ROBL-CRG	**Experiment title:** **Chemical speciation of metals in shooting-range soils**	**Experiment number**: **20-01-622**
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Names and affiliations of applicants (* indicates experimentalists):

A. SCHEINOST[1]*, CH. HENNIG[1]*, D. VANTELON[2]*, I. XIFRA[2]*

[1]Institute of Radiochemistry, FZD, Dresden, Germany
[2]Department of Environmental Sciences, ETH Zurich, Switzerland

Report:

Scheinost, A. C., Rossberg, A., Vantelon, D., Xifra, I., Kretzschmar, R., Funke, H., and Johnson, C. A. (2006). Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* **70**, 3299-3312.

Abstract: The Sb speciation in soil samples from Swiss shooting ranges was determined using Sb K-edge X-ray Absorption Spectroscopy (XAS) and advanced statistical data analysis methods (Iterative Transformation Factor Analysis, ITFA). The XAS analysis was supported by a spectral data set of 13 Sb minerals and 4 sorption complexes. In spite of a high variability in geology, soil pH (3.1 – 7.5), Sb concentrations (1000 – 17000 mg/kg) and shooting range history, only two Sb species were identified. In the first species, Sb is surrounded solely by other Sb atoms at radial distances of 2.90, 3.35, 4.30 and 4.51 Å, indicative of metallic Sb(0). While part of this Sb(0) may be hosted by unweathered bullet fragments consisting of PbSb alloy, Pb L_{III}-edge XAS of the soil with the highest fraction (0.75) of Sb(0) showed no metallic Pb, but only Pb^{2+} bound to soil organic matter. This suggests a preferential oxidation of Pb in the alloy, driven by the higher standard reduction potential of Sb. In the second species, Sb is coordinated to 6 O atoms at a distance of 1.98 Å, indicative of Sb(V). This oxidation state is further supported by an edge energy of 30496-30497 eV for the soil samples with < 10 % Sb(0). Iron atoms at radial distances of 3.10 and 3.56 Å from Sb atoms are in line with edge-sharing and bidentate corner-sharing linkages between $Sb(O,OH)_6$ and $Fe(O,OH)_6$ octahedra. While similar structural units exist in tripuhyite, the absence of Sb neighbors contradicts formation of this Fe antimonate. Hence the second species most likely consists of inner-sphere sorption complexes on Fe oxides, with edge and corner-sharing configuration occurring simultaneously. This pentavalent Sb

species was present in all samples, suggesting that it is the prevailing species after weathering of metallic Sb(0) in oxic soils. No indication of Sb(III) was found.

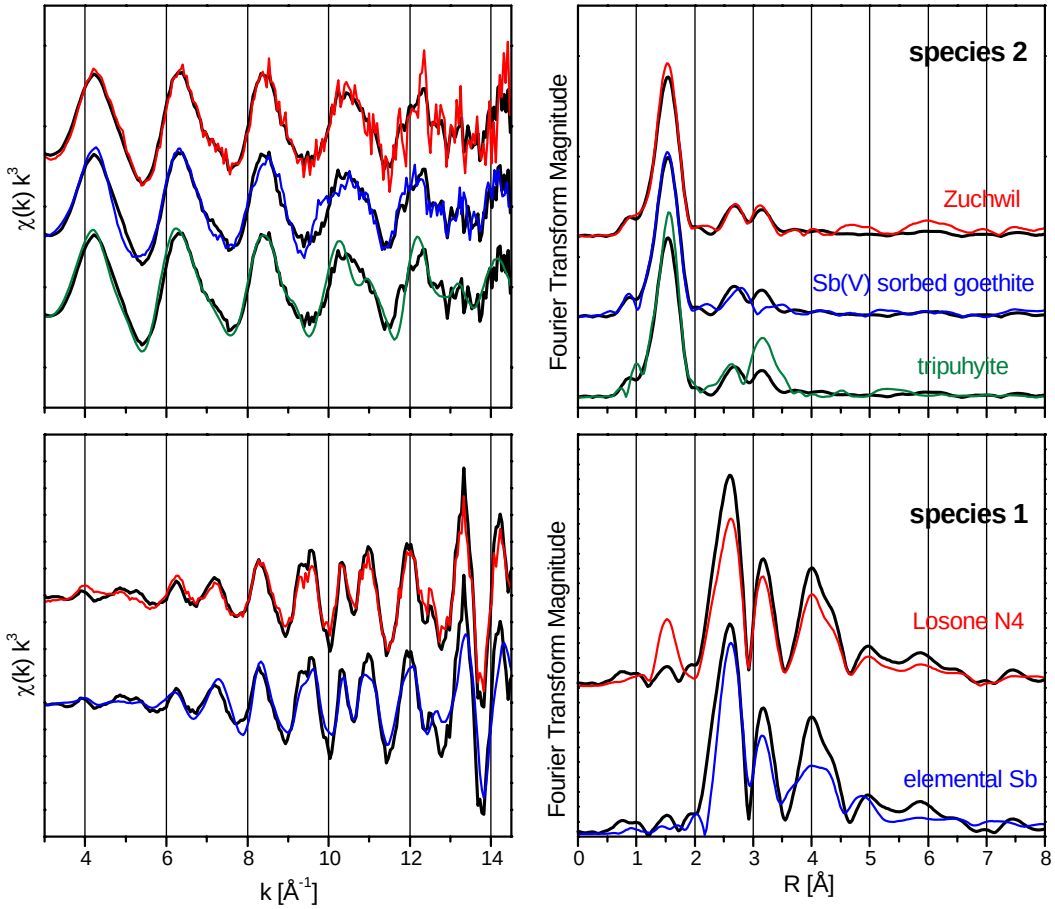

Fig. 1. ITFA-derived Sb K-edge EXAFS spectra of the two Sb species in the soil samples (black lines). For comparison are shown the experimental spectra of the soil samples with the largest fraction of the respective species (red), and of selected reference species (blue and .green lines).

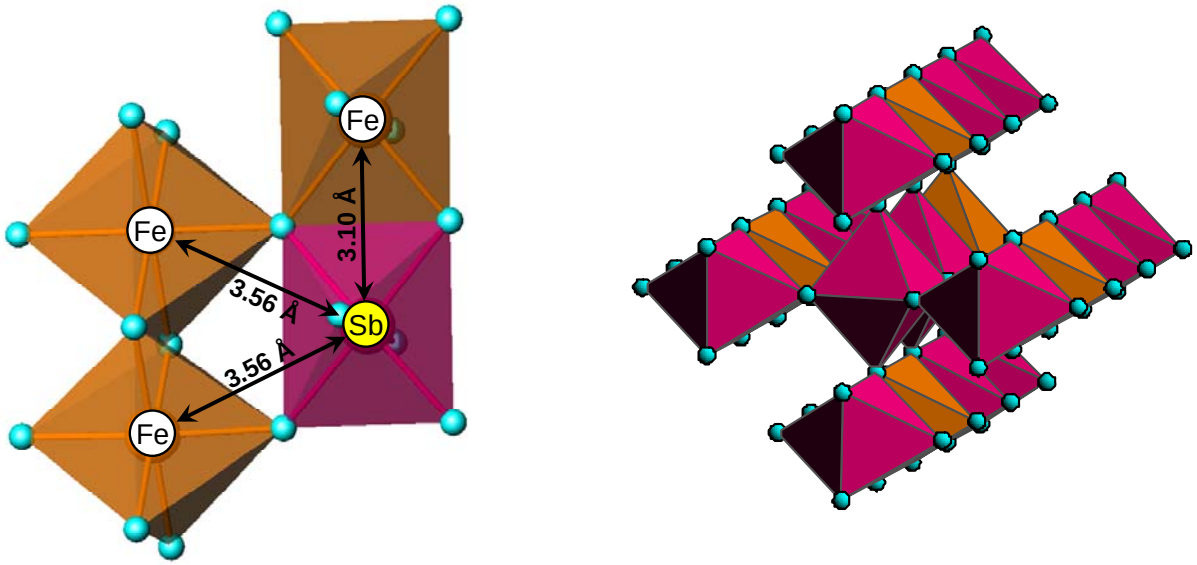

Fig. 2. Structural model of species 2 (left) and of tripuhyite, $Fe^{III}Sb^{V}0_4$ (right). Sb octahedra are shown in pink, Fe octahedra in orange.