

Antimony and Cu isotope variations in the Sb-Au orogenic deposit Dúbrava (Slovakia)

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The Dúbrava Sb-Au deposit is located in the Tatric Superunit of the Western Carpathians (Slovakia). It consists of hydrothermal veins hosted by the Variscan granodiorites and migmatites. The deposit can be subdivided into five hydrothermal mineralization stages [1]. The most prominent stage called “stibnite-sphalerite-Pb-Sb sulfosalts” comprises predominately stibnite (Sb₂S₃), zinkenite (Pb₉Sb₂₂S₄₂), senarmontite (Sb₂O₃) and chalcostibite (CuSbS₂). To characterize the Sb and Cu sources and to understand factors responsible for fractionation of Sb and Cu isotopes, we investigated various primary minerals from this mineralization stage at Dúbrava.

The Sb and Cu isotopic composition of selected minerals was measured *in-situ* by deep UV-fs laser ablation ($\lambda = 194$ nm) system coupled with MC-ICP-MS. Instrumental mass bias for Cu and Sb was monitored with Sn NIST 3161a and Ni NIST 986 standard solution, respectively, which were simultaneously aspirated during LA-MC-ICP-MS analyses. All $\delta^{123}\text{Sb}$ values were measured in bracketing to a stibnite in-house standard and reported relative to NIST 3102a and $\delta^{65}\text{Cu}$ relative to NIST 976 [2]. Using this technique isotopic variations larger than 0.1 ‰ can be distinguished.

The $\delta^{123}\text{Sb}$ values of the primary minerals of the “stibnite-sphalerite-Pb-Sb sulfosalts” stage, including stibnite, zinkenite, senarmontite and chalcostibite display a range of ≈ 0.6 ‰. Stibnite and zinkenite formed simultaneously but stibnite has ≈ 0.2 ‰ heavier Sb isotopic composition than zinkenite. The evolution in this stage was influenced by the influx of cooler, low-salinity fluids of likely meteoric origin, as evidenced by $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values [1]. Oxygenation of the fluids caused the late primary precipitation of senarmontite with much heavier $\delta^{123}\text{Sb}$ values than the sulfides. A possible explanation of the heavy $\delta^{123}\text{Sb}$ values in senarmontite is the massive precipitation of Sb minerals upon cooling of the fluid and the corresponding shift in the Sb isotopic composition in the fluid. Chalcostibite shows Sb isotopic values intermediate between stibnite and zinkenite, suggesting that it formed by mobilization of Sb from the pre-existing ores. Heavy $\delta^{65}\text{Cu}$ values (0.30-0.45 ‰) of chalcostibite may indicate a recycled heavy Cu source.

[1] Majzlan et al. (2020), *Geol. Carpath.* **71**, 85-112.

[2] Lazarov and Horn (2015), *Spectroch. Acta Part B* **111**, 64-73.