

## CHEMICAL COMPOSITION OF Ni, Co AND Fe SULPHOARSENIDES AND ARSENIDES IN THE HYDROTHERMAL SIDERITE VEINS IN THE WESTERN CARPATHIANS (SLOVAKIA)

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There are Ni-Co minerals occurring mainly in the hydrothermal siderite veins of Alpine age in the Western Carpathians. The mineral succession scheme is the following: alteration → siderite → alpine paragenesis → Ni-Co-Fe-As minerals → quartz with Cu-Bi-Fe-Sb-Hg sulphides. The most abundant are in the sulphide (sulphoarsenide, arsenide) stage with less contents of carbonates and silicates. There are often occurred with the Cu minerals – tetrahedrite, tennantite, chalcopyrite and with the others sulphides mainly pyrite and galena. Those were described on numerous deposits and occurrences in the Slovak Republic. Ni-Co-Fe-Cu-As minerals are represented by gersdorffite, cobaltite, arsenopyrite, rammelsbergite, paramrammelsbergite, krutovite, ullmannite, skutterudite, nickeline and carrollite which were studied in details at the following localities: Vyšná Boca, Dobšiná and Častá.

Optical zoning is a characteristic feature of all the mentioned Ni-Co minerals, but mainly of the sulphoarsenides and diarsenides. It may be oscillatory, concentric or sector zoning. The typical oscillatory zoning was developed probably in a non-steady system under the influence of locally changing physico-chemical conditions or by diffusion in solid state. The dominant components in the chemical zoning in the sulphoarsenides are As and S over the also varying Ni, Co and Fe.

The most abundant minerals are sulphoarsenides represented mainly by arsenopyrite and gersdorffite. Based on chemical composition of sulphoarsenides we described 3 basic types of gersdorffite. The 1<sup>st</sup> type is represented by euhedral, homogenous gersdorffite from Vyšná Boca, with typical strong isomorphism of Ni vs. Co ( $\pm$  Fe) and a less pronounced variation of As vs. S. That type forms rims around arsenopyrite crystals and was crystallized close to the temperature of the arsenopyrite formation. Higher temperature sulphoarsenides, including cubic gersdorffites and cobaltites with strongly disordered structure and space group Pa3, were formed at a temperature of 500–550 °C (KLEMM, 1965). The 2<sup>nd</sup> type from Dobšiná deposit is characterized by smooth transition from arsenopyrite to gersdorffite. Gersdorffite formed by metasomatic replacement of arsenopyrite, thus both minerals might have crystallized in the triclinic space group P1 (ČVILEVA *et al.*, 1988), at temperature of 550–650 °C (KLEMM, 1965). During that replacement the primary crystal shape of arsenopyrite is preserved. The intensive zonal (but smooth) arsenopyrite-cobaltite transition samples may also belong to this type. The 3<sup>rd</sup> type is repre-

sented by gersdorffites from Vyšná Boca and Dobšiná. In these samples a smooth transition to krutovite is observed, with strong variation of As vs. S and a less characteristic isomorphous substitution of Fe vs. Co. Both minerals crystallized in the space group P2<sub>1</sub>3, a space group of gersdorffite of temperature lower than 300 °C (KLEMM, 1965). In the euhedral crystals intensive oscillatory zoning is typical. The cores of the crystals are formed by krutovite and the rims by gersdorffite. Krutovite was identified by X-ray diffraction. Gersdorffites from Častá belong also to that type. They were formed together with ullmannite by solid solution decomposition. They show strong isomorphous substitution of Sb, As and S. Space group is P2<sub>1</sub>3. Their formation temperature was relatively low, probably under 300 °C.

Most arsenopyrites contain no isomorphous substitution and are close to stoichiometric formula. Isomorphous substitution of Fe vs. Co or Ni respectively indicated a higher temperature of formation (KLEMM, 1965). Antimony rarely substitute in the arsenopyrite crystal lattice. Arsenopyrite-gudmundite smooth transition was not observed (Vyšná Boca), but zonal arsenopyrite contains zones, mainly in the crystal core, enormously enriched in Sb (up to 11.81 wt.% Sb; (=5.59 at.% Sb)). This is the maximum Sb substitution in arsenopyrite reported from the Western Carpathians. Sb replaces As in the lattice. These Sb substituted arsenopyrites might formed at a lower temperature.

Based on this chemical variation, (successive precipitation from solid solution; substitution of cations (Ni, Co, Fe) and anions (As, Sb, S)), we can say, that with increasing temperature arsenopyrite began to precipitate; later gersdorffite and cobaltite, with strong substitution of cations. On the reverse path ullmannite and gersdorffite was crystallized by solid solution decomposition. Fluid inclusion studies of these hydrothermal veins (HURAI *et al.*, 2002) confirmed a temperature increase during the crystallization of quartz and siderite from the core to the rim.

### References

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