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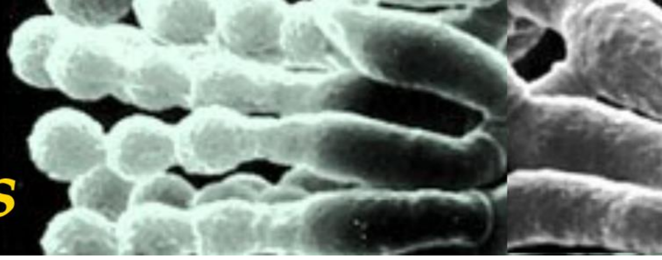

Biorecovery of valuable elements by fungi

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Many important metal resources are threatened by over-exploitation, inadequate recycling and reclamation, and geopolitical issues. Consumption of metals and minerals has increased steadily in recent decades and rising population growth ensures that demand will accelerate. Furthermore, the increasing need for energy production from renewable resources, such as solar and wind power, and energy-efficient electronic materials, including those used in computers, mobile phones and televisions, are highly dependent on a range of valuable metal and mineral resources. Such “E-tech elements” include cobalt, platinum group metals and rare earth elements, as well as metalloids like selenium and tellurium. Some of these elements are already in short supply, can be difficult to recover by conventional mining and extraction, and may be found in only a small number of geographic locations therefore rendering the supply chain vulnerable to economic and political forces. The EU is almost wholly dependent on imported supplies. There is therefore an urgent need to improve the supply of important elements while balancing new mining processes with minimizing environmental impacts such as pollution and increased greenhouse gas emissions. Of the many worldwide initiatives considered to address this problem, microbial bioprocessing is seen as an essential component of the approaches that may be used to improve metal recovery.

The ability of microorganisms to change the chemical state of metals and minerals is of profound significance in the natural environment being part of natural cycles for metals and associated elements in rocks, minerals, and soil. The growing discipline of geomicrobiology encompasses many such aspects of microbial metal and mineral biotransformations. Species from all microbial groups can be involved, with the great metabolic diversity of bacteria and archaea ensuring that these organisms receive considerable research attention. Despite this, appreciation of fungi is growing because of their profound importance in the terrestrial environment and capabilities for many metal and mineral transformations. Many geomycological processes are relevant to natural cycling of elements, rock and mineral transformations, plant productivity and biodeterioration, as well as applications in the context of metal and mineral transformations, bioremediation and element biorecovery.

Fungi are ideally suited as geoactive agents and the vast majority exhibit a branching filamentous explorative lifestyle. They utilize organic substrates for growth and energy and excrete a variety of extracellular enzymes and other substances that interact with organic and inorganic substrates. They can directly and indirectly mediate the formation of many kinds of minerals, including oxides, phosphates, carbonates and oxalates (**Figure 1**), as well as elemental forms of metals and metalloids such as silver (Ag), selenium (Se) and tellurium (Te). Such biomineralization largely depends on the organism modifying its local microenvironment to create appropriate chemical conditions for precipitation to take place, and this depends on their metabolism.

Compared to the simpler bacterial cell form, the filamentous fungal growth habit additionally provides more framework support and stability as a reactive network for biomineralization (**Figure 2**).

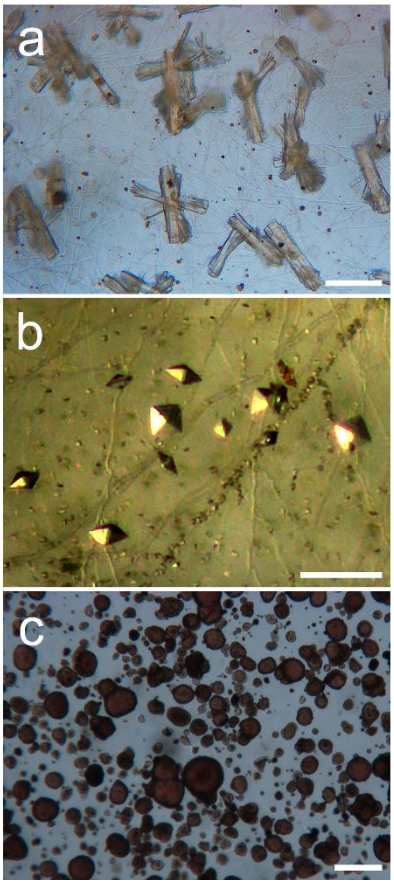

Figure 1. Oxalate mineral formation by fungi. (a) cobalt oxalate formed in cobalt carbonate-amended agar medium by *Aspergillus niger* (Bar = 50 µm). (b) calcium oxalate formed in calcium hydroxide-amended agar medium by *A. niger* (Bar = 100 µm). (c) cobalt carbonate formed in cobalt chloride and urea-amended agar medium by *Neurospora crassa* (Bar = 50 µm).

Fungi are very important biodegraders of organic materials, and this can result in mineral formation where biodegradation products react with available metals. For example, the action of phosphatase enzymes on phosphorus-containing organic substrates results in the release of inorganic phosphate which can then precipitate with available metals. Several filamentous fungi and yeasts can extensively precipitate lead or uranium phosphates on their surfaces during growth on a source of organic phosphorus in the presence of soluble lead (Pb) and uranium (U) (**Figure 3**). Such removal from solution of potentially toxic or radioactive elements is of bioremedial potential. A recent discovery was the fungal-mediated formation of pyromorphite, a highly insoluble lead phosphate, the phosphate arising from both organic and inorganic sources. Similarly, the formation of stable uranium phosphate minerals during fungal growth in the presence of uranium oxides or depleted uranium has also been demonstrated.

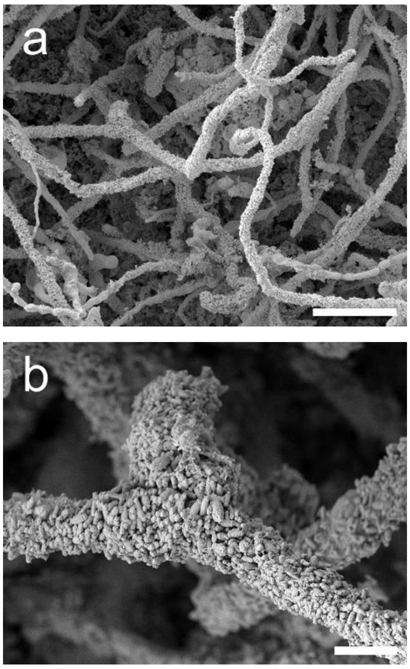

Figure 2. Scanning electron microscopy images of rhodochrosite ($MnCO_3$) precipitation on hyphae of *Neurospora crassa* grown in urea- and $MnCl_2$-amended medium (Bars = 30 and 5 µm, respectively).

Microbially-mediated carbonate precipitation has been used for metal and radionuclide bioremediation, soil stabilization and the reinforcement of concrete. This system also provides a promising method for biorecovery of toxic or valuable metals *e.g*. cobalt (Co), nickel (Ni), and lanthanum (La). Many free-living fungi can degrade urea which results in extensive production of carbonate which will precipitate with any susceptible metals present (**Figure 3**).

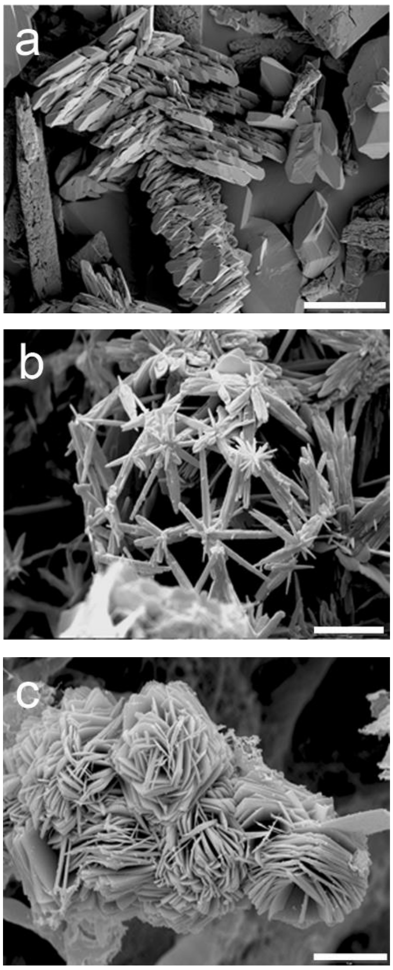

Figure 3. Formation of lead or uranium phosphate minerals after growth of fungi on an organic phosphorus-containing substrate (glycerol 2-phosphate) in the presence of soluble $Pb(NO_3)_2$ or $UO_2(NO_3)_2$. (a) Pb minerals produced by *Aspergillus niger* (Bar = 50 µm) (b) Pb minerals produced by *Paecilomyces javanicus* (Bar = 5 µm) (c) U minerals produced by *A. niger* (Bar = 5 µm).

Biomass-free culture supernatants also have precipitative properties which enables metal biorecovery from solution in pure form. Pure otavite (cadmium carbonate, $CdCO_3$) was recovered in this way, with a proportion of the particles of nanoscale dimensions (**Figure 4**). Fungal isolates from calcareous soil could precipitate calcite ($CaCO_3$) and strontianite ($SrCO_3$) as well as olekminskite ($Sr(Sr,Ca)(CO_3)_2$) and Sr-containing vaterite ($(Ca_xSr_{1-x})CO_3$), resulting in almost complete removal of strontium (Sr) from solution. Metal carbonates have several industrial applications and are also used as precursors for important metal oxides. In an imaginative demonstration, thermal de-composition of fungal biomass and precipitated manganese carbonate ($MnCO_3$) resulted in a carbonized biomass-manganese oxide composite material which was used as electrode material in supercapacitors and lithium ion batteries. This was found to have excellent electrochemical properties in comparison with other Mn oxide materials prepared by abiotic means, and in lithium ion batteries retained ~90% charge capacity after 200 charge-discharge cycles.

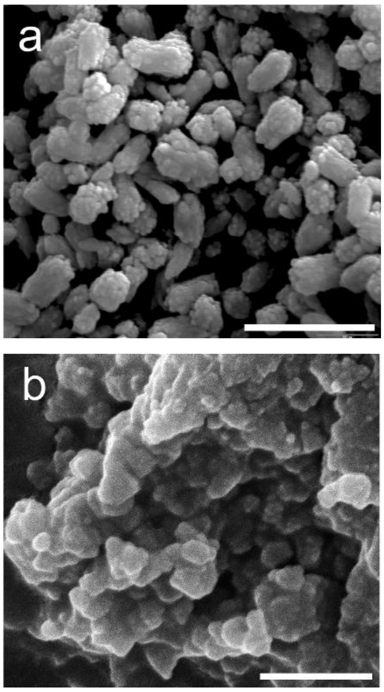

Figure 4. Scanning electron microscopy images of micro- and nanoscale metal carbonate minerals derived by mixture of soluble metal chlorides with fungal growth supernatant obtained after growth of *Neurospora crassa* in urea-amended medium. (a) otavite ($CdCO_3$) (Bar = 1 µm). (b) cobalt carbonate ($CoCO_3$) (Bar = 300 nm).

Metal-containing micro-nanoparticles have a variety of applications. The use of metal-transforming microbes, including fungi, for production of nanoparticles may allow some control over size, morphology, and composition. This is relevant to the production of new advanced biomaterials with applications in metal and radionuclide bioremediation, metal biorecovery, anti-microbial treatments (*e.g.* nano-silver), solar energy, electrical batteries and microelectronics. Many fungi precipitate nano-elemental forms of metals and metalloids through bioreduction, *e.g.* Ag(I) reduction to elemental silver Ag(0); selenate [Se(VI)] and selenite [Se(IV)] to elemental selenium [Se(0)]; tellurite [Te(IV)] to elemental tellurium [Te(0)] (**Figure 5**). Many of the fungal biominerals mentioned previously can be nanoscale or microscale (**Figures 4** & **5**) which imparts additional physical and chemical properties apart from metal sequestration. For example, fungal Mn oxides can sequester metals like Pb, zinc (Zn), Co, Ni, and chromium (Cr) and also oxidize certain organic pollutants. Many fungi produce insoluble metal oxalates on interacting with a variety of different metals and metal-bearing minerals, *e.g.* those of Ca, Cd, Co, copper (Cu), magnesium (Mg), Mn, Sr, Zn, Ni and Pb and these have various industrial uses as well as providing another metal biorecovery mechanism.

As ubiquitous inhabitants of soil and rock surfaces, fungi are engaged in a suite of metal and mineral transformations through such mechanisms as complexation, mineral dissolution and secondary mineral formation. These are also of negative human impact with the same mechanisms being involved in the biodeterioration of rock and mineral-based materials in the built environment and cultural heritage. On the positive side, their interactions with metals and minerals are of applied significance in land bioremediation, revegetation, and detoxification of industrial effluents and waste streams, and an important component of the overall microbial repertoire of mechanisms that are being applied to metal biorecovery and the production of useful biomaterials. With growing concern over the management, conservation and recycling of world metal and mineral resources, it is clear that fungal capabilities may offer potentially useful solutions to an apparently insoluble problem.

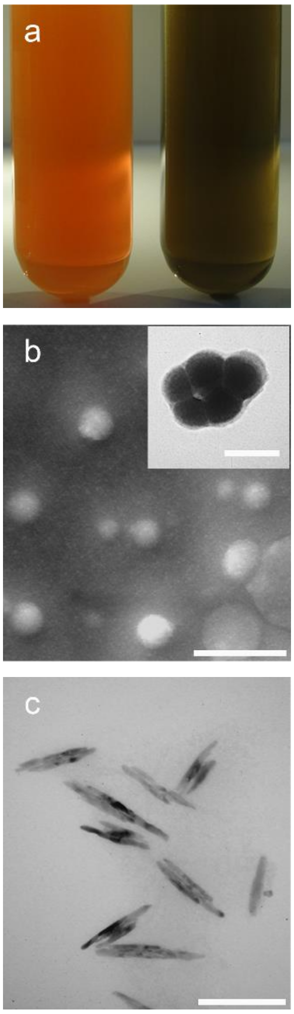

Figure 5. Fungal production of nanoscale metalloids. (a) suspensions of elemental Se (red) and elemental tellurium (black) obtained after reduction of sodium selenite or tellurite by a fungal growth supernatant (b) scanning electron microscopy image of selenium nanoparticles (Bar = 500 nm). The inset is a transmission electron microscopy image of a nanoparticle aggregate (Bar = 200 nm) (c) transmission electron microscopy image of tellurium nanorods (Bar = 400 nm).

Further Reading

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