

Silver accumulation in macrofungi

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Fungi are intimately involved in the cycling of elements and transformations of both organic and inorganic substrates [1]. Despite the Ag content in soils being very low, Ag concentrations in macrofungal fruit-bodies commonly reach units or tens of mg kg⁻¹ (dry mass). In general, saprobic species are more efficient Ag-accumulators than ectomycorrhizal species. High Ag contents (up to hundreds of mg kg⁻¹) are found in macrofungi from Ag-polluted areas. Recently, hyperaccumulation of Ag by two European *Amanita* species was found [2]; the highest reported Ag content was 1253 mg kg⁻¹. Whereas metal-hyperaccumulating plants typically grow on substrates with high levels of accumulated elements such as serpentinites, Ag-hyperaccumulating macrofungi are found in non-metalliferous unpolluted areas. The mechanism and importance of the accumulation process itself are unknown. However, the importance of Ag hyperaccumulation might be attributed to the “defense hypothesis” [3]. The majority of fruit-body Ag was present in complexes of molecular weight of 7 and 3 kDa composed of sulfhydryl-containing low molecular weight peptides. Obviously, macrofungi play a significant role in mobilization and redistribution of Ag and Au [4] in soils.

[1] Gadd (2007) *Mycol. Res.* **111**, 3-49. [2] Borovička *et al.* (2007) *Mycol. Res.* **111**, 1339-1344. [3] Boyd (2007) *Plant Soil* **293**, 153-176. [4] Borovička *et al.* (2005) *Mycol. Res.* **109**, 951-955.

Isotopic fractionation of Cu and Zn during adsorption onto bacterial surfaces

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The distribution, cycling, and fate of metals in nature can be impacted by complexation reactions with organic-acid functional groups on bacterial surfaces. The stable isotopes of metals like Cu and Zn may be fractionated during these interactions, and if so, the fractionation factors for these reactions need to be quantified to properly interpret Cu and Zn isotopic signatures in natural systems. Moreover, Cu and Zn isotopes could be used as a tool to gain new insights into the chemical nature of bacterial surface-metal complexation.

Bacterial surface adsorption experiments were conducted with Cu and Zn. Samples for isotopic analysis were collected as a function of the fraction of metal adsorbed, which increased with increasing pH. Samples were centrifuged, filtered (0.1µm) and processed using anion-exchange column chemistry to isolate Cu and Zn for isotopic analysis. Isotopic measurements for ^{65/63}Cu and ^{66/64}Zn were conducted using a MC-ICP-MS, and are reported in delta notation relative to the SRM-976 (Cu) and JMC-3-0749-L (Zn) reference materials (also passed through the ion exchange column chemistry).

Bacterial-surface complexes preferentially incorporated the heavier Cu and Zn isotopes, leaving the solution enriched in the lighter isotopes by 0.6‰ and 0.5‰, respectively. Isotopic changes progressed linearly as a function of the total metal adsorbed, which is suggestive of a reversible, equilibrium fractionation process. The apparent fractionation factors ($\alpha_{\text{solution-bacteria}}$) were 0.9994 ± 0.0001 and 0.99951 ± 0.00014 for Cu and Zn, respectively. The magnitudes and directions of isotopic fractionation for bacterial-surface complexation are similar to those recently described for Cu and Zn adsorption onto ferrihydrite. This may provide some insight into the relative bonding strengths in these environments. Our results suggest that metal complexation with organic-acid functional groups on bacterial surfaces should be considered when interpreting the metal isotopic record in near-surface geologic environments. This is a particularly important finding if one considers that bacterial surface interactions are often a precursor for other processes such as mineral precipitation or metabolic uptake.