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

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

In the middle part of Allchar, there is a prevalence of Sb-mineralization accompanied with As, followed by 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 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 barite, followed by muscovite, kaolinite-group minerals and various Sb-oxides. Tl-sulfosalts fangite, Tl_3AsS_4, lorándite, $TlAsS_2$ and pierrotite, $Tl(Sb,As)_{10}S_{12}$ are the primary Tl-sources and are mostly hosted in realgar. Tl dissolved during weathering under cicumneutral conditions is precipitated as As-beraing avicennite (0.55-6 at% of As), Tl_2O_3, crystallizing in massive aggregates up to 200 μm in length and tiny, fibrous Tl-bearing todorokite- or birnessite-type Mn-oxides (up to 8.5 at% of Tl) intregrown with avicennite and dolomite. Furthermore, sperulitic crystals of tiny (up to 3μm) Tl-Sb-oxides (Tl:Sb ~ 3:1) (unknown mineral species) have been found intergrown with quartz, muscovite and minor dolomite. Thallium dissolved during weathering under acidic conditions (pH ~2.8-3.1) didn't precipitate at all. In these samples jarosite-group minerals, scorodite, tripuhyite and oxycalcioroméite have been formed.

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 (ammonium nitrate and phosphate) mobilized up to xx% of the total Tl, xx% of the total Sb and xx% of the total As, indicating that large fraction of Tl is weakly bound and could be easily mobilized 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 storage and preservation of toxic Tl in mine wastes and contaminated environments.

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