

Antimony isotope evolution during hydrothermal precipitation and during oxidative weathering of diverse antimony mineralization in the Western Carpathians (Slovakia)

A. Kaufmann^{1,2}, M. Lazarov^{1*}, S. Weyer¹, J. Majzlan²

¹ Institute of Mineralogy, Leibniz University Hannover, Germany

² Institute of Geosciences, Friedrich Schiller University Jena, Germany

*e-mail: m.lazarov@mineralogie.uni-hannover.de

Numerous hydrothermal Sb or Sb-Au mineralization and ore deposits are seated in a Variscan basement of the Western Carpathians (Slovakia). Stibnite is the most common mineral in all of them. However, each deposit has its specific mineralization association and Sb is found in a variety of sulfides, sulfosalts, or oxides, in combination with Cu, Pb, Fe, or Ag. All these minerals, on macro- or microscale, carry information about the ore-forming processes. In this study, a variety of Sb minerals from four ore deposits: Dve Vody, Magurka, Dúbrava and Pezinok, are investigated for their Sb isotope composition. Measurements were conducted *in-situ* by deep UV-fs laser ablation system coupled with MC-ICP-MS following the procedure of Kaufmann et al. (2021).

The $\delta^{123}\text{Sb}$ values of all investigated primary hydrothermal minerals show a range of -0.8 to +1.0 ‰. Variations of $\delta^{123}\text{Sb}$ for each deposit do not exceed 0.8 ‰. Combining information from textural relationships and Sb isotope compositions, in some cases also mineral trace-element contents, implies that mineral $\delta^{123}\text{Sb}$ can be correlated with the mineral precipitation sequence. This relationship can be observed on hand-specimen as well as on ore body and ore deposit scale. The systematic increase of $\delta^{123}\text{Sb}$ values during progressive precipitation of primary Sb minerals can be rationalized by a Rayleigh crystallization model, applying a uniform isotope fractionation factor for all minerals that was determined for stibnite by Zhai et al. (2021).

Each ore deposit has its own distinct mean of $\delta^{123}\text{Sb}$. Dúbrava displays the lowest values of around -0.11 ± 0.56 ‰, followed by Magurka and Pezinok with a mean of 0.08 ± 0.59 ‰ and 0.24 ± 0.48 ‰, respectively. The overall heaviest isotopic compositions are observed for Dve Vody $\sim 0.53 \pm 0.88$ ‰. These differences may indicate that either different sources or differently developed fluids, or both were responsible for each deposit formation.

A similar spread of $\delta^{123}\text{Sb}$ (-0.50 to +0.8 ‰) was observed for secondary Sb minerals formed near surface as the result of weathering. Depending on the amount of leached, primary mineral, and redox changes during transport and formation of secondary minerals, Sb isotope fractionation of more than 0.3 ‰ was observed. While the Sb oxides tend to become isotopically heavier, Sb hydroxides, Fe,Sb oxides or silicates prefer the ^{121}Sb isotope and display lower $\delta^{123}\text{Sb}$ signatures, compared to the coexisting primary minerals.

Thus, considering all studied deposits, mineral $\delta^{123}\text{Sb}$ may help to constrain the precipitation sequences in primary ore deposits, to decipher hydrothermal remobilization or near-surface weathering of primary ores and to constrain the potential source(s) of the metalloid.

Kaufmann AB, Lazarov M, Kiefer S, Majzlan J, Weyer S. (2021): In-situ determination of antimony isotope ratios in Sb minerals by femtosecond LA-MC-ICP-MS. - JAAS 36, 1554-1567

Zhai D, Mathur R, Liu SA, Liu J, Godfrey L, Wang K, Vervoort J. (2021): Antimony isotope fractionation in hydrothermal systems. - Geochim Cosmochim Acta 306, 84-97