

Mobility of Tl and Hg in the As-rich waste dumps of adit no. 25, former Allchar mine, North Macedonia

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In the northern part of the As–Sb–Tl–Au Allchar deposit, there is a prevalence of As–Tl mineralization accompanied with minor Sb and Hg. We used PXRD, SEM-EDS, EMPA, Raman spectroscopy, pore-water analysis, and chemical extractions to determine the distribution and speciation of Tl and Hg in the As-rich waste dumps of adit no. 25.

The As- and Tl-rich waste material (As: 0.48–14.7 wt.%; Tl: 0.02–1.44 wt.%) is mostly composed of orpiment, quartz, realgar, and scorodite, followed by gypsum and kaolinite-group minerals. The Tl–As sulfosalts lorandite, fangite, and raguinite are the primary Tl-sources and are mostly hosted in orpiment or realgar. The Hg–Tl–As(–Sb) sulfosalts vrbaite, simonite, and christite are the primary sources of both Tl and Hg. After leaching of Tl, As, and Sb from the latter, Hg immediately reacts to form fine-grained cinnabar. This secondary cinnabar and its oxidation products form thin alteration rims (< 10–15 μm) around the affected sulfosalt grains. The most common Tl-bearing precipitate is dorallcharite [TlFe³⁺₃(SO₄)₂(OH)₆]. Its tiny crystals and spherulitic aggregates are often embedded in P-bearing (up to 2 at.%) scorodite. Tl is also accumulated in Mn oxides (up to 5 at.%) and thalliumpharmacosiderite.

The pore water (pH: 2.6–8.1) shows high concentrations of Tl (up to 55 mg·L⁻¹) and As (up to 213 mg·L⁻¹). Mild extractions (ammonium nitrate and phosphate) mobilized up to 54% of the total Tl and 12% of the total As, indicating that large amounts of Tl are weakly bound and could be easily mobilized into the surrounding ecosystems.

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