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MINERALOGICAL AND GEOCHEMICAL DIVERSITY WITHIN THE STAN TERG DEPOSIT, KOSOVO

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ABSTRACT

Detailed mineralogical and geochemical analyses were done on the samples from various mineralization styles collected from the Stan Terg Pb-Zn mine, Kosovo.

The application of electron probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) allowed for the determination for obtaining major, minor, and trace element chemical compositions of selected mineral phases, including submicroscopic inclusions, and at very low concentrations (as low as around 1 ppm) that can be linked in the crystal chemistry of the main sulphides. Galena is the main host of Bi, Ag, Au, Sb, Sn and Tl, sphalerite hosts Sn, In, Ga, Cd and Hg, pyrite hosts Co and Ni, arsenopyrite Ge, Au, and Co, chalcopyrite Ag, Ge, Cd, Sn, Ni, tetrahedrite Ag and Hg. Pyrrhotite does not incorporate significant minor or trace elements in its structure.

Several Bi-bearing sulphosalts, previously unknown in Kosovo, have been identified in the Stan Terg deposit using the EPMA analyses done on samples associated with skarn mineral paragenesis. Tetradymite group minerals, mainly ikunolite and babkinite, show low degree of S and Se substitution and higher concentrations of Pb for Bi. Joséite-A is the first Te mineral described from this locality. Lillianite homologues include lillianite (N=4) and heyrovskýite (N=7) with a low degree of AgBi for $2Pb^{2+}$ substitution, average x = 0.21 and 0.17, respectively. Izoklakeite, the fourth member of the kobellite homologous series with average Sb/(Sb+Bi) ratio about 0.43, is also described. Other Bi-bearing minerals identified include cannizzarite, cosalite, native bismuth, and bismuthinite. All minerals described are associated with galena with elevated Bi and Ag contents (0.02 Bi+Ag *apfu*). The presence of native gold is spatially related with Bi mineralization. The physico-forming conditions for bismuth-related mineralization suggests temperatures between 350-400°C.

Investigation of sulphotelluride phases indicate a presence of joséite-A, joséite-B and two unidentified minerals: phase A, with chemical formula $(Bi,Pb)_2(TeS)_2$, and phase B, with chemical formula $(Bi,Pb)_{2.5}Te_{1.5}S_{1.5}$. Sulphotellurides occur in association with cosalite, Sb-rich lillianite, kobellite homologeus series and Bi-rich jamesonite. In situ analyses of the tellurides or the accompanying sulphosalts do not reveal significant concentrations of Ag or Au, and Ag tellurides have not been found in the Stan Terg deposit. The hydrothermal fluids were likely depleted in precious metals limiting the precipitation of Au and Ag from this hydrothermal system.

Also reported are results from recently discovered Ag mineral association in the Stan Terg deposit, located in the Vardar Zone (in the northern Kosovo). The mineralization described comprises pyrargyrite, freieslebenite, high-Ag bearing tetrahedrite, freibergite and native compounds (electrum, native Ag, native Sb). Ag minerals occur in vugs and cracks in massive galena ore that suggests these are the latest precipitated minerals in the deposit. The chemical composition of those minerals was determined with the EPMA. Freibergite from the

Stan Terg deposit is chemically zoned and contains between 13.91-20.28 at. % of Ag. High Ag solutions are also indicated by relatively high Ag content in electrum, which is between 47.02 and 73.19 at. % of Ag. The Ag association is thought to be an epithermal equivalent of precious metal mineralization which could be located in the external part of the Stan Terg hydrothermal system. This association occurs at low temperatures, below 200˚C. The Ag minerals may be part of an epithermal vein system from the external part of the Stan Terg deposit. Similarly to other known Pb-Zn-Ag hydrothermal systems, silver association is related to formation of the rhodochrosite banded ore and Ag-Au-Sb±Hg dominated mineralization.

Tin is a common minor element in the hydrothermal base metal deposits in Kosovo. Stannite commonly occurs at Stan Terg deposit in small amounts in association with sphalerite, chalcopyrite, galena, pyrite and pyrrhotite. Sphalerite from Stan Terg, commonly overgrown by stannite contains the lowest Sn content (few ppm) and may have been precipitated before Sn-enrichment from the hydrothermal fluids. The highest value of Sn (520 ppm) in Stan Terg sphalerite was obtained in close proximity to a stannite rim, and indicates a rapid increase of Sn concentration in the later hydrothermal fluids. Stannite-sphalerite geothermometry revealed the following ore-forming temperatures 240° to 390 °C for Stan Terg. Sphalerite, chalcopyrite, and stannite, precipitated simultaneously during cooling from reduced hydrothermal fluids and under low-sulfidation fluid states. Fluctuations in physico-chemical fluid conditions are revealed by the presence of stannite group minerals along growth zones in sphalerite crystals and may be related to short interval of magmatic pulses during ore deposition.

The results obtained from *in situ* detailed geochemical analyses of the main sulphides occurring in the deposit and their paragenetic relationship with the other minerals are a foundation for a new paragenetic sequence model for the ore mineralization at the Stan Terg deposit. At least four generations of galena and sphalerite, three generations of pyrrhotite, arsenopyrite, and chalcopyrite, and at least five groups of tetrahedrite were identified.

The first mineral generation may be related to precipitation in a matrix within the limestone breccias near by central pipe, and comprises galena, Bi-minerals, arsenopyrite, pyrite, native gold and chalcopyrite. The skarn-related mineralization, occurring in association with gangue skarn minerals (like hedenbergite, ilvaite, garnet) comprises galena, at least two Bi-associations (one with sulphotellurides), pyrite, two pyrrhotite generations, sphalerite and less commonly tennantite and As-rich tetrahedrite. During the main hydrothermal replacement phase of precipitation, most of the mineralization occurred. This consists of the main phases hosting Pb and Zn mineralization, include galena, arsenopyrite, pyrite, chalcopyrite, pyrrhotite, and at least two generations of sphalerite and tetrahedrite. The period of mineralization with Cu is postdates the main Pb and Zn stage, and comprises galena overgrown by bournonite, and younger generations of arsenopyrite, pyrite, chalcopyrite, sphalerite, stannite, and tetrahedrite. Ag mineralization comprises native gold/electrum (with high Ag content), Ag minerals, Ag-rich tetrahedrite, freibergite and chalcopyrite. The youngest ore mineral is boulangerite, occurring primarily in the oligonite zone, but also occurs covering most of minerals precipitating in cavities. There are few secondary minerals, since the supergenic stage is weakly developed even at the surface. Minerals hosted in the vein and brecciated style of mineralization, have similar geochemical signature as ore minerals in skarn-related and primary replacement mineralization, which suggests that these mineralizations have precipitated during the whole episode of ore deposition.