Gold content of ectomycorrhizal and saprobic macrofungi – an update

J. Borovicka$^{1,2,3}$, Z. Řanda$^2$ and E. Jelínek$^1$

$^1$ Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, CZ-128 43 Prague 2, Czech Republic
$^2$ Nuclear Physics Institute, Academy of Sciences of the Czech Republic, CZ-250 68 Řež near Prague, Czech Republic
$^3$ Czech Mycological Society, Karmelitská 14, CZ-118 00 Prague 1, Czech Republic

E-mail: jan.borovicka@myko.cz

Abstract. Species of macrofungi growing in the wild were collected from non-auriferous and unpolluted areas, and analyzed for gold. In addition, preliminary results of samples originated from an auriferous area are presented. Gold was determined using long-term instrumental neutron activation analysis (INAA). In total, 108 samples, including 49 species of ectomycorrhizal fungi and 30 species of terrestrial saprobes, were examined. The highest concentrations (expressed in dry weight) were found in ectomycorrhizal species Russula nigricans (235 ng g$^{-1}$) and Suillus variegatus (1070 ng g$^{-1}$). Among the saprobic macrofungi, an extraordinary high value 2250 ng g$^{-1}$ was found in Lepiota cf. clypeolaria. Gold content of saprobic macrofungi originated from the auriferous area was obviously higher than that of macrofungi from non-auriferous areas. The highest contents were found in Agaricus silvaticus (4230 ng g$^{-1}$) and in two samples of Lycoperdon perlatum (6955 and 7739 ng g$^{-1}$).

1. Introduction

Macrofungi (commonly called mushrooms) are well-known as accumulators of many trace elements such as various heavy metals (Hg, Cd), metalloids (As, Se) and radionuclides ($^{137}$Cs). Among the noble metals, mushrooms are well-known as accumulators of silver [1-4]. Several authors have formerly reported a few results on gold content of macrofungi [2,4,5]. Results of a large investigation on gold content of macrofungi from non-auriferous and unpolluted areas have been recently published [6].

The aim of this study was to update our knowledge of the gold content of ectomycorrhizal and saprobic macrofungi originated from non-auriferous areas and, in addition, to present preliminary data on gold content in saprobic macrofungi originated from an auriferous area.

2. Materials and methods

Macrofungi were collected in non-auriferous and unpolluted areas (84 samples including 49 ectomycorrhizal and 19 saprobic species). On the other hand, 24 macrofungal samples including 15 species of terrestrial saprobes were collected in the auriferous area in vicinity of Mokrsko deposit (Central Bohemia, Czech Republic). In this area, gold contents in soils are very high and reach lower units of mg kg$^{-1}$ [7]. The macrofungal fruiting bodies were isolated from substrate debris using a
stainless steel or plastic knife, rinsed with distilled water, cut into thin slices, and dried. Drying was initially at room temperature, and later in an oven at 65°C. The analyses were performed on whole fruiting bodies, without discriminating between the different parts. Dry samples were then pulverized and perfectly homogenized. All possible precautions to prevent contamination of the samples were kept.

Gold concentrations were determined using long-term instrumental neutron activation analysis (INAA). Peletized samples with a mass of about 500 mg were analyzed. Irradiation was performed at a nuclear reactor LVR-15 at the Nuclear Research Institute, Rež near Prague plc. at fluence rates of $8 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ and $3 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ for thermal and fast neutrons, respectively. Irradiation time was 2-3 hours, counting was after 10 days of decaying. Gamma-ray spectra of the samples, multielement standards and monitors irradiated by neutrons were measured using several coaxial HPGe detectors with relative efficiency of 20-53%, resolution FWHM 1.8 keV for the 1332.5 keV photons of $^{60}$Co. For gold determination, the gamma line of 411.8 keV of the radionuclide $^{198}$Au was measured. The complete procedure has been described in detail by Řanda & Kučera (2004). Common result uncertainty was in the range of 1–10 %.

3. Results and discussion
According to their ecology, macrofungi were divided to two groups – ectomycorrhizal fungi and terrestrial saprobes. Gold contents (ng g$^{-1}$ of dry weight) of the macrofungal samples from unpolluted and non-auriferous areas belonging to both groups are presented in Tables 1 and 2. Gold content of samples from the auriferous area (including only terrestrial saprobes) is presented in Table 3. The distribution of gold among ectomycorrhizal fungi and terrestrial saprobes based on our results and those of the former study [6] is illustrated in Figure 1.

**Table 1.** Gold content (ng g$^{-1}$ of dry weight) of ectomycorrhizal fungi from non-auriferous and unpolluted areas.

| Sample | Species                | Au  | Sample | Species                | Au  |
|--------|------------------------|-----|--------|------------------------|-----|
| M 163  | *Albatrellus ovinus*   | 9.00| M 186  | *L. subdulcis*         | 131 |
| B 170  | *Amanita ceciliae*     | 5.67| B 177  | *A. echinocephala*     | 10.3|
| B 200  | *A. echinocephala*     | 36.0| B 209  | *A. echinocephala*     | 10.0|
| B 211  | *A. echinocephala*     | 7.67| B 217  | *A. echinocephala*     | 2.90|
| B 218  | *A. echinocephala*     | 11.1| B 158  | *A. pantherina*        | 17.0|
| B 207a | *A. strobliformis*     | 8.38| M 207  | *R. chloroides*        | 12.4|
| B 207b | *A. strobliformis*     | 5.32| B 156  | *R. laurocerasi*       | 3.41|
| M 202  | *A. strobliformis*     | 15.3| M 208  | *R. laurocerasi*       | 14.4|
| M 180  | *Boletinus cavipes*    | 19.3| B 162  | *R. nigricans*         | 9.59|
| M 161  | *Boletus badius*       | 14.7| M 193  | *R. nigricans*         | 235 |
| M 160  | *B. calopus*           | 12.0| M 170  | *R. ochroleuca*        | 12.8|
| M 158  | *B. luridus*           | 15.8| B 157  | *R. queletii*          | 8.84|
| M 182  | *Cantharellus tubaeformis* | 24.4| B 159  | *R. risigallina*       | 3.57|
| M 195  | *Dermocybe semisanguinea* | 65.0| M 207  | *R. subfoetens*        | 13.5|
| M 152  | *Entoloma clypeatum*   | 26.1| B 215a | *R. viscida*           | 5.59|
| M 157  | *Entoloma sp.*         | 31.0| B 215b | *R. viscida*           | 4.14|
| M 179  | *Entoloma sp.*         | 29.0| B 216a | *R. viscida*           | 7.66|
| M 155  | *Hebeloma sp.*         | 22.8| B 216b | *R. viscida*           | 4.17|
| B 192  | *Chalciporus piperatus*| 4.82| B 155  | *R. xerampelina*       | 2.76|
| M 213  | *C. piperatus*         | 76.0| B 187  | *Sarcodon imbricatus*  | 7.32|
| Sample | Species                  | Au  | Sample | Species                  | Au  |
|--------|--------------------------|-----|--------|--------------------------|-----|
| B 164  | Choiromyces venosus      | 3.66| B 186  | Suillus bovinus          | 6.85|
| M 190  | Laccaria amethystina     | 16.3| M 188  | S. bovinus               | 11.3|
| M 154  | Laccaria sp.             | 23.0| B 190  | S. collinitus            | 7.69|
| M 194  | L. aff. proxima          | 12.2| M 189  | S. collinitus            | 27.2|
| B 167  | Lactarius circellatus    | 2.52| M 197  | S. collinitus            | 10.0|
| M 158  | L. hypsinus              | 28.0| B 191  | S. luteus                | 8.89|
| M 162  | L. piperatus             | 9.30| M 191  | S. variegatus            | 1070|
| M 187  | L. quietus               | 13.0| M 167  | Tricholoma album         | 6.30|

**Table 2.** Gold content (ng g⁻¹ of dry weight) of terrestrial saprobes from non-auriferous and unpolluted areas.

| Sample | Species                     | Au  |
|--------|-----------------------------|-----|
| M 173  | Agaricus arvensis           | 44.0|
| M 183  | A. silvaticus               | 20.3|
| M 223  | Clitopilus prunulus         | 18.7|
| M 176  | Collybia asema              | 22.0|
| M 171  | Coprinus comatus            | 57.0|
| B 154  | Geastrum triplex            | 20.6|
| M 177  | Hygrophoropsis aurantiaca   | 18.0|
| M 178  | Hygrophorus postulatus      | 12.0|
| M 166  | Lactomyces velutina         | 6.70|
| B 165  | Leucoagaricus cf. clypeolaria | 4.71 |

| Sample | Species                     | Au  |
|--------|-----------------------------|-----|
| B 34   | Agaricus campestris         | 151 |
| B 91 a | A. campestris               | 162 |
| B 94 a | A. campestris               | 114 |
| B 94 b | A. campestris               | 103 |
| B 94 c | A. campestris               | 137 |
| B 86   | A. silvaticus               | 114 |
| B 49   | Bovista plumbea             | 47.9|
| B 89   | B. plumbea                  | 196 |
| B 96   | B. plumbea                  | 164 |
| B 43   | Calvatia excipuliformis     | 209 |
| B 87   | Clitocybe odora             | 21.6|
| B 113  | Hygrophoropsis aurantiaca   | 14.8|

**Table 3.** Gold content of terrestrial saprobes from the auriferous area Mokrsko (ng g⁻¹ of dry weight).

| Sample | Species                     | Au  |
|--------|-----------------------------|-----|
| B 34   | Agaricus campestris         | 151 |
| B 93 a | Leucoagaricus leucothites   | 69.8|
| B 97   | Leucopaxillus giganteus     | 10.9|
| B 39   | Lycoperdon perlatum         | 6955|
| B 42   | L. perlatum                 | 7739|
| B 37   | L. pyriforme                | 14.5|
| B 46   | Macrolepiota procera       | 277 |
| B 38 a | M. rachodes                | 187 |
| B 38 b | M. rachodes                | 149 |
| B 92   | Mycena epityrgia            | 14.1|
| B 35   | M. pura                    | 11.5|
| B 48   | Vascellum pratense          | 64.3|
| B 90   | V. pratense                | 218 |
Figure 1. Distribution of gold in ectomycorrhizal fungi and terrestrial saprobics from non-auriferous and unpolluted areas. Data based on new results and former study [6].

Results of gold content in macrofungi newly obtained from non-auriferous areas are in a good agreement with formerly published data [2,4,6]. However, extraordinary high gold levels were found in single collection of ectomycorrhizal species *Suillus variegatus* (1070 ng g\(^{-1}\)) and saprobe *Lepiota cf. clypeolaria* (2250 ng g\(^{-1}\)). Surprisingly, low values (< 20 ng g\(^{-1}\)) were determined for other samples of these two species (collected in different sites) as well as during this or previous study [6]. The gold content of macrofungi is known to vary in a large range probably because of a lot of factors which may influence the ability of macrofungi to accumulate Au [6]. However, these two extremely high levels are the highest concentrations ever found in macrofungi growing in non-auriferous area and further investigation on their localities is required.

Figure 2. Distribution of gold in terrestrial saprobic macrofungi from non-auriferous areas (data from Figure 1) and the Mokrsko deposit.

Gold content of saprobic macrofungi found in the auriferous area is very high, mostly above 100 ng g\(^{-1}\). A comparison between saprobic macrofungi growing in non-auriferous and auriferous area is presented in Figure 2. The highest contents were found in *Agaricus silvaticus* (4230 ng g\(^{-1}\)) and in
two samples of *Lycoperdon perlatum* (6955 and 7739 ng g\(^{-1}\)). Au content of saprobic macrofungi growing in auriferous area is much higher than that commonly found in vascular plants from such places (up to tens of ng g\(^{-1}\) [8-10]).

Our results obtained for saprobic macrofungi from Mokrsko are much higher than those formerly reported from an auriferous area [5]. However, these authors investigated only few ectomycorrhizal species and the gold content in the soil profile of the investigated auriferous locality was very low (the maximum total concentration of Au reported by the original authors was approximately 40 ng g\(^{-1}\)).

Speciation of gold in macrofungal fruit bodies and the mechanism of accumulation are unknown.

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