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Minor and trace elements in tennantite-tetrahedrites and coexisting sulphides from the Madan Pb-Zn hydrothermal deposits, Central Rhodopes, Bulgaria

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The tennantite-tetrahedrites are the most common among the sulfosalt minerals in the Madan base metal deposits, Central Rhodopes. Due to their chemical diversity and compositional variations in natural settings they have been recognized as a potentially important petrogenetic indicator of hydrothermal mineralizing environment. Tennantite-tetrahedrites are formed in the late phases of the main quartz-sulphide stage with galena, sphalerite, pyrite and chalcopyrite, showing complex mineral textures and chemical compositions. We have used EPMA and LA-ICP-MS techniques to determined minor and trace elements and investigate their distribution in tennantite-tetrahedrites and coexisting sulphides.

Because the content of Cu is higher than 10 apfu in studied tenanntite-terahedrites, Cu can be considerably substituted by Zn, and less commonly by Fe and Ag. Average Ag content is 0.75 wt.% and reach up to 1.91 wt.% in the samples from the Petrovitsa deposit.

Minor elements are detected in the sulphosalt minerals, such as Cd (up to 0.45 wt.%) and Co (0.17 wt.%). Concentrations of up to several ppm Ni have been measured. Although the Mn is not a foreign element for the natural tennantite-tetrahedrites, it has not been detected in the studied sulphosalts. Bismuth and Te were below the limit of detection of the EMPA, however detected by LA-ICP-MS at a ppm level. The trace amounts of Pb range from 10 to 50 ppm. In rare cases the concentration of Se reaches 0.26 wt.%, probably substitutes for S. Vanadium, Mo, Ga, Ge and Cr concentrations in sulphosalts are typically close to the limit of detection.

Concentrations of minor and trace elements in associated sulphides vary over several orders of magnitude between different deposits and samples. Ag, Sb and Bi are the most important minor elements and have uneven distribution in the galena. Argentum and Sb were found in variable amounts in the ranges 10-1000 ppm for Ag, and 70-600 ppm for Sb. In coexisting sphalerite detected are: Cd up to 1.51 wt.%; Cu up to 1.16 wt.%; Fe 0.11-1.10 wt.%; Mn $\sim$2000 ppm, Co 750 ppm and few ppm Ga and Ge. In associated chalcopyrite concentrations of Zn 0.30 wt.% and Sb 1.94 wt.% are analyzed by EPMA. The chalcopyrite from the Gradishte deposit reveals: As up to 1300 ppm, Ni (in the range of 350-450 ppm, Ge ($\sim$ 60 ppm). The enhanced Zn can be due to sphalerite micro-inclusions within the host crystals. LA-ICP-MS single spot spectra, showing both smooth and irregular profiles, suggest two possible types of incorporation of minor and trace elements in the studied sulphides: 1) homogeneous along the analyzed volume reflected in smooth ablation profiles for most of the elements; 2) inhomogeneous, due to zonation or solid inclusions. Chemical determination of minor and trace element concentrations in tenanntite-tetrahedrites and associated sulphides is a step towards understanding the mechanisms controlling exsolution relative to retention of elements in crystal structure.

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