

Elemental and Mg-Cu-Zn isotopic features of bay bolete (*Imleria badia*) mushrooms collected over the extended period from the contrasting substrates

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Mushrooms may serve as a determinant of environmental response to various extreme events on both elemental and isotopic levels. We studied elemental and Mg-Cu-Zn isotope compositions of the *I. badia* mushrooms collected during the two consecutive harvesting seasons from three forested sites in the Czech Republic. The sites were almost unpolluted by recent human activities, and are underlain by contrasting bedrock (granite, amphibolite, and serpentinite). Elements such as Ag, Cd, K, P, Rb, S, Se, and Zn were enriched in the mushroom's fruiting bodies relative to substrates of any type. Concentrations of most elements were not site-dependent, with only Ag, As, Rb, and Se concentrations depending on the bedrock composition. No systematic temporal variations were observed for individual elements. Most analyzed elements were distributed unevenly within the mushroom's fruiting bodies, with apical parts enriched in mobile elements. Soils were depleted in the ^{26}Mg isotope ($\delta^{26}\text{Mg} = -0.78$ to -0.30‰) and displayed a wide range of the $\delta^{65}\text{Cu}$ values (-0.85 to $+0.67\text{‰}$). Values of $\delta^{66}\text{Zn}$ were mostly negative for the granite-based soils (-0.33 to $+0.07\text{‰}$), positive for the amphibolite-based soils ($+0.03$ to $+0.12\text{‰}$), and slightly deviated from zero for the serpentinite-based soils (-0.09 to $+0.09\text{‰}$). The studied mushrooms fractionated isotopes of Mg, Cu, and Zn both at the soil-to-mushroom interface and within the fruiting bodies. Mushrooms preferably uptake lighter Mg isotopes ($\Delta^{26}\text{Mg}_{\text{mushroom-soil}} = -0.19$ to -0.79‰), heavier Zn isotopes ($\Delta^{66}\text{Zn}_{\text{mushroom-soil}} = +0.43$ to $+0.61\text{‰}$), and both lighter and heavier Cu isotopes ($\Delta^{65}\text{Cu}_{\text{mushroom-soil}} = -0.33$ to $+0.60\text{‰}$). For copper, significant isotope fractionation on the soil-to-mushroom interface could be explained by redox reactions, both reduction (negative fractionation) and reoxidation (positive fractionation). Isotope fractionation of Mg (only negative) and Zn (only positive) can be due to preferable incorporation of the heavier Zn and lighter Mg isotopes mobilized from the substrate. The mushroom samples were characterized mostly by the $\delta^{26}\text{Mg}_{\text{stipe}} < \delta^{26}\text{Mg}_{\text{cap}} < \delta^{26}\text{Mg}_{\text{sporophore}}$ and $\delta^{65}\text{Cu}_{\text{stipe}} > \delta^{65}\text{Cu}_{\text{cap}} > \delta^{65}\text{Cu}_{\text{sporophore}}$ isotope fractionation schemes whereas Zn always displayed a $\delta^{66}\text{Zn}_{\text{stipe}} > \delta^{66}\text{Zn}_{\text{cap}} < \delta^{66}\text{Zn}_{\text{sporophore}}$ isotope fractionation scheme. Within-mushroom isotope fractionation was not season- or annual-dependent. This study may offer a new perspective for understanding partitioning of elements between biologic and mineral geochemical reservoirs. The studied sites may serve as a reference point for unpolluted environment for further studies dealing with biogeochemical response to various environmental events. Funded by the Czech Geological Survey (Grants # 311040 and 311450).