

## GEOGENIC THALLIUM-EXTREME ENVIRONMENTS: IN WHICH SECONDARY PHASES IS Tl(I) INCORPORATED?

Dorđević, T.<sup>1</sup>, Drahota, P.<sup>2</sup>, Kolitsch, U.<sup>3,1</sup>, Majzlan, J.<sup>4</sup>, Kiefer, S.<sup>4</sup>, Tepe, N.<sup>5</sup>, Hofmann, T.<sup>5</sup>,  
Serafimovski, T.<sup>6</sup>, Tasev, G.<sup>6</sup>, Boev, I.<sup>6</sup>, Boev, B.<sup>6</sup>

<sup>1</sup>Institut für Mineralogie und Kristallographie, Universität Wien, Althanstraße 14, 1090 Wien, Austria

<sup>2</sup>Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University,  
Albertov 6, 128 43 Prague 2, Czech Republic

<sup>3</sup>Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum, Burgring 7, 1010 Wien, Austria

<sup>4</sup>Institute of Geosciences, Department of Mineralogy, Friedrich-Schiller-Universität, Carl-Zeiss-Promenade 10,  
07745 Jena, Germany

<sup>5</sup>Centre for Microbiology and Environmental Systems Science, University of Vienna,  
Althanstraße 14, 1090 Wien, Austria

<sup>6</sup>Department of Mineral Deposits, Faculty of Natural Sciences, University "Goce Delčev"-Štip,  
Goce Delčev 89, 2000 Štip, North Macedonia  
e-mail: tamara.djordjevic@univie.ac.at

Although the oxidation zones of the majority of naturally Tl-rich localities represent a great threat to surrounding ecosystems, they have not been investigated so far in much detail. Since the remediative treatment of highly Tl-contaminated soils depends on the character of the Tl-bearing phases, it is necessary to fully characterize Tl retention through secondary minerals in affected areas, in order to build a sound basis for successful remediation.

In this study we identified Tl reservoirs in waste dumps and soils of the naturally thallium richest locality in the world, the Crven Dol locality (Tl-As-Sb-Au Allchar deposit, North Macedonia). Tl speciation differs to a certain extent from that observed in similar localities, and is reflected by a very well-developed secondary mineralogy. Thallium dissolved during weathering is precipitated mostly as novel poorly crystalline to amorphous thallium arsenates or as dorallcharite (Tl-Fe sulfate). In traces, Tl also appears as a nano-sized Tl(I) oxide (Tl<sub>2</sub>O) and as thalliumpharmacosiderite (Tl-Fe arsenate). Furthermore, Tl is accumulated in supergene Mn oxides, pharmacosiderite, and jarosite.

Pore waters contain high aqueous concentrations of Tl (up to 660 µg/L) and As (up to 196 mg/L). 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 mobilized up to 44 % of the total Tl and 23 % of the total As, indicating that a large amount of these toxic elements is only bound weakly (sorption) to solids and can be easily mobilized.

In general, in soil horizons lacking secondary Tl-bearing minerals, Tl(I) adsorption onto micaceous phyllosilicates (mostly illite), followed by Tl(I) and Tl(III) adsorption onto Mn oxides has previously been identified as the dominant Tl retention mechanism (WICK et al., 2018, 2019 and references therein). However, in Tl-extreme environments, when illite and Mn oxides are either absent or exhausted, discrete secondary Tl minerals form and store Tl.

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WICK, S., BAEYENS, B., FERNADES, M.M., VOEGELIN, A. (2018): *Environ. Sci. Technol.*, 52, 571-580.

WICK, S., PEÑA, J., VOEGELIN, A. (2019): *Environ. Sci. Technol.*, 53, 13168-13178.