Thallium mobility in mining wastes at the Crven Dol locality, Allchar deposit, North Macedonia

Tamara Đorđević1, Uwe Kolitsch1,2, Petr Drahota3, Magdaléna Knappová3, Juraj Majzlan4, Stefan Kiefer5, Tomáš Mikuš5, Goran Tasev6, Todor Serafimovski6, Ivan Boev6, and Blažo Boev6

1Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 14, A-1090 Wien, Austria
2Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria
3Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic
4Institute of Geosciences, Department of Mineralogy, Friedrich-Schiller-Universität, Carl-Zeiss-Promenade 10, 07745 Jena, Germany
5Earth Science Institute, Slovak Academy of Sciences, Geological Division, Ďumbierska 1, 974 01 Banská Bystrica, Slovakia
6Department of Mineral Deposits, Faculty of Natural Sciences, University “Goce Delčev”-Štip, Goce Delčev 89, 2000 Štip, North Macedonia

In order to better understand the environmental behaviour of thallium, we have chosen the abandoned As–Sb–Tl–Au Allchar deposit (North Macedonia) with unique mineral composition and high thallium grades of the ore. We used pore water analyses, selective extractions, single-crystal and powder X-ray diffraction (PXRD), SEM-EDS, electron microprobe analysis (EMPA), and Raman spectroscopy to determine the distribution and speciation of thallium in waste dump material at the Tl-rich Crven Dol locality in the northern part of the Allchar deposit.

PXRD studies showed that the various solid waste samples are comprised mostly of carbonates (dolomite and calcite), gypsum, quartz, muscovite, kaolinite-group minerals followed by orpiment, realgar, pyrite, marcasite, lorandite, and various iron and calcium arsenates and iron (hydro)oxides, both amorphous and crystalline. Raman spectra, SEM-EDS and EMPA also showed the presence of Ca-Fe-, Ca-Mn-, and Ca-Mg-arsenates.

The main primary source of Tl in the waste is lorandite (TlAsS₂), which occurs as prismatic crystals and anhedral grains up to 1 mm and is frequently intergrown with realgar. Other Tl sources, included in either realgar or orpiment, are minor Tl sulphosalts such as fangite (Tl₂AsS₄), raguinite (TlFeS₃), picotpaulite (TlFe₂S₃) and jankovičite (Tl₂Sb₄(As,Sb)₄S₂₂). The Tl dissolved during weathering is precipitated as micaceous subparallel crystals of poorly crystalline to amorphous thallium arsenates (representing previously unknown mineral species), forming porous aggregates up to 100 µm. These Tl arsenates are intergrown with dolomite and Ca-Fe-arsenates and appear as two chemically different phases. The first, more common phase shows a variable Tl:As ratio ranging from ca. 2.1 to 4.1 and a variable Ca content (2.2 to 4.1 at.%). In the second, Tl-richer phase, the Tl:As ratio varies from ca. 5.1 to 8.4. Raman spectra of the Tl arsenates display broad bands and may be divided in the fingerprint region into two relevant ranges, 350–600 and 700–900 cm⁻¹, both
attributed to arsenate tetrahedral complexes showing As–O(X) symmetric stretching with X = H+ or H2O.

Another relatively common Tl precipitate is dorallcharite [TlFe3+(SO4)2(OH)6], crystallizing in the form of tiny, well-formed platelets that are grouped into aggregates up to 400 µm in size. Tl is also accumulated in (probably cryptomelane-type) Mn oxides (up to 3.6 at.%), pharmacosiderite (up to 0.9 at.%), and jarosite (up to 0.9 at.%).

The pore water contained high aqueous concentrations of Tl (up to 660 μg·L⁻¹) and As (up to 196 mg·L⁻¹). Although these concentrations are low with respect to their total concentrations in the solid phase (Tl: 0.07-1.44 wt. %; As: 0.72-8.67 wt. %), mild extractions (ammonium nitrate and phosphate) mobilized up to 44% of the total Tl and 23% of the total As, indicating that a large amount of these toxic elements is bound weakly (sorption) to solids and can be easily mobilized into the pore water.

Financial support of the Austrian Science Fund (FWF) [P 30900-N28] is gratefully acknowledged.