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Ore mineralogy and mineral chemistry of quartz-polymetallic veins in Caleta Argentina, Livingston Island, Antarctica

Рудна минералогия и химизъм на минерали от кварц-полиметални жили от Калета Архентина, остров Ливингстън, Антарктика

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Abstract. The quartz-polymetallic veins from Caleta Argentina, Livingston Island, Antarctica consist of pyrite, chalcopyrite, galena, and sphalerite. Chalcopyrite is the most common ore mineral and with concentrations of Ag (average 240.51 ppm). Sphalerite contains Ag (average 50.82) and Au (average 0.31 ppm), and pyrite – Au from not detectable to 1.03 ppm (average 0.59 ppm) and Ag from not detectable to 54.33 ppm (average 32.52 ppm). Caleta Argentina, as one of the ore occurrences in Hurd Peninsula, has to be correlated with the other research area such as the Bulgarian Antarctic Base, the Bulgarian Beach, and Sally Rocks.

Keywords: ore mineralogy, mineral chemistry, ore veins, Livingston, Antarctica.

Introduction

The current research is part of a scientific project in the Antarctic season 2019/2020, aiming to document the ore veins in Hurd Peninsula. We present new data on the ore minerals and mineral chemistry from quartz-polymetallic veins in the area of Caleta Argentina Bay, for which there is preliminary and unpublished data. The results from this study will help to constrain the ore potential of the Hurd Peninsula.

Materials and methods

The samples are collected from quartz-polymetallic veins. Polished sections were prepared to determine the paragenetic relationships and optical characteristics. X-ray powder diffraction (XRD) analyses were done at the Sofia University St. Kliment Ohridski,. TUR M62 diffractometer use filtered Co-Kα radiation in the 2Θ range 4–80°, step size 1.5°. Electron microprobe analyses (EMPA) and back-scattered electron imaging were done on carbon-coated polished sections in the certified laboratory "Eurotest-Control". Analyzes were performed according to ISO 22309:2011 "Microbeam analysis – Quantitative analysis using energy dispersive spectrometry (EDS) for elements with atomic number 11 (Na) or higher". The equipment used is based on a SEM – Jeol JSM 35 CF, upgraded with a digital scanning system for SEM – "DISS5+", an energy dispersive X-ray system – "IDFIXe" with software for qualitative and quantitative analysis, and an energy dispersive detector with a resolution of 129 eV of Mn-Kα and analytical range from Boron to U. For quantitative analysis using MAC standards – microanalysis consultants – natural minerals – chalcopyrite, galena, pyrite, arsenopyrite, antimonite, zinc selenide, lead telluride and pure substances – gold, silver, cadmium, nickel, cobalt, manganese. The operating conditions of the apparatus are as follow: accelerating voltage 20 keV, probe current 4.10^{-9} A, spectrum acquisition time 100 s, without "dead time".

Trace element concentrations in ore minerals are measured by LA-ICP-MS on polished sections at the Geological Institute (Bulgarian Academy of Sciences). The analyses were performed on Perkin Elmer ELAN DRC-e ICP-MS equipped with a New

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Wave UP193-FX excimer laser ablation system. NIST SRM 610 glass and MASS 1 was used as external standard and stoichiometric Fe as internal. The laser system was operated at constant 10 Hz pulse rate; laser energy was 10.10 J/cm^2 on SRM 610 glass and 1.90–3.06 J/cm^2 on sample. Spot size was 50 µm in diameter. Acquisition dwell time for all masses was set to 0.01 s. Data reduction was undertaken using SILLS ver. 1.1.0 software (Guillong et al., 2008).

Geology of Caleta Argentina and morphological features of the ore veins

Livingston Island is one of the South Shetland Islands which regionally belongs to the South Shetland Block. It represents a continental fragment situated between the South Shetland Trench zone to the NW and Bransfield Back-arc Basin to the SE. There is a broad consensus that since the early Mesozoic, the South Shetland Block represents a magmatic arc related to the subduction of the oceanic lithosphere of the Phoenix Plate (Smellie et al., 1984).

Caleta Argentina, as a part of the Hurd Peninsula, is built up mainly of sedimentary sequences of the Miers Bluff Formation (MBF), consisting of five members. Terrigenous and aleuro-pelitic mixed rocks (mudstones) formed at different depositional environments – from turbiditic to delta and alluvial fans are recognized (Pimpirev et al., 2015; Stefanov, Pimpirev, 2015).

The ore veins in the studied area are hosted by the rocks of MBF and mostly by the sedimentary sequences of the South Bay member, consisting of medium- to coarse-grained massive sandstones alternating with thick mudstones and fine-grained sandstones. Layers of breccia-conglomerates are randomly presented (Pimpirev et al., 2015).

Several quartz-polymetallic veins build an ore zone with a thickness of about 3–4 m. The veins have similar features to those exposed in the area of the Bulgarian Antarctic Base (BAB) (Sabeva et al., 2020). The veins are structurally controlled, probably following strike-slip faults. They mainly consist of quartz and ore minerals. Primary ore minerals are pyrite and chalcopyrite, and less commonly galena and sphalerite. In the weathering zone, malachite is most common, probably formed at the expense of chalcopyrite, as well as azurite, which is in a subordinate amount.

Ore mineralogy and mineral chemistry

The main ore stage is represented by pyrite, chalcopyrite, galena, and sphalerite, but in all the studied samples chalcopyrite dominates. The depositional sequence is: 1, pyrite; 2, galena; 3, chalcopyrite and sphalerite. The gangue minerals are quartz, clinochlore, and sericite (proven also by XRD).

Chalcopyrite is the most common ore mineral. It occurs as anhedral small grains with size mostly around 50–100 µm and as large aggregates, forming nests and veinlets up to 7–8 mm. It encloses pyrite and galena and associates with the synchronously formed sphalerite. Chalcopyrite is usually fractured and porous. Some of the grains are oxidized and altered along the periphery and cracks, and replaced by secondary copper minerals.

Electron microprobe analyses show chemical composition close to stoichiometry. The LA-ICP-MS analyses also show that chalcopyrite is a poor host for trace elements. The most abundant is Zn (from 371.88 to 10 551.67 ppm, average 2939.60 ppm). Concentrations exceeding 2000 ppm Zn and irregular profiles of the depth spectra are probably the result of micro-inclusions of sphalerite (Huston et al., 1995; George et al., 2018). Silver and selenium are the trace elements most commonly reported in chalcopyrite and typically structurally-bond in the lattice. Ag has concentrations from 223.54 ppm to 283.3 with an average of 240.51 ppm and substitutes Cu in the lattice of chalcopyrite. Chalcopyrite often hosts Se due to the possibility of formation of solid solution with eskebornite (CuFeSe2) above 390 °C (Bethke, Barton, 1971). Se contents in samples from Caleta Argentina are from not detectable (bdl) to 139.95 ppm with average 70.10 ppm. Cd, Mn, In, Sn, Bi are with very low concentrations (average < 20 ppm).

Sphalerite is the second-most abundant sulfide mineral in the quartz-polymetallic veins and occurs mainly as anhedral aggregates. Irregularly distributed small chalcopyrite inclusions with spherical or drop-like forms, known as "chalcopyrite disease" are observed in sphalerite.

EPMA reveal certain deviations in stoichiometry – high contents of S, which is probably due to unsuitable analytical spot. The LA-ICP-MS dataset shows variable concentrations of trace elements in sphalerite. Structurally-bonded in the lattice are Fe (from 17 851.79 to 42 890.89 ppm, average 29 606.01 ppm; almost 3%), Cu (from 860.65 to 45 465.46 ppm, average 24 307.86 ppm; 2.5%), Cd (from 1274.33 to 1796.92 ppm, average 1489.24 ppm), Co (from 70.82 to 589.21 ppm, average 301.80 ppm) and Mn (from 36.11 to 636.60 ppm, average 225.88 ppm). These element substitutions in sphalerite are governed by the similarity of the size of a relatively large number of other ions to that of tetrahedrally-coordinated Zn^{2+}, as well as their affinity for tetrahedral coordination. The chemical structure of ZnS doped with Fe^{2+}, Cd^{2+} and other bivalent cations. Iron is almost always present in sphalerite and the high Fe contents define sphalerite as Fe-rich which indicate ore-forming conditions with higher fS_2 (Cook et al., 2009). Chemical behavior and irregular depth spectra of Pb (average 114 ppm), Se (average 68.70 ppm), Ag (average 50.82), Au (average 0.31 ppm) and probably part of Cu suggest they are inclusion-related. High contents of silver correspond with these of gold. The elements with average concentrations < 30 ppm are Hg, As, Bi, Sb, Ti, In, Sn, Ga.

Galena occurs as anhedral crystals with size of 200–1000 μm, also as smaller inclusions in chalcopyrite. Triangular pits along cleavage lines are observed, which are determined by its perfect tenacity in three directions. On the periphery of some crystals, alteration rims of secondary minerals as linarite and cerussite are observed (proved by XRD).

Electron microprobe analyses reveal the presence of 1.35 wt% Ag, 0.16 wt% Mn, 0.30 wt% Co, 0.32 wt% Ni and 0.35% Fe as trace elements. These elements are inherent for the galena and probably are due to inclusions of sulfide minerals (Blackburn, Schwendeman, 1977).

Pyrite is the rarest ore mineral in quartz-polymetallic veins and is deposited first and enclosed by chalcopyrite and galena. It occurs as euhedral crystals with cubic and pentagondecahedral forms and subhedral crystals. The size of the grains is mostly up to 100 μm but individual grains with size up to 200–250 μm are also observed.

Electron microprobe analyses of pyrite show chemical composition close to stoichiometry $Fe_{0.99}S_{2.01}$. Low contents of copper (0.07 wt%) are established. The LA-ICP-MS dataset shows variable concentrations of trace elements in pyrite. High concentrations of Zn (from 726.96 to 6188.45 ppm, average 2766.85), Cu (from 594.48 to 2781.26 ppm, average 1361.23), and Pb (from 1.09 to 487.18 ppm, average161.81) are detected and represented as micro-inclusions of sphalerite, galena and chalcopyrite. As (average 205.90 ppm) and Co (average 106.54 ppm) are structurally-bound. Trace elements with concentrations < 100 ppm are Se, Bi, Mn, Cr, Sb, Ge, Ti, Cd, Sn, In, Tl, Hg. Pyrite contains Au from not detectable to 1.03 ppm (average 0.59 ppm) and Ag from not detectable to 54.33 ppm (average 32.52 ppm). These elements display irregular profiles with spikes, which suggest the presence of micro-inclusions of native gold and electrum.

Conclusions

The area of the Hurd Peninsula, which in regional aspect belongs to the Andean metallogenic province (Guild et al., 1998) hosts a number of hydrothermal veins, breccias and hydrothermal altered rocks (Willan, 1994; Velev et al., 2016; Sabeva et al., 2020). Caleta Argentina, as one of these ore mineralizations, has to be correlated with the other research area from the Hurd Peninsula such as BAB, the Bulgarian Beach, and Sally Rocks. More detailed studies are needed to clarify the ore-forming conditions and to prove that these ore bodies are probably products of a single process but due to different hydrothermal events.

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