. Distribution of ore elements, ore paragenesis and succession according to the depth.

2. Presence of uraninite, enargîte and tetrahedrit-tennantite in the mineral paragenesis.

3. Absence of telescopy which is typical of subvolcanic deposits. In other words, absence of mutual existence of high and low temperature minerals at the same time.

4. Absence of metal-oxides which are also characteristic of subvolcanic deposits.

5. Restriction of minerals to a few mineral types in a vein.

6. Structural and textural observations on ore minerals are in favor of high temperature crystallization.

7. Absence of gel-like structures in ore and gangue minerals.

Additionally, the following also indicate that the origin of the Bakacak ore is not volcanic or subvolcanic:

— Considerable length and thickness of the ore veins,

— Presence of definitive contacts between ore veins and the wall rock and existence of a crushed, clayey zone “letten bestege” at their contacts.

— Coarser grain size of the gangue minerals which indicate higher temperatures of formation,
— Presence of quartz as a gangue mineral in the deeper Zones.

— Presence of typomorphic amethyst crystals as a gangue mineral indicating a 200° – 300 °C temperature range.

In summary, the Bakacak ore deposit is a meso-thermal deposit based on its mineral association, paragenesis, succession and structural and textural findings under the ore microscope.

ACKNOWLEDGEMENTS

Author would like to thank to Prof. Dr. Güner Göymen, from Gazi University and Dr. Taner Ünlü, from the Mineral Research and Exploration Institute of Turkey (M.T.A. Enstitüsü) for their critical reviews and stimulating discussions.

REFERENCES


