

## Biogenic formation of realgar in the shallow subsurface soil

PETR DRAHOTA<sup>1</sup>, LUKÁŠ FALTEISEK<sup>1</sup>,  
VOJTĚCH DUCHOSLAV<sup>1</sup>, KAREL ŽÁK<sup>2</sup> AND VÍT PENÍŽEK<sup>3</sup>

<sup>1</sup>Faculty of Science, Charles University in Prague, Czech Republic

<sup>2</sup>Institute of Geology of the ASCR, Prague, Czech Republic

<sup>3</sup>Faculty of Agrobiolgy, Food and Natural Resources, Czech University of Life Sciences, Prague, Czech Republic

The origin of many low-temperature metal sulfides has been the topic of numerous prior studies. Given the dramatic inhibition of thermochemical sulfate reduction at low temperatures, the potential role of microorganisms in sulfide mineralization has been proposed [1]. In this study, we have identified macroscopic realgar ( $\alpha$ -As<sub>4</sub>S<sub>4</sub>) deposits in a naturally As-enriched wetland soil located at the Mokrsko Geochemical Anomaly (Czech Republic). Distribution of the elements in the soil profiles showed distinct accumulation of As (up to 2.21 wt.%), S (up to 0.91 wt.%), and C<sub>org</sub> (up to 19.4 wt.%) in the shallow subsurface (60-80 cm). In this slightly alkaline, anoxic to suboxic environment ( $E_h$ : -56 to 157 mV; pH: 7.1-8.0) arsenic sulfide occurs as aggregates of nanocrystalline realgar crystallites (mean dimension: 76 nm) associated with particulate organic matter (roots, organic aggregates, etc.). Realgar is depleted in <sup>34</sup>S ( $\delta^{34}\text{S}_{\text{realgar}}$ : -11.23 ‰) by 15.6-17.4 per mill compared to aqueous sulfate, the oxidized sulfur source for biological reduction supplied to the wetland. Extraction of microbial community DNA from wetland samples yielded diverse PCR amplicons from dissimilatory sulfate reductase (*dsrB*) genes [2], indicating varied bacterial taxa capable of reducing forms of oxidized sulfur. Results of this preliminary investigation consistently support the biogenesis of realgar in the wetland. Our findings also provide insight into the conditions necessary to promote the immobilization of As in engineered systems for the treatment of mine drainage and wastewater effluents.

[1] Pósfai and Dunin-Borkowski (2006) *Rev. Mineral. Geochem.* **61**, 679-714. [2] Drahota *et al.* (2013) *Environ. Pollut.* **180**, 84-91.