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Tl sequestration in the middle part of the Allchar Sb–As–Tl–Au deposit, North Macedonia

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In geogenic Tl-extreme environments, such as Tl-rich sulfide deposits, secondary Tl minerals play a crucial role in the mobility and fate of this toxic element.

In the middle part of the Allchar Sb–As–Tl–Au deposit, there is a prevalence of Sb mineralization accompanied by As and very minor Tl, Ba, Hg and Au. We used PXRD, SEM-EDS, Raman spectroscopy, pore-water analysis and chemical extractions to determine the distribution and speciation of Tl in the As- and Sb-rich waste dumps and associated soils (As: 3.8-17.7 g/kg; Sb: 0.9-16.4 g/kg and Tl: 127-837 mg/kg). Soil samples and waste-dump material are composed mostly of dolomite, quartz, gypsum, pyrite, marcasite, stibnite, realgar and baryte, followed by muscovite, kaolinite-group minerals and various metal-Sb-oxides. The Tl sulfosalts fangite, lorándite and pierrotite are the primary Tl-sources and are mostly hosted in realgar. Thallium dissolved during weathering under circumneutral conditions is reprecipitated as As-bearing (0.55-6 at.% of As) avicennite, crystallizing in massive aggregates up to 200 μm in length, and as tiny, fibrous Tl-bearing todorokite- or birnessite-type Mn oxides (up to 8.5 at.% of Tl) intergrown with avicennite and dolomite. Furthermore, tiny spherulitic aggregates (up to 3 μm) of a Tl-Sb-oxide (Tl:Sb ~ 3:1) (unknown mineral species) have been found intergrown with quartz, muscovite and minor dolomite. In contrast, thallium dissolved during weathering under acidic conditions (pH ~2.8-3.1) did not reprecipitate at all. In such samples jarosite-group minerals, scorodite, tripuhyite and hydroxycalcioroméite crystallised.

The pore water (pH: 2.8-7.8) contained large aqueous concentrations of Sb (up to 14 mg/l), As (up to 8.5 mg/l) and Tl (up to 464 μg/l). Mild extractions mobilised up to 25% of the total Tl, 3% of the total Sb and 11% of the total As, indicating that a large fraction of Tl is weakly bound and could be easily mobilised into the surrounding ecosystems.

The identification of avicennite, Tl-Mn oxides and Tl-Sb oxides in near-neutral soils points to their stability at near-neutral soil pH and indicates their potential for the immobilisation of toxic Tl in various contaminated environments.

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