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Antimony isotope signature of hydrothermal ore formation and weathering of antimony ore deposits

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Several medium-large antimony ore deposits occur in the Central Western Carpathians in Slovakia. The Variscan hydrothermal mineralizations are hosted in granites, metapelitic, and meta-carbonaceous rocks. All deposits contain several similar main mineralization stages, signs of Alpine re-working and poorly developed oxidation zones.

Various primary and secondary Sb minerals from four Sb and Sb-Au orogenic deposits (Dve Vody, Magurka, DÃºbrava and Pezinok) were analysed for their Sb isotope composition. Measurements were performed *in situ* by the deep UV-fs laser ablation system coupled with MC-ICP-MS. Instrumental mass bias was corrected by simultaneously aspirated Sn (NIST 3161a) standard solution and results were reported relative to Sb (NIST 3102a) standard. Using this technique, isotopic variations larger than 0.1 ‰ can be distinguished.

Total range of $\delta^{123}Sb$ in primary ore minerals is around 1.4 ‰. The largest variation (~1 ‰) is observed for the most abundant stibnite and can be related to its successive precipitation from the fluid. Stibnite from the main mineralization stage has $\delta^{123}Sb$ from –0.2 to +0.4 ‰ while the less abundant, later stibnite tends to be isotopically lighter. The primary Sb oxides (senarmontite, valentinite Sb_2O_3 and kermesite Sb_2S_2O) formed during the main Sb deposition stage and consistently display distinctly higher $\delta^{123}Sb$ values than the associated Sb sulfides. This conforms to the textural evidence that the Sb oxides postdate stibnite and other Sb sulfides.

Late hydrothermal overprint produced locally chapmanite ($Fe_2Sb(SiO_4)_2(OH)$) and weathering led to the formation of brandholzite [$MgSb_2(OH)_{12}$Â·$6H_2O$] and tripuhyite ($FeSbO_4$). These minerals display extremes in Sb isotope compositions. The factors responsible for these signatures are the amount of the leached primary ores, transport of the dissolved solution and the redox changes during the mineral precipitation. Thus, Sb isotopic composition is an excellent tool for further understanding of the evolution of antimony deposits, from initial reduced stages to the surficial weathering.