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Tetrahedrite-tennantite series in the Pb-Zn deposits from the Central Rhodopes: textural relationships, mineral chemistry and conditions of formation

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The tennantite-tetrahedrite minerals are important although in minor quantities in the Madan base metal deposits, South Bulgaria. Found in veins and metasomatic orebodies of the Petrovitsa and Gradishte deposits, these minerals closely associate with the main sulphides – galena, sphalerite, chalcopyrite and pyrite. Large compositional variations are responsible for the observed fine oscillatory zoning of the crystals.

The studied sulphosalts are presented as remarkable in size crystals with polyhedral morphologies.

In the Gradishte samples they are observed as idiomorphic crystals postdating aggregates of large chalcopyrite, pyrite and quartz. Crystals are developed by negative and small positive tetrahedra, the {110} acting mostly as a modifying form. Tenantite-tetrahedrites overgrow (112) chalcopyrite faces with parallel mutual orientation, due to the similar basic structural motifs. Characteristic penetration twins on {111} are observed. Macroscopically, the tetrahedrite from Petrovitsa occurs as well-shaped crystals with two characteristic morphologies: 1) Peculiar crust of tennantite-tetrahedrite, completely overgrowing and resembling the shape of the main sulphides. Such perimorhoses are composed by subparallel crystals (0.5-1 up to 3-4 mm) with tetrahedral habit and bounded by the faces o {111}, d {110}, a {100} and n {211}. The crusts aggregate reveal central parts of chalcopyrite-galena-sphalerite-tetrahedrite association, together with carbonates and minor quartz; 2) Single crystals observed preferably on cubo-octahedral galena crystals. Such overgrowths follow the scheme galena (100) [100] // tetrahedrite (001) [110]. According to the textural characteristics and spatial position these tetrahedrites are formed shortly after the polyhedral crusts.

Based on microprobe analyses the following average crystal-chemical formulae can be assigned:

Gradishte: $(Cu_{5.99-6.00}Ag_{0-0.01})_6Cu_4(Fe_{0.08-0.45}Zn_{1.61-1.93}Cu_{0.06-0.2}Cd_{0.01})_2(Sb_{0.03-2.85}As_{1.12-3.98})_4(S_{12.73-12.93}Se_{0-0.05})$

Petrovitsa: $(Cu_{5.70-5.86}Ag_{0.11-0.30})_6Cu_4(Fe_{0.06-0.21}Zn_{1.81-1.95}Cu_{0.10-0.25})_2(Sb_{2.23-3.66}As_{0.33-1.74})_4(S_{12.71-12.90}Se_{0-0.03})_{13}$

In the Madan samples Cu content is considerably substituted by Zn, and less commonly by Fe and Ag. Such compositions correspond to zincian varieties (to 1.95 *apfu* Zn) with low Fe-content (<0.45 *apfu*). Silver is characteristic for the Petrovitsa samples, reaching 0.30 *apfu*. The Gradishte samples reveal highly variable As/Sb ratios, mostly belonging in composition to the tennantite and intermediate members of the solid solution. Tennantite-tetrahedrite$_{ss}$ from Petrovitsa have As/Sb ratio <0.78, in the range of 0.10-0.55, corresponding to tetrahedrite.

The presence of tennantite-tetrahedrite$_{ss}$ in the hydrothermal mineralization suggests increased activity of Sb and As in the fluids, as well as increased fS_2. Important Zn-incorporation in the studied samples is indicative for high fO_2, resulting in enhanced Cu^{2+}/Me^{2+} ratios. A vertical zonation in the Madan hydrothermal system is observed, consisting of As-rich members (mostly zincian tennantite), typically found at depth (Gradishte ~400 m.a.s.l.), while in the upper levels (Petrovitsa mine ~970 m.a.s.l.) tetrahedrite compositions tend to prevail. Silver incorporation is often related to the late stage of formation of tetrahedrite, compared to the main sulphide paragenesis. Textural characteristics, mineral relationships and fluid inclusion studies suggest that tennantite-tetrahedrite$_{ss}$ at Madan precipitated in the late stages of mineralization at temperatures close to 200°C.

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