Mineralogical control of synergetic thallium and antimony weathering

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As metals and metalloids have a strong impact on the environment, methods for their detection and speciation have received a particular attention in the last few years. Thallium (Tl), antimony (Sb) and arsenic (As) are important examples of such toxic elements. Their speciation is of the particular interest owing to their toxicity, bioavailability and reactivity. One of the world most famous deposit hosting all these three elements is Sb-As-Tl-Au Allchar deposit in North Macedonia, which mining waste dumps and technosoils served us as an ideal natural laboratory for the investigations of the oxidative processes on the primary sulfide and sulfosalt minerals. Of the particular interest were the weathering processes in the Sb-rich (Sb: 1000–16500 ppm) central part of the deposit, where Tl-concentrations have been measured in the range between 120-840 ppm (Đorđević et al. 2021).

In the scope of our previous study (Đorđević et al. 2021) we have identified primary and secondary mineralogy of the technosoils in the central part of Allchar deposit. As the main primary Tl-sources we have identified sulfosalts fangite, lorándite and pierrotite. Tl dissolved during weathering under circumneutral conditions is reprecipitated as avicennite and as tiny, fibrous Tl-bearing Mn oxides (up to 8.5 at.% of Tl). Furthermore, tiny spherulitic aggregates (up to 3 µm) of a Tl-Sb-oxide (unknown mineral species) have been found intergrown with quartz, muscovite and minor dolomite. Due to their small aggregate size, we have not been able to closer identify these oxides. Therefore, we have decided to take a closer look at these phases using transmission electron microscopy (TEM). The TEM-lamellae were prepared by means of focused ion beam (FIB) and were investigated under cryogenic condition (–184 °C) using high-resolution scanning transmission microscopy (HR-STEM) coupled with electron dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD). Just after a short electron exposure, Tl_2O_3 crystals in the size up to 100 nm formed on the surfaces of the Tl-Sb-oxides. EBSD on Tl-Sb-oxide particles confirmed that the Tl-Sb-oxide is crystalline and the EDS-line and area scans confirmed Tl:Sb ratio of 2.5, meaning that Tl enters the crystal structure of the new Tl-Sb oxides and is not hosted as the nanophase.

Both nano- and microcrystalline Tl-minerals are important products of oxidative weathering of Tl-bearing metal-sulphides. Our future study focused on the formation and dissolution of these phases will provide a much deeper insight into the mechanisms of formation of specific mineral association and will help to interpret common features in the alteration paths in general.

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