Synchrotron-based X-ray spectroscopy study of thallium partitioning and retention in metal-sulfide deposits

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ABSTRACT

Technosols near the former Sb-As-Tl-Au Allchar mine in North Macedonia formed on Tl- and Sb-rich sulfidic mining wastes. Thallium (Tl) contents in these soils can reach up to 17,000 mg/kg (Đorđević et al., 2021). At these high contents, Tl is primarily retained in secondary Tl minerals, both as monovalent Tl(I) and trivalent Tl(III).

In this study, we characterized the distribution and speciation of Tl in antimony (Sb) and manganese (Mn) oxides found in technosols from the central part of the Allchar deposit, using nano-focused X-ray fluorescence (nano-XRF) and X-ray absorption spectroscopy (nano-XAS) at the I14 beamline at the Diamond Light Source (DLS, UK). Because both Tl and Mn are susceptible to X-ray induced speciation changes, chemical imaging was performed using the sparse XANES mode available at I14 to minimize sample exposure to X-rays (Townsend at al., 2022). Data obtained via this approach did not reveal marked changes in Tl or Mn oxidation state over the course of sample analysis, indicative of only minor X-ray-induced artifacts. Averaged XANES spectra over homogeneous sample regions were extracted for analysis by linear combination fitting using Tl or Mn reference spectra.

Preliminary analyses indicated that Tl was primarily Tl(I) in all probed areas, both in low and high Mn regions that correspond to Sb- and Mn-oxides, and irrespective of local variations in Tl loading. With respect to Tl in technosols and mining wastes, this study provides spectroscopic evidence for the importance of Tl(I)-bearing Mn- and Sb-oxides and indicates the need for further studies on the structure and reactivity of these oxides.

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