# COMPOSITIONAL VARIATIONS OF THE TENNANTITE-TETRAHEDRITE SERIES FROM THE MADAN Pb-Zn DEPOSITS, BULGARIA: OSCILLATORY ZONING AND CONDITIONS OF FORMATION

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The tennantite-tetrahedrite solid solution series is the most common among the sulphosalt minerals in the Madan base metal deposits, Central Rhodopes, Bulgaria. Found in veins and metasomatic orebodies of the Petrovitsa and Gradishte deposits, these minerals closely associated with the main sulphides – galena, sphalerite, chalcopyrite and pyrite. 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. Large compositional variations are responsible for the observed fine oscillatory zoning of the crystals, according to EPMA and LA-ICP-MS investigations.

A generalized formula for the tennantite-tetrahedrite$_{ss}$ was proposed by JOHNSON *et al.* (1986): $(Cu,Ag)_6\,Cu_4\,(Fe,Zn,Cu,Hg,Cd)_2\,(Sb,As,Bi,Te)_4(S,Se)_{13}$. Although in the Madan samples Cu content is always higher than 10 *apfu*, Cu can be considerably substituted by Zn, and less commonly by Fe and Ag. Such compositions correspond to zincian varieties (1.7–1.95 *apfu* Zn) with low Fe-content (0.08–0.45 *apfu*). Silver is characteristic of 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 (Fig. 1). Tennantite-tetrahedrite$_{ss}$ from Petrovitsa have As/Sb ratio < 0.78, generally in the range of 0.10–0.55, corresponding to tetrahedrite. Bismuth and tellurium were below the limit of detection of the EPMA, however detected by LA-ICP-MS analyses at a ppm level. Selenium commonly substitutes for S.

Based on microprobe analyses the following average crystal-chemical formulae can be assigned: *Gradishte*: $(Cu^{+}_{5.99–6.00}Ag_{0–0.01})_{\Sigma6}Cu^{2+}_{4}(Fe_{0.08–0.45}Zn_{1.61–1.93}Cu^{2+}_{0.06–0.2}Cd_{0.01})_{\Sigma2}(Sb_{0.03–2.85}As_{1.12–3.98})_{\Sigma4}(S_{12.73–12.93}Se_{0–0.05})_{\Sigma13}$. *Petrovitsa*: $(Cu^{+}_{5.70–5.86}Ag_{0.11–0.30})_{\Sigma6}Cu^{2+}_{4}(Fe_{0.06–0.21}Zn_{1.81–1.95}Cu^{2+}_{0.10–0.25})_{\Sigma2}(Sb_{2.23–3.66}As_{0.33–1.74})_{\Sigma4}(S_{12.71–12.90}Se_{0-0.03})_{\Sigma13}$.

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 $fO_2$ (SPIRIDONOV *et al.* 2005), 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.

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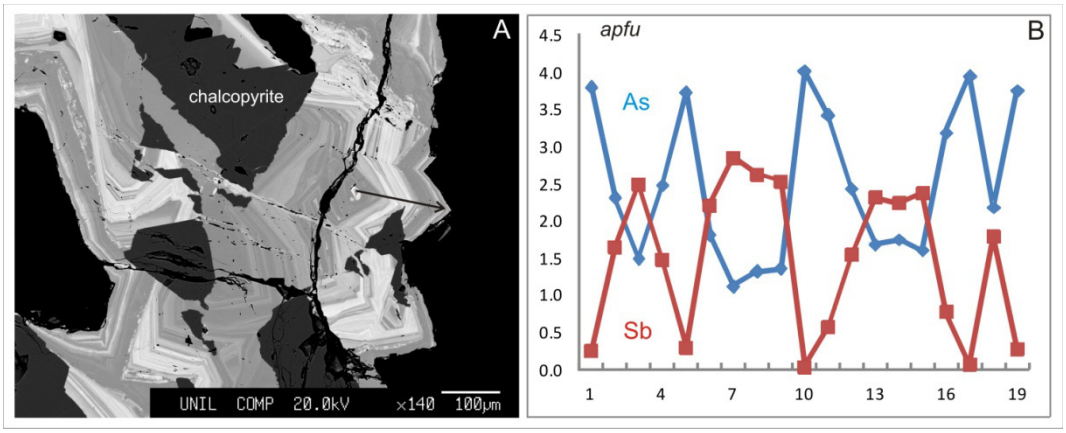


***Fig. 1.*** *BSE image of Gradishte tennantite-tetrahedrite$_{ss}$ reveals typical oscillatory zoning (A), controlled by As and Sb fluctuation (B). Location of the profile is indicated on the BSE image.*