X-ray spectroscopic characterization of As(V)-rich Tl(III)-particles in a weathered Tl-As-Fe-sulfide mineralization

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Thallium is a highly toxic trace metal of growing environmental concern. In Erzmatt (Swiss Jura mountains) soils were found to contain high levels of Tl and As due to their formation from carbonate rock hosting a weathered hydrothermal Tl-As-Fe mineralization. Although Tl in this site was constrained to a limited area, it is ideally suited to study the long-term transformation of Tl at contaminated sites and its speciation in soils.

In a previous study, the Erzmatt soils were found to contain Tl^{I}-substituted jarosite and avicennite ($Tl^{III}_2O_3$) as important secondary Tl-bearing minerals [1]. The dominant soil-formed Tl species was Tl^{I} associated with illite. Elevated levels of Tl^{III} were associated with soil Mn concretions, but accounted for only a minor fraction of total soil Tl. Circumstantial evidence suggested that another unidentified Tl^{III}-rich phase is present in the Erzmatt soils.

In continuing work, we identified and characterized the unknown Tl^{III}-rich phase by examining soil and rock thin sections as well as individual particles isolated from soil and rock combining laboratory X-ray fluorescence spectrometry (XRF) and X-ray diffraction (XRD) with synchrotron-based bulk X-ray absorption spectroscopy (XAS) and micro-resolved XRF/XRD tomography.

Our results suggest that the composition of the Tl-rich particles corresponds to Tl_2O_3 with up to 0.25 As(V)/Tl. Extended X-ray absorption fine structure (EXAFS) spectra in combination with XRD data suggest that the As^{V}-rich $Tl^{III}_2O_3$ grains are amorphous or nanocrystalline precursors of crystalline avicennite. We speculate that these particles form by the oxidation of Tl-As sulfide minerals such as lorandite ($TlAsS_2$) or ellisite (Tl_3AsS_4) and that the As^{V} inhibits the crystallization of Tl_2O_3 into avicennite.

Avicennite and As^{V}-rich Tl_2O_3 particles in the Erzmatt soils are coated with Mn-oxides that we identified as layered MnO_2, possibly in association with a tectomanganate. The MnO_2-crusts contain up to 0.2 Tl/Mn as Tl(I) and may have formed via a redox reaction between dissolved Mn^{2+} and Tl^{III}.

The results from this work provide new insights into the processes that control the release of Tl from Tl-bearing sulfide minerals and the sequestration of Tl in soils, and are relevant with respect to the assessment of risks arising from geogenically and anthropogenically Tl-contaminated sites.

REFERENCES

1. Voegelin, A.; Pfenninger, N.; Petrikis, J.; Majzlan, J.; Plotze, M.; Senn, A. C.; Mangold, S.; Steininger, R.; Gottlicher, J., Thallium speciation and extractability in a thallium- and arsenic-rich soil developed from mineralized carbonate rock. Environ Sci Technol 2015, 49, 5390-5398.