



## Minor and trace elements in ore minerals from the Chelopech deposit: LA-ICP-MS study on pyrite, enargite and sphalerite

### Второстепенни и елементи-следи в рудни минерали от находище Челопеч: LA-ICP-MS изследване на пирит, енаргит и сфалерит

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**Keywords:** economic ore mineralization, beneficial elements, LA-ICP-MS, Srednogorie zone, Bulgaria.

### Introduction

The Panagyurishte mineral district, being an important metallogenic region in Eastern Europe, has supplied about 95% of the recent Bulgarian copper and gold production (Moritz et al., 2004 and references therein). It displays some of the best examples of Upper Cretaceous porphyry-Cu and high-sulfidation epithermal ore deposit association. The largest epithermal deposit in the district is exploited since 1954 at the Chelopech underground mine, which currently has 31.4 Mt of measured and indicated resources at an average grade of 1.14% Cu, 3.73 g/t Au, and 9.27 g/t Ag (Marton et al., 2016). The question about the possible beneficial elements in the ores and the regularities of their distribution was addressed from the early years of exploitation being still of interest nowadays. Pilot systematic study on the trace elements in the main ore minerals was published by Terziev (1966). The present study reports preliminary LA-ICP-MS data about the trace element concentration in pyrite, enargite and sphalerite from different levels of the Chelopech deposit.

### Geological background

The Chelopech deposit is hosted by a Upper Cretaceous volcanic and volcano-sedimentary complex, progressively overlying Precambrian and Palaeozoic metamorphic rocks (Moritz et al., 2004). Recently, in accordance with the extensive underground mining, a new genetic model revealed that the ore-hosting magmatic environment at Chelopech is dominated by a multiphase intrusive complex (Marton et al., 2016), although Bogdanov (1987) has suggested similar genetic model. The high-sulfidation hydrothermal system is formed within a shallow intrusive multistage porphyritic diorite/microdiorite system pierced by

several vertically extended, intrusion-related breccia bodies (including numerous blind breccia pipes) and at least one large surface-reaching maar-diatreme eruptive center, which is related to a granodiorite phase associated with: 1) porphyry Cu-Mo-Au stockwork and potassic-phyllitic, 2) distal base metal sulfide veins, and 3) high-sulfidation Cu-Au mineralization (Marton et al., 2016). The high-sulfidation mineralization occurs within sulfide- and sulfosalt-rich zones of replacement silicification surrounded by halos of advanced argillic alteration (Georgieva, 2014). The orebodies (complex branched hydrothermal breccia bodies and discrete pipes) vary from 150 to 300 m in length, and 30–20 m thickness.

### Materials and methods

The trace element concentration in the sulfide minerals was studied by LA-ICP-MS analytical system at Geological Institute, BAS (energy density of 5–6 J/cm<sup>2</sup>; laser pulse frequency of 5–2 Hz; 50 or 75 μm beam diameters; external standardization on Mass 1 and internal standardization from EPMA were applied).

Several representative samples with pyrite, sphalerite and enargite were involved in the compositional determination. Drill cores materials from drill holes (DH): 500 (1692 m), 503 (468 m) and ext. 19 (350 m) and samples from 405 mine level were analyzed.

### Results

*Pyrite* is widespread in the ore bodies, associating mainly with enargite and sphalerite in the studied samples. It forms veinlets crosscutting massive enargite or occurs as disseminated small grains in the groundmass, together with other sulphides and gangue minerals. An important compositional characteristic of this pyrite is the increased Cu and As-content. Arsenic incorpo-

ration varies in different orders of magnitude from 3.30 ppm (deeper levels) to ~914 ppm, although most of the values are within 107–800 ppm. The extremely high measured values of ~6000 ppm As correspond to pyrites intimately associating with enargite. The copper incorporation in the deeper levels of the deposit (DH 500) is in the range 134–1746 ppm, being relatively limited compared to other pyrites with Cu-content generally varying within 5141–12171 ppm limits. The highest values of Cu (up to 3 wt%) are detected in the pyrite veinlets. Apart from the enhanced Cu, which in some cases might be due to small impregnations of chalcopyrite (sometimes seen under microscope), pyrite is characterized by almost constant Ge (74–88), Mn (37–55), Cr (33–82), Ni (4–11 ppm) amounts. Certain contents of Sb (3–927), Bi (2–164), Pb (14–4294), Zn (2–476), Ga (1–843), Ag (2–50 ppm) are possibly owing to microinclusions of other ore minerals, considering their wide variation. There is no clear evidence for a positive correlation between Ge and Zn, Ag and Pb, suggesting incorporation of galena and sphalerite if present, although such intergrowths are observed. The Au-incorporation (generally 3–31 ppm, averages 8 ppm), reaching its maximum of 109 ppm shows correlation with As and Tl (up to 99 ppm) content. Together with As, Se (3–500 ppm) decreases in depth. Small grains of pyrite (1692 m) show significant Ti-content (up to 150 ppm), probably owing to rutile.

*Enargite* is among the main minerals of the sulphide-sulphosalt paragenesis in the Chelopech, closely associating with pyrite in different temporal relationships. Significant amounts of Sb and Bi – 1.3–7 wt%, 2900–8041 ppm (DH 503); 1–5 wt%, 1837–11554 ppm (405 mine level); up to 2200, 1594–6695 ppm (DH ext. 19), respectively, were detected in the studied enargites. Important constituents are Fe (generally 1100–4100), Ni (255–273), Se (260–2080), Sn (120–4660), Pb (76–654 ppm) as well. Among the other elements Zn (up to 1970), Ge (up to 262) and Ag (averages 43 ppm) are well expressed. Gold incorporation is significant (mean amounts of 30 ppm); the increased content in some points (123 ppm) correlates with Tl reaching 241 ppm. An obvious increase of Se and Sn in depth is detected (in accordance with the observation of Terziev, 1966). Constant incorporation of Ni in all samples and crystals indicates its isomorphic presence in the enargite structure.

*Sphalerite* is typical for the base-metal stage of the formation of the deposit, together with galena, pyrite and some chalcopyrite. Common constituents of the studied sphalerites are Mn, Fe, Cu, Ga, Cd and Hg. Dark sphalerite from the deeper levels of the deposit (DH 500) contains Fe generally in the range 1000–4300 ppm, Cd (1800–2300 ppm), and Hg up to

41 ppm. On the other hand, the zonal aggregate of brownish sphalerite from 405 mine level shows wide variety of elements, where Cd (1100–1900 ppm), Pb (up to 2040 ppm) and Hg (up to 1144 ppm) are among the major ones. Typical correlation between Fe-content and the color of the sphalerite is observed (lighter zones contain 42 ppm Fe). Arsenic incorporation up to 890 ppm is probably due to fine intergrowths with pyrite. The zonal distribution of the elements in the aggregate reveals general decreasing (in accordance with Fe-decrease) of almost all measured elements from the central parts to the periphery: Cu (2447–775), Mn (125–38), Ga (1041–103), Ge (536–220), Ag (317–146), Te (10–1), Au (4–1), Hg (1144–130), Tl (27–13), Pb (2040–495) and Bi (14–3 ppm). Elements like Se (~12), Cd (average 1395), In (up to 213) and Ti (average 267 ppm) do not suffer that zonal distribution.

### Concluding remarks

The ore mineralization of Chelopech deposit displays qualitative and quantitative diversity of elements compared to those from other Bulgarian ore districts. Apart from the increased Cu-content, corresponding to the Cu-Au geochemical specialization of the deposit, wide variety of elements is presented with various orders of magnitude. The systematic variation in concentration and regularities in the distribution provides potential for development of mineral vectors of exploration in such epithermal systems.

*Acknowledgements:* The study is supported by the Valentin Grozdev's grant of the WFS Scholarship Program 2013–2014.

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