

Minireview

Geomycology: metals, actinides and biominerals

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Summary

Geomycology can be simply defined as ‘the scientific study of the roles of fungi in processes of fundamental importance to geology’ and the biogeochemical importance of fungi is significant in several key areas. These include nutrient and element cycling, rock and mineral transformations, bioweathering, mycogenic biomineral formation and interactions of fungi with clay minerals and metals. Such processes can occur in aquatic and terrestrial habitats, but it is in the terrestrial environment where fungi probably have the greatest geochemical influence. Of special significance are the mutualistic relationships with phototrophic organisms, lichens (algae, cyanobacteria) and mycorrhizas (plants). Central to many geomycological processes are transformations of metals and minerals, and fungi possess a variety of properties that can effect changes in metal speciation, toxicity and mobility, as well as mineral formation or mineral dissolution or deterioration. Some fungal transformations have beneficial applications in environmental biotechnology, e.g. in metal and radionuclide leaching, recovery, detoxification and bioremediation, and in the production or deposition of biominerals or metallic elements with catalytic or other properties. Metal and mineral transformations may also result in adverse effects when these processes result in spoilage and destruction of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), acid mine drainage and associated metal pollution, biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment. The ubiquity and importance of fungi in

biosphere processes underlines the importance of geomycology as an interdisciplinary subject area within microbiology and mycology.

Introduction

Fungi are ubiquitous chemoorganotrophic (heterotrophic) organisms and their importance as animal and plant symbionts and pathogens, and spoilage organisms of natural and manufactured materials is profound (Gadd, 1993a; 1999; 2006; 2008a; Burford *et al.*, 2003a). However, appreciation of fungi as agents of biogeochemical change is less pronounced and they are frequently neglected within broader geomicrobiological contexts (Gadd, 2008b). While geochemical activities of bacteria and archaea receive considerable attention, especially in relation to carbon-limited and/or anaerobic environments, in aerobic terrestrial environments fungi are of great importance, especially when considering rock surfaces, soil and the plant root-soil interface. For example, mycorrhizal fungi are associated with most plant species and are involved in major redistributions of inorganic nutrients (Fomina and Gadd, 2007; Finlay *et al.*, 2009). Free-living fungi have major roles in the decomposition of plant and other organic materials, including xenobiotics, and therefore in the biogeochemical cycling of all the elements comprising such substances (e.g. C, N, P, S, metals) (Gadd, 2004a; 2007a; 2008a). Lichens commonly inhabit exposed rock (and other) substrates, and play fundamental roles in early stages of rock colonization and mineral soil formation (Haas and Purvis, 2006). Fungi are also major biodeteriorative agents of stone, wood, plaster, cement and other building materials, and important components of rock-inhabiting microbial communities, participating in mineral dissolution and secondary mineral formation (Burford *et al.*, 2003a,b; 2006; Gadd *et al.*, 2005; 2007; Fomina *et al.*, 2005a,b; Gadd, 2007a) (Fig. 1). Fungi also have a role in the maintenance of soil structure due to their predominantly filamentous branching growth habit and frequent exopolymer production (Ritz and Young, 2004). In the aquatic environment, fungi are important decomposers, with evidence of their occurrence and activity even within deep marine sediments (Reitner *et al.*, 2006; Edgcomb *et al.*, 2011).

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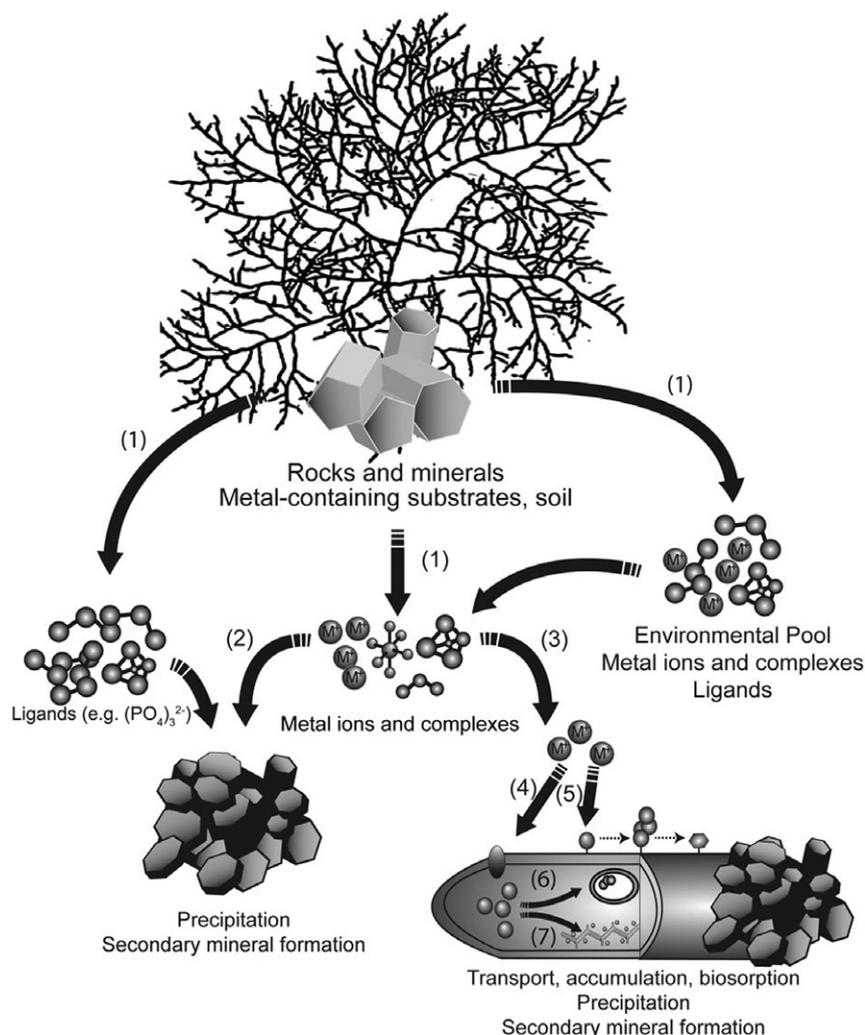


Fig. 1. Simple model of fungal interactions with rocks and minerals, and other metal-containing substrates, that lead to mobilization or immobilization of metals. (1) Fungal physical (e.g. penetration, cleavage) and biochemical activities [e.g. production of inorganic and organic metabolites, e.g. H^+ , CO_2 , organic acids, siderophores, phenolic compounds, amino acids; reductive dissolution] mobilize metal ions, complexes and associated elements and ligands (e.g. $PO_4)_3^{2-}$]. Such activities will contribute to the environmental pool of such substances. (2) Interaction of mobilized metal species with released ligands or those in environmental pools result in precipitation and formation of secondary minerals that can include oxalates, phosphates, carbonates. (3) Mobile metal ions and other species can be taken up by fungal biomass by (4) specific and non-specific transport processes and (5) surface association (e.g. biosorption to cell wall components, such as chitin, melanin, glucans or extracellular materials, such as polysaccharides), which can result in nucleation and deposition of mineral phases; mineral phases, including clays, can also be 'sorbed' by fungal biomass, while mineral deposition may also be enhanced by metabolite excretion and redox reactions. Intracellular metals may be localized within vacuolar compartments (6) or sequestered by metal-binding peptides, such as metallothioneins or phytochelatins, or other molecules (7). A variety of other specific and non-specific interactions may also occur which are not shown here (see also Gadd, 2007a; 2008a, 2010; fungal colony image taken by Karl Ritz).

This article outlines some important fungal roles and functions in rock, mineral, metal and soil transformations, and will emphasize the importance of fungi as agents of geochemical change, and the applied significance of these processes in environmental biotechnology. Such roles can all be included under the term 'geomycology', which can be simply defined as 'the scientific study of the roles of fungi in processes of fundamental importance to geology' (Gadd, 2007a; 2011). This includes such topics as the alteration and weathering of rocks and minerals, soil formation, the transformation and accumulation of metals, decomposition

and nutrient cycling. The decomposition of organic substances can be included under the heading of 'geomycology' since this results in major geochemical cycling of elements in the biosphere, with the metabolism of organic compounds underpinning all fungal activities and interactions with environmental components. 'Geomycology' can be considered to be a subset of 'geomicrobiology', namely the roles of microorganisms in geological and geochemical processes (Ehrlich and Newman, 2009; Gadd, 2010). A variety of inorganic or organic products of fungal metabolism can serve as chemical reagents in reactions such as

metal precipitation, metal solubilization, mineral weathering and dissolution while biophysical and biomechanical effects on the substratum may ensue from the fungal branching filamentous growth form (Burford *et al.*, 2003a; Gadd, 2007a). While the majority of processes discussed pertain to the terrestrial environment, it should be noted that the same processes may also occur in aquatic environments and sediments, though their significance may be different as well as being influenced strongly by spatial and environmental factors.

Fungal processes influenced by minerals

Many important microbial processes can be influenced by minerals including energy generation, nutrient acquisition, cell adhesion and biofilm formation (Brown *et al.*, 2008). Essential nutrients may be acquired from mineral surfaces, e.g. C, N, P, Fe, essential metals, and various organic compounds (Vaughan *et al.*, 2002). Environmental contaminants, including metals, may also be sorbed to mineral surfaces and these can be displaced by fungal activity (Kraemer *et al.*, 1999; Huang *et al.*, 2004; Chorover *et al.*, 2007; Theng and Yuan, 2008). Potentially toxic metals released from minerals as a result of physicochemical and biological processes may in turn affect microbial communities (Gadd, 2005; Fomina *et al.*, 2005c). Such properties of mineral surfaces as microtopography, surface composition, surface charge and hydrophobicity play an important role in thigmotropism, microbial attachment and detachment, and are therefore critical for colonization and biofilm formation, and the ecology of microbial populations associated with mineral substrates (Vaughan *et al.*, 2002; Gleeson *et al.*, 2005; 2006, 2007; 2010; Bowen *et al.*, 2007a,b; Brown *et al.*, 2008; Hutchens, 2009).

Mineral transformations

Fungi are involved in the formation and deterioration of minerals, including those produced biogenically. The majority of such interactions are probably accompanied by changes in metal speciation and mobility, especially when metals are a component of the interacting mineral, or are present in the cellular microenvironment.

Mineral formation

Biomineralization refers to the processes by which organisms form minerals and is usually categorized into biologically-induced mineralization (BIM) and biologically-controlled mineralization (BCM). Biologically-induced mineralization is where an organism modifies the local microenvironment creating conditions that favour extracellular chemical precipitation of mineral phases. The organism does not appear to control the biomineralization

process in BIM while a great degree of control over biomineralization is exerted in BCM, e.g. complex cellular biomineral structures in certain eukaryotes (Gadd and Raven, 2010). Fungal biomineralization examples therefore usually refer to biologically-induced mineralization. This can result from oxidation or reduction of a metal species, and metabolite excretion, e.g. CO₂, oxalate (Figs 1–4). It can also result from organic matter decomposition where released substances re-precipitate with metals in the microenvironment and *vice versa*, with fungal surfaces providing reactive sites for sorption (\equiv biosorption), which can also lead to nucleation and formation of mineral precipitates (Lloyd *et al.*, 2008; Gadd, 2009a; 2010). Fungi have especially important roles in the terrestrial environment regarding mineral dissolution, metal and anion cycling, and also mineral formation by free-living and symbiotic forms (see later), which can occur through metabolism-independent and -dependent processes (Gadd, 2007a; 2008a). Precipitation, nucleation and deposition of crystalline material on and within cell walls are influenced by factors such as pH and wall composition. Cationic species of Si(IV), Fe(III), Al(III) and Ca(II), which may be released through dissolution mechanisms, stimulate precipitation of compounds that may bond soil particles: precipitation of carbonates, phosphates and hydroxides increases soil aggregation. Hyphae and associated exopolymeric material can also enmesh soil particles, and also release organic metabolites that enhance aggregate stability (Bronick and Lal, 2005). Apart from the more detailed biomineral examples that follow, a variety of other fungal-associated minerals have been recorded, e.g. birnessite, ferrihydrite, iron gluconate, calcium formate, forsterite, goethite, halloysite, hydrocerussite, todorokite, moolooite, montmorillonite and uranium phosphates (Burford *et al.*, 2003a,b; Fomina *et al.*, 2007a,b; 2008; Gadd, 2007a; 2010; Gadd and Raven, 2010) (Figs 2 and 3).

Mineral biodeterioration

Direct and indirect physical, chemical and biochemical mechanisms are involved in mineral biodeterioration (Sand, 1997; Edwards *et al.*, 2005; Lian *et al.*, 2008) (Fig. 1). Biomechanical deterioration of rocks and minerals can occur through penetration, boring and burrowing into decaying material and along crystal planes in, e.g. calcitic and dolomitic rocks (Sterflinger, 2000; Golubic *et al.*, 2005; Smits, 2006; Gadd, 2007a; Cockell and Herrera, 2008). Cleavage penetration can occur with lichens (Banfield *et al.*, 1999; Adamo and Violante, 2000; Chen *et al.*, 2000). However, biochemical actions are believed to be more important than mechanical degradation. Biochemical weathering of rocks and minerals can occur through excretion of, e.g., H⁺, CO₂,

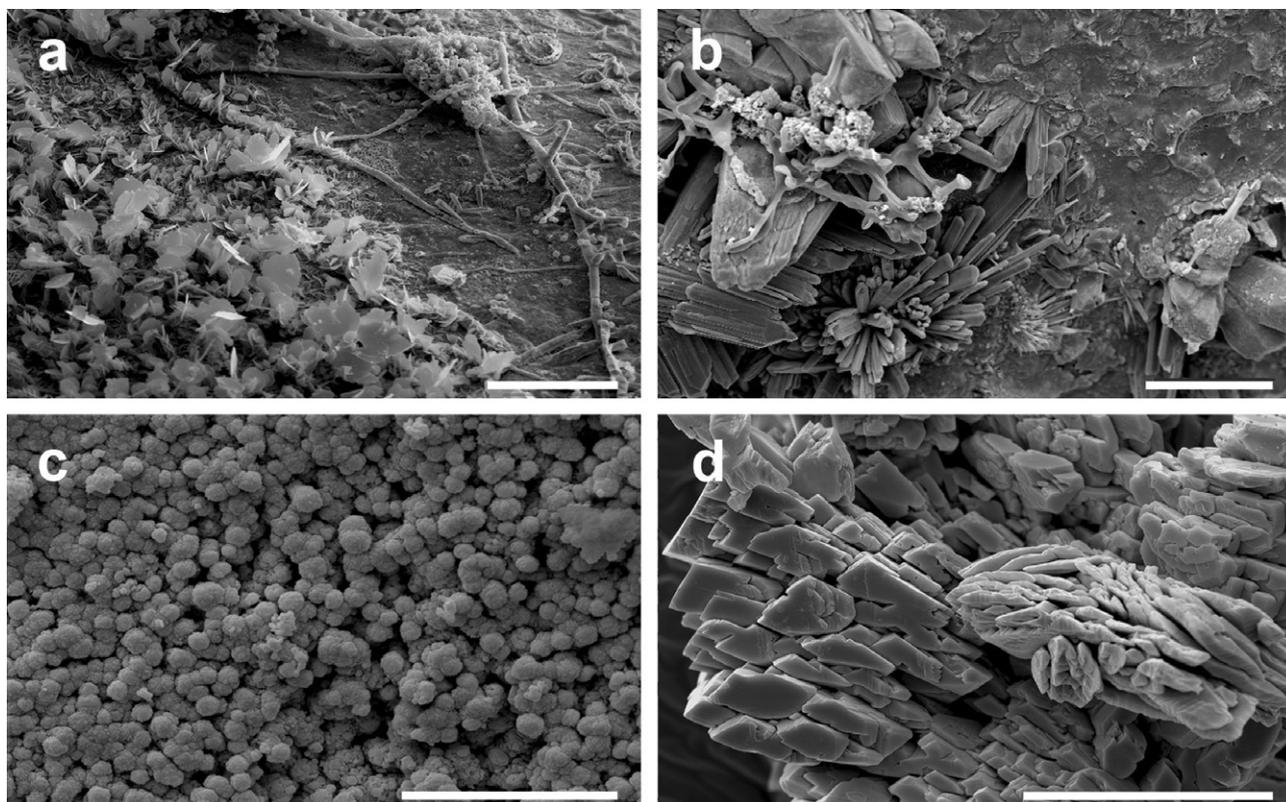


Fig. 2. Scanning electron micrographs of fungal production of secondary lead minerals and surface corrosion of lead metal. Fungal isolates were incubated in the presence of lead metal for 1 month at 25°C: images were taken using a Philips XL30 environmental scanning electron microscope (ESEM) operating at an accelerating voltage of 15 kV. (a) Fungal growth on the surface of lead metal as well as secondary lead mineral formation. Bar = 50 μm . (b) fungal mediated surface corrosion and mineral formation on lead surface. Bar = 20 μm . (c and d) different morphologies of secondary lead minerals collected from corroded lead metal surfaces. Bars = 10 μm and 20 μm respectively (Y.J. Rhee and G.M. Gadd, unpubl. data).

organic acids, siderophores and other metabolites. This can result in changes in mineral microtopography through pitting and etching to complete dissolution (Drever and Stillings, 1997; Ehrlich, 1998; Gharieb *et al.*, 1998; Kumar and Kumar, 1999; Adamo and Violante, 2000; Adeyemi and Gadd, 2005; Edwards *et al.*, 2005). Oxalate production was particularly important in the bio-deterioration of uranium oxides and depleted uranium (Fomina *et al.*, 2007a,b; 2008; Gadd and Fomina, 2011). Mineral dissolution may result in release of toxic (Sayer *et al.*, 1999) or essential metals like K (Lian *et al.*, 2008). Fungi can acidify their micro-environment via a number of mechanisms, which include the excretion of protons and organic acids, while respiratory CO_2 can result in carbonic acid formation. In addition, fungi excrete a variety of other metal-complexing metabolites (e.g. siderophores, carboxylic acids, amino acids and phenolic compounds) (Burgstaller and Schinner, 1993) (Fig. 1). The origin of fungal tunnels within soil minerals has been explained as a result of dissolution and 'boring' within the mineral matrix – the 'rock-eating fungi' hypothesis (Jongmans *et al.*, 1997; Landeweert

et al., 2001; Golubic *et al.*, 2005; Cockell and Herrera, 2008). An additional 'rock-building fungi' hypothesis has also been presented, which explains how fungal tunnels may occur inside minerals (Fomina *et al.*, 2010). This proposes that fungi can explore within pre-existing cracks, fissures, pores and weak points in weatherable minerals and, during colonization and mineral dissolution, build a matrix of secondary minerals of the same or different chemical composition as the substrate, e.g. secondary CaCO_3 precipitation in calcareous soil and rock (Verrecchia, 2000) or oxalate formation (Fomina *et al.*, 2010). As a result, fissures and cracks become secondarily cemented with mycogenic minerals. In less easily weathered silicate minerals, such as feldspars, fungal-mediated precipitation of amorphous aluminosilicates (Van Breemen *et al.*, 2000) may modify the appearance of pre-existing cracks and fissures in an analogous manner. After death and degradation of fungal hyphae, tunnels may be left within surficial patinas and crusts representing distinct fossil signatures of previous biogeochemical fungal activity (Fomina *et al.*, 2010).

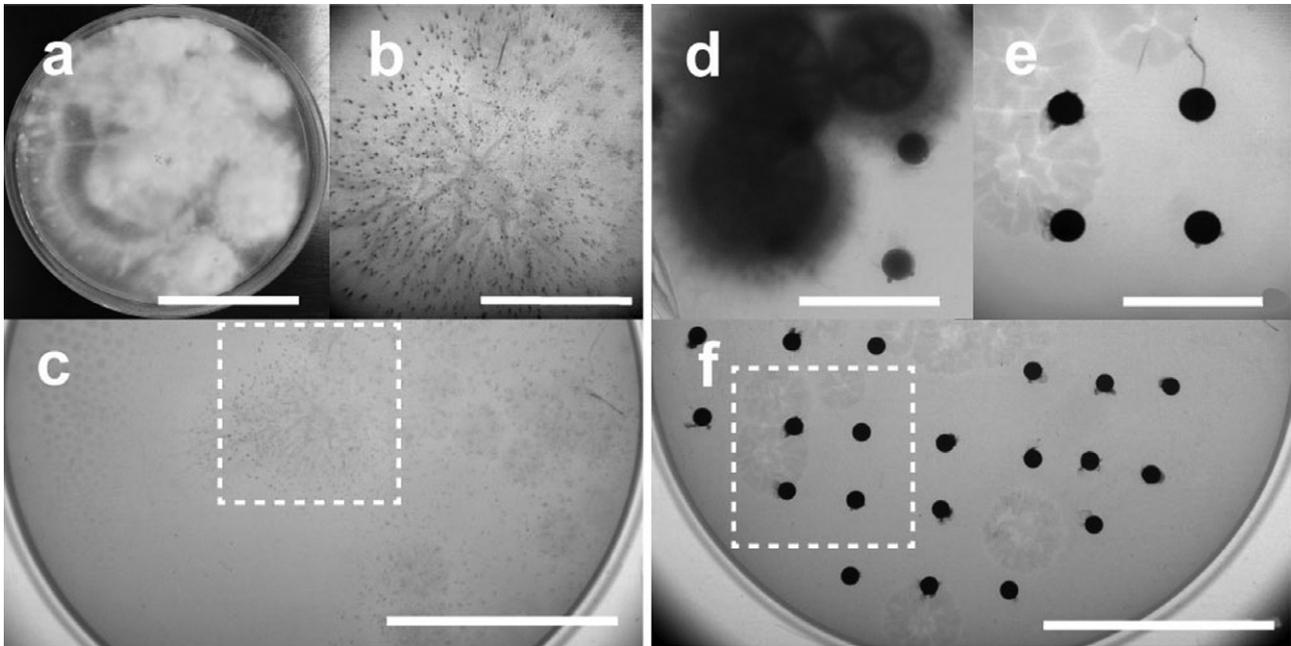


Fig. 3. Fungal transformations of lead as revealed by X-ray *in vivo* imaging (*in vivo* FX system, Kodak). Experimental fungi were allowed to grow over lead nitrate-amended malt extract agar [MEA; 7.5 mM $\text{Pb}(\text{NO}_3)_2$] (a, b and c) or over lead shot placed on top of MEA (d, e and f) for 1 month at 25°C.

a. Digital image of fungal biomass on lead nitrate-amended media.

b and c. X-ray irradiation images of the same fungal biomass showing X-ray dense deposits indicating formation of lead secondary minerals in the medium and around hyphae.

d. Digital image of fungal colonies showing lead shot embedded within the fungal biomass.

e and f. X-ray irradiation images showing evidence of corrosion of the lead metal under fungal biomass (for all X-ray images, exposure time = 6 min, f-stop = 7.5, X-ray E = 35 KVP). Bar markers are (a) 40 mm, (b, d and e) 10 mm, (c and f) 35 mm. The dashed-line squares in (c) and (f) indicate the areas shown at higher magnification in (b) and (e) respectively (Y.J. Rhee and G.M. Gadd, unpubl. data).

Common mineral and biomineral transformations by fungi

Fungi can potentially be involved in many different kinds of non-specific mineral transformations in the environment at differing scales (Rosling *et al.*, 2009; Smits, 2009), especially when considering their ubiquity and capacity for production of mineral-transforming metabolites, their symbiotic associations, and the consequences of their significant environmental properties such as organic matter decomposition and resultant element cycling. Only a few examples will be given here.

Bauxite

The major constituents of bauxite are Al_2O_3 , Fe_2O_3 and SiO_2 or aluminosilicate in various forms. Weathering of source rock (formation of protobauxite) is promoted by activities of those bacteria and fungi that can mobilize Al, Fe and Si that are then subsequently precipitated as oxides, silica and silicate minerals. Maturation of protobauxite to bauxite is promoted by iron-reducing and fermentative bacteria under anaerobic conditions (Ehrlich and Newman, 2009).

Carbonates

A significant proportion of insoluble carbonate at the Earth's surface is of biogenic origin. Certain fungi can deposit calcium carbonate extracellularly (Verrecchia *et al.*, 1990; Burford *et al.*, 2006). Insoluble carbonates may be broken down by fungal attack, usually the result of acid formation but may also involve physical processes (Lian *et al.*, 2008), and various fungi and lichens have this property (Adamo and Violante, 2000; Cockell and Herrera, 2008; Lian *et al.*, 2008). Such activity is particularly evident on limestones and marble used in building construction, but may also occur in natural limestone formations (Golubic *et al.*, 2005; Cockell and Herrera, 2008). Fungal attack on carbonate substrates (dolomites and limestones) can result in diagenesis of these substrates to neo-dolomite, glushinskite, weddellite, whewellite and possibly struvite, as well as intense substrate 'de-micritization' and 'micritization' with oxalates, grain bridging and cementation, open space filling, formation of intergranular and intragranular porosity, and permeability enhancement. Advanced stages of diagenesis may be characterized by dissolution and replacement of original minerals by the new substrates

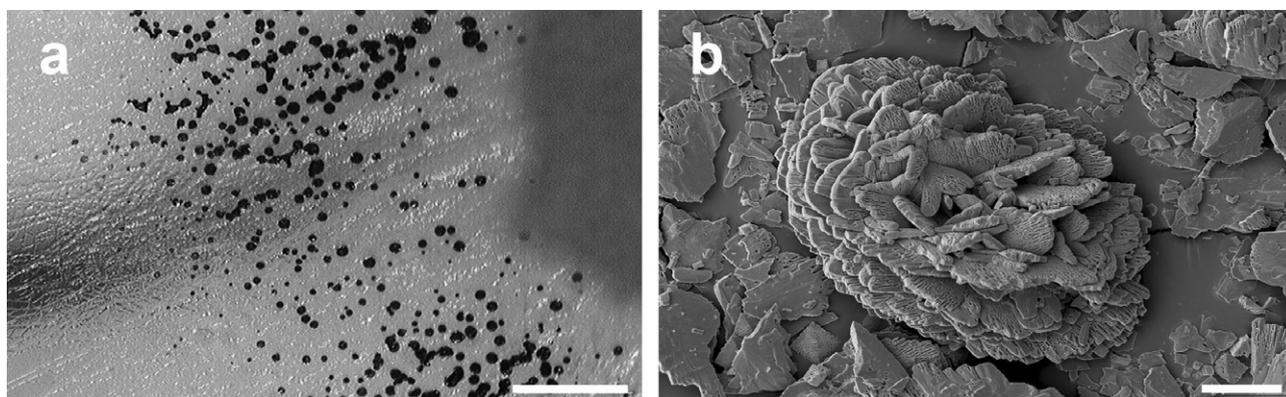


Fig. 4. Fungal production of manganese biominerals.

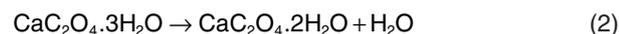
a. Light microscope image of MnO_x deposition in malt extract agar media around a colony of an *Acremonium* sp. incubated in the presence of 20 mM MnSO_4 for 10 days at 25°C. Bar = 0.8 cm.

b. Scanning electron micrograph of manganese oxalate produced by *Serpula himantioides* after growth on MnSO_4 (20 mM) amended malt extract agar medium for 15 days at 25°C in the dark. Bar = 100 μm . (Z. Wei and G.M. Gadd, unpublished).

produced by fungal biomineralization activities (Kolo *et al.*, 2007).

Oxalates

Calcium oxalate is the most common environmental form of oxalate, occurring as the dihydrate (weddellite) or the more stable monohydrate (whewellite) (Gadd, 1999). The initial precipitation phase is the trihydrate (Eq. 1), which loses water of crystallization to form either the dihydrate (Eq. 2) or monohydrate (Eqs 3 and 4), depending on conditions:

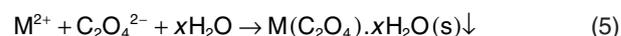


or



Calcium oxalate crystals can be associated with free-living, pathogenic and plant symbiotic fungi and lichens, and are formed by precipitation of solubilized calcium as the oxalate (Gharieb *et al.*, 1998; Gadd, 1999; Adamo and Violante, 2000; Adamo *et al.*, 2002). Biotic fungal calcium oxalate can exhibit a variety of crystalline forms (tetragonal, bipyramidal, plate-like, rhombohedral or needles) (Arnott, 1995). Calcium oxalate precipitation has an important influence on biogeochemical processes in soils, acting as a calcium reservoir, and also influences phosphate availability. Fungi can produce other metal oxalates (Fig. 4) on interacting with a variety of different metals and metal-bearing minerals, e.g. Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (Sayer and Gadd, 1997; Gadd, 1999; 2007a; Sayer *et al.*, 1999). Precipitation may occur

according to the following equation for divalent metal cations (Eq. 5):



The formation of toxic metal oxalates may contribute to fungal metal tolerance (Gadd, 1993a; Jarosz-Wilkolazka and Gadd, 2003).

In many arid and semi-arid regions, calcareous soils and near surface limestones (calcretes) are secondarily cemented with calcite (CaCO_3) and whewellite (calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and the presence of fungal filaments mineralized with these substances has been reported in a range of localities (Verrecchia, 2000). Calcium oxalate can also be degraded to calcium carbonate, and this may again cement pre-existing limestones (Verrecchia *et al.*, 2006). During the decomposition of fungal hyphae, calcite crystals can act as sites of further secondary calcite precipitation. Other experimental work has demonstrated fungal precipitation of secondary calcite, whewellite and glushkinskite ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (Burford *et al.*, 2003a,b; 2006; Gadd, 2007a). Fungal attack on dolomitic and seawater substrates resulted in the formation of Ca-oxalates (weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and glushkinskite ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (Kolo and Claeys, 2005).

Oxides

Several fungi can promote Mn(II) oxidation to $\text{Mn}(\text{IV})\text{O}_2$ including *Acremonium* spp. (Miyata *et al.*, 2004; 2007; Saratovsky *et al.*, 2009) (Fig. 4). In many cases, fungal oxidation is probably non-enzymatic and due to interaction with a metabolic product (e.g. a hydroxy acid) or a cellular component (Ehrlich and Newman, 2009), although the involvement of laccase and/or multicopper

oxidases has been shown in ascomycetes (Miyata *et al.*, 2004; 2007). For some basidiomycete white-rot fungi like *Phanerochaete chrysosporium*, redox transformations of Mn occur during lignin degradation, but this is thought to be of minor biogeochemical significance (Ehrlich and Newman, 2009). The MnO_x material produced by *Acremonium* KR21-2 is manifest as small crystalline particles which adopt a todorokite-like tunnel structure, which is in contrast to previously reported microbial MnO_x materials which adopt layered birnessite-type structures (Saratovsky *et al.*, 2009). Non-enzymatic microbial Mn²⁺ oxidation may be effected through production of metabolites, e.g. hydroxycarboxylic acids such as citrate, lactate, malate, gluconate or tartrate. Some fungi can oxidize Mn(II) and Fe(II) in metal-bearing minerals such as siderite (FeCO₃) and rhodochrosite (MnCO₃) and precipitate them as oxides (Grote and Krumbein, 1992). Manganese and iron oxides are major components (20–30%) along with clay (~60%) and various trace elements in the brown-to-black veneers known as desert varnish or rock varnish (Grote and Krumbein, 1992; Gorbushina, 2007).

Conversely, manganese-reducing microbes may mobilize oxidized or fixed manganese, releasing it into the aqueous phase. Most of those fungi that reduce Mn(IV) oxides such as MnO₂ reduce them indirectly (non-enzymatically) with the likely mechanism being the production of metabolic products that can act as reductants for Mn(IV) oxides such as oxalate (Ehrlich and Newman, 2009).

Phosphates

Phosphorus occurs primarily as organic phosphate esters and inorganic forms, e.g. calcium, aluminium, and iron phosphates. Organic phosphates are hydrolysed by phosphatases which liberate orthophosphate during microbial decomposition of organic material. Fungi also liberate free orthophosphate from insoluble inorganic phosphates by producing acids or chelators, e.g. gluconate, citrate, oxalate and lactate, which complex the metal resulting in dissociation. Phosphate-solubilizing activity is very important in the plant mycorrhizosphere (Whitelaw *et al.*, 1999).

Microbes can also play a role in the formation of phosphate minerals such as vivianite [Fe₃(PO₄)₂·8H₂O], strengite (FePO₄·2H₂O) and variscite (AlPO₄·2H₂O). Here, the orthophosphate may arise from organic phosphate degradation while Fe or Al may arise from microbial solubilization of other minerals. Such formation of phosphate minerals is probably most common in soil (Ehrlich and Newman, 2009). Secondary mycogenic uranium mineral precipitates on fungal mycelia growing in the presence of uranium oxides or depleted uranium were found to be uranyl phosphate minerals of the meta-autunite group,

uramphite and/or chernikovite (Fomina *et al.*, 2007a; 2008; Gadd and Fomina, 2011).

Silicates

Silicon dioxide, when combined with oxides of magnesium, aluminium, calcium and iron, forms the silicate minerals in rocks and soil and these are weathered by biological, chemical and physical processes (Brehm *et al.*, 2005). Silicates are the largest class of minerals comprising 30% of all minerals and making up 90% of the Earth's crust (Ehrlich, 1998; Ehrlich and Newman, 2009). Silicate minerals are unstable in the biosphere and break down readily to form clays (Adamo *et al.*, 2002; Tazaki, 2006). Many kinds of fungi and lichens play an important role in the dissolution of silicates and therefore in the genesis of clay minerals, and in soil and sediment formation (Barker and Banfield, 1996; 1998; Arocena *et al.*, 1999; 2003; Banfield *et al.*, 1999; Adamo and Violante, 2000; Tazaki, 2006; Theng and Yuan, 2008). In fact, the presence of clay minerals can be a typical symptom of biogeochemically weathered rocks, and this has been observed for lichens and ectomycorrhizas (Barker and Banfield, 1998; Arocena *et al.*, 1999). Even silicates of great physical and chemical resistance can be attacked, e.g. quartz sand, crystalline quartz and commercial glass (Brehm *et al.*, 2005). Bioweathering action is mainly indirect, either through the production of chelates or the production of acids (mineral or organic), or other metabolites, together with biomechanical effects (Cromack *et al.*, 1979; De La Torre *et al.* 1993; Mandal *et al.*, 2002). Metabolic agents may be excreted into the bulk phase but may also involve adhering organisms and biofilms on surfaces of silica or silicates resulting in etching (Bennett *et al.*, 2001; Wei *et al.*, 2011). After colonization of muscovite, a phyllosilicate mineral, in the form of a mineral sheet model system by *Aspergillus niger*, a network of hyphae covered the surface of the muscovite, and mineral dissolution or degradation was clearly evidenced by a network of fungal 'footprints' that reflected coverage by the mycelium (Wei *et al.*, 2011) (Fig. 5). Such mechanisms of silicate dissolution may be instrumental in releasing limiting nutrients like bound P and Fe. Quartz (SiO₂) can be subject to slow dissolution by organic acids such as citric and oxalic acid, the mechanism of action being chelation rather than protonation (Bennett *et al.*, 2001).

In lichen weathering of silicate minerals, calcium, potassium, iron, clay minerals and nanocrystalline aluminous iron oxyhydroxides become mixed with fungal organic polymers such as extracellular polysaccharides (Barker and Banfield, 1998), while biotite was interpenetrated by fungal hyphae along cleavages, partially converting it to vermiculite (Barker and Banfield, 1996). The fungal partner has also been reported to be involved in formation

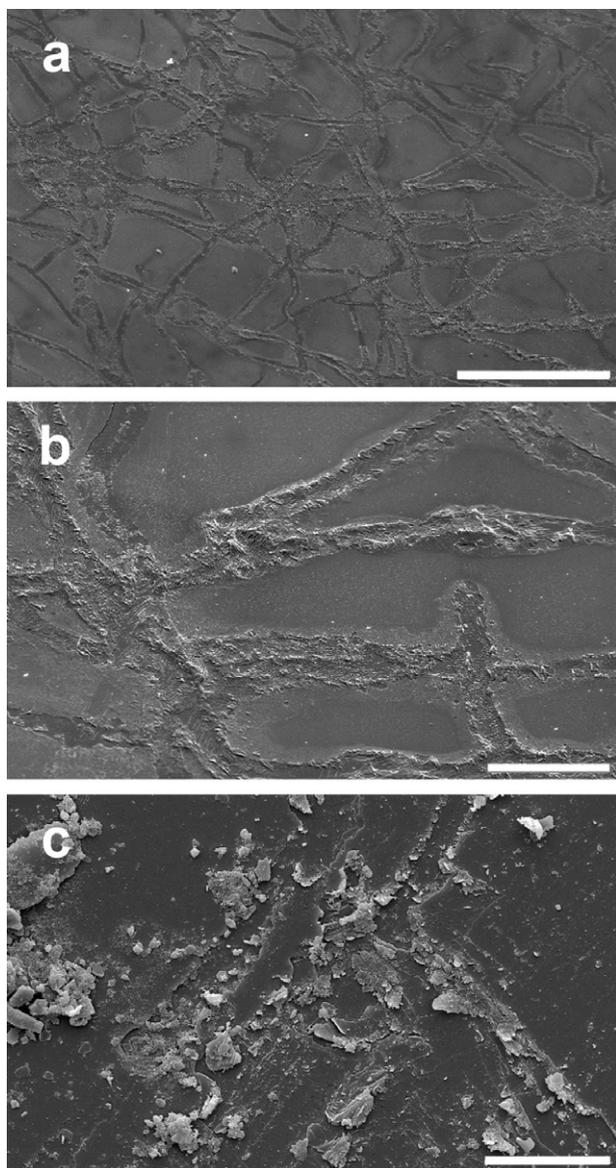


Fig. 5. Fungal biodeterioration of a silicate mineral (muscovite). a. Scanning electron micrographs of a network of fungal 'footprints' after growth of *Aspergillus niger* on a muscovite surface for 12-weeks and removal of the biomass. Bar = 100 μm . b. Higher magnification image of the degradation channels caused by the fungal hyphae. Bar = 20 μm . c. Scanning electron micrograph of bioweathering of muscovite incubated in natural soil for approximately four years. Bar = 20 μm . Specimens were examined using a Philips XL30 ESEM operating at an accelerating voltage of 15 kV (see Wei *et al.*, 2011).

of secondary silicates, such as opal and forsterite, in lichen thalli (Gorbushina *et al.*, 2001). The transformation rate of mica and chlorite to 2:1 expandable clays was pronounced in ectomycorrhizosphere soil and probably a result of the high production of organic acids and direct extraction of K^+ and Mg^{2+} by fungal hyphae (Arocena *et al.*, 1999).

Fungal–clay mineral interactions also play an important role in soil development, aggregation and stabilization (Burford *et al.*, 2003a). Fungi entangle soil particles in their hyphae-forming microaggregates and also effect exopolysaccharide-mediated aggregation. Interactions between hyphae and solid particles are subject to forces of both a physicochemical (electrostatic, ionic, hydrophobic effects, etc.) and biological nature (chemotropism, production of specific enzymes, polysaccharides, lectins and other adhesins, etc.) (Ritz and Young, 2004). Such interactions between clay minerals and fungi alter the adsorptive properties of both the clay minerals and fungal hyphae (Morley and Gadd, 1995; Fomina and Gadd, 2002b).

Silicon compounds in the form of clays (aluminosilicates) can exert many effects on microbes in soil and stimulate or inhibit metabolism (Theng and Yuan, 2008). Effects of clays are mostly indirect and arise from physicochemical effects of clays on the microenvironment, e.g. action as buffers, and as sorptive agents for cells, metabolites, ions and enzymes (Tazaki, 2006; Ehrlich and Newman, 2009). Clay minerals (bentonite, palygorskite and kaolinite) can also influence the size, shape and structure of fungal mycelial pellets (Fomina and Gadd, 2002a).

Reduction or oxidation of metals and metalloids

Many fungi precipitate reduced forms of metals and metalloids, 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)] (Kierans *et al.*, 1991; Gharieb *et al.*, 1995; 1999). Reduction of Hg(II) to volatile Hg(0) can also be mediated by fungi (Gadd, 1993b; 2000a). An *Aspergillus* sp. was able to grow at arsenate concentrations of 0.2 M and it was suggested that increased arsenate reduction contributed to tolerance (Canovas *et al.*, 2003a,b). Mn oxidation/reduction has been mentioned previously.

Other mycogenic minerals

A range of other minerals have been found in association with fungal communities. Apart from those detailed above, mycogenic secondary minerals associated with fungal hyphae and lichen thalli include desert varnish (MnO and FeO), ferrihydrite, iron gluconate, calcium formate, forsterite, goethite, halloysite and hydroserussite (Grote and Krumbein, 1992; Hirsch *et al.*, 1995; Verrecchia, 2000; Gorbushina *et al.*, 2001; Arocena *et al.*, 2003; Burford *et al.*, 2003b). *Lichenothelia* spp. can oxidize manganese and iron in metal-bearing minerals, such as siderite (FeCO_3) and rhodochrosite (MnCO_3), and precipitate them as oxides (Grote and Krumbein, 1992). Similar oxidation of Fe(II) and Mn(II) by fungi leads to the formation of dark patinas on glass surfaces (Eckhardt, 1985).

Another biogenic mineral (tepius) has been identified in association with a lichen carpet that covers high mountain ranges in Venezuela (Gorbushina *et al.*, 2001).

Metal–fungal interactions

Metals, metalloids, metal radionuclides, organometals and organometalloids, and their compounds, interact with fungi in various ways depending on chemical speciation, organism and environment, with fungal metabolic activity also capable of influencing metal speciation and mobility (Gadd and Griffiths, 1978; Gadd, 1992; 1993a; 2004a,b; 2005; 2007a,b; 2008c; 2009b). Many metals are essential for life, e.g. Na, K, Cu, Zn, Co, Ca, Mg, Mn and Fe, but all can exert toxicity when present above certain threshold concentrations. Other metals, e.g. Cs, Al, Cd, Hg and Pb, have no known metabolic function in fungi but all can be accumulated. Metal toxicity is affected by environmental conditions and the chemical behaviour of the particular metal species. Metals exert toxic effects in many ways and can inhibit enzymes, displace or substitute for essential metal ions, cause disruption of membranes, interact with systems which normally protect against the harmful effects of free radicals, inhibit growth and spore germination of fungi, affect reproduction and metabolism, and reduce the ability of mycorrhizal fungi to colonize host plant roots (Gadd, 1993a; Howlett and Avery, 1997; Fomina *et al.* 2005c). However, many fungi are found in metal-polluted locations and a variety of mechanisms, both active and incidental, contribute to tolerance. Mechanisms of toxic metal tolerance in fungi include reduction of metal uptake and/or increased efflux, metal immobilization (e.g. cell wall adsorption, extracellular precipitation of secondary minerals, extracellular binding by polysaccharides and extracellular metabolites, and intracellular sequestration by, e.g. metallothioneins and phytochelatins (PCs), and localization in vacuoles (Gadd *et al.*, 1984; Gadd, 1993a; Blaudez *et al.*, 2000a; Perotto and Martino, 2001; Baldrian, 2003; Meharg, 2003).

Fungal communities in metal-polluted soils and metal-rich environments

Many studies have shown that metal toxicity reduces microbial populations and activity and can affect microbe-mediated processes in soil ecosystems, such as organic matter decomposition (Brookes and McGrath, 1984). The frequency of tolerant microorganisms may increase with an increase in toxic metal levels, and this can lead to a decrease in species diversity and therefore a shift in microbiota composition (Pennanen *et al.*, 1996). However, fungi show considerable interspecific responses to toxic metals, and the extent to which intra-

specific (adaptive) resistance occurs remains unclear (Meharg and Cairney, 2000). In many cases, several direct and indirect mechanisms, both physicochemical and biological, can contribute to survival. Thus, although metal pollution can qualitatively and quantitatively affect fungal (and other microbial) populations in the environment, it may be difficult to distinguish metal effects from those of environmental components, environmental influence on metal speciation and toxicity, and the nature of any microbial resistance/tolerance mechanisms involved (Gadd, 1992).

Mycelial fungi can develop a significant biomass in soil and may sequester significant amounts of metals (Massaccesi *et al.*, 2002). Several studies have shown that microbial population responses to toxic metals are characterized by a shift from single-celled bacteria and streptomycetes to fungi (Olayinka and Babalola, 2001). A population shift to fungi can lead to increased decomposition of organic matter and reduced assimilation of released N (Khan and Scullion, 2002).

All nutritional groups of fungi (saprotrophs, biotrophs and necrotrophs) can be affected by toxic metals. Toxic metal (Cd, Cr, Cu, Ni, Pb and Zn) contamination of soil led to a significant decrease in the number of arbuscular mycorrhizal fungi and low colonization of plant roots and, as a result, to changes in species diversity (Moynahan *et al.*, 2002; Mozafar *et al.*, 2002). The most frequent soil saprotrophic microfungi isolated from heavily metal polluted habitats in Argentina, Czech Republic and Ukraine were species of *Penicillium*, *Aspergillus*, *Trichoderma*, *Fusarium*, *Rhizopus* and *Mucor*, as well as *Paecilomyces lilacinus*, *Acrostalagmus luteo-albus* (as '*Nectria inventa*'), *Cladosporium cladosporioides*, *Alternaria alternata* and *Phoma fimeti* (Kubatova *et al.*, 2002; Massaccesi *et al.*, 2002). Melanized fungi (e.g. *Cladosporium* spp., *Alternaria alternata*, *Aureobasidium pullulans*) are often isolated from soil samples treated with toxic industrial wastes containing high concentrations of copper and mercury (Zhdanova *et al.*, 1986, 2000), and may also be dominant members of the mycobiota of metal-contaminated phylloplanes (Mowll and Gadd, 1985). Fungal colony-forming units were 10 times lower in Pb-enriched soils, the species composition was widely different from that in control soils, and the isolated fungi had a high Pb tolerance. The most commonly isolated fungus in Pb-enriched soils was *Tolyposcladium inflatum*. Comparison of isolates from Pb-enriched soil and isolates from unpolluted soils showed that *T. inflatum* was intrinsically Pb-tolerant, and that the prolonged conditions with high Pb had not selected for any increased tolerance (Baath *et al.*, 2005). This is similar for *A. pullulans*, ubiquitous on Pb-contaminated phylloplanes, where adaptation was not necessary for tolerant behaviour (Gadd, 1984).

Investigations on metal toxicity in mycorrhizal fungi have also revealed inter- and intraspecific variations in metal sensitivity, especially in ectomycorrhizal species (Jones and Muehlchen, 1994; Hartley *et al.*, 1997; Vodnik *et al.*, 1998; Meharg and Cairney, 2000; Blaudez *et al.*, 2000b). Clearly, metal effects on natural soil communities are difficult to characterize because of the complex array of contributing factors. For example, many contaminated sites contain mixtures of metals as well as organic pollutants and each may have reciprocal physical and chemical effects on the other with complexation and other phenomena affecting toxicity, bioavailability and degradation (Hong *et al.*, 2010a,b). In several mycorrhizal fungi, metal-tolerant fungal strains solubilized toxic metal minerals more efficiently than sensitive strains (Fomina *et al.*, 2004).

Morphological and growth strategies in response to toxic metals

Effects of toxic metals on fungal growth have shown intra- and interspecific variability and dependence on metal species and speciation (Gadd, 1993a; Plaza *et al.*, 1998). For *T. virens* and *Clonostachys rosea* colonizing spatially discrete toxic metal containing domains, colonization distance, hyphal extension rates and the efficacy of carbon substrate utilization decreased with increasing concentrations of copper and cadmium (Fomina *et al.*, 2003). A decrease in metal toxicity may be correlated with an increase in available carbon source (Ramsay *et al.*, 1999; Fomina *et al.*, 2003).

Several toxic metals can induce or accelerate melanin production in fungi, leading to blackening of colonies and chlamydospore development (Gadd and Griffiths, 1980). Chlamydospores and other melanized forms have high capacities for metal biosorption, the majority of metal remaining within the wall (Gadd, 1984; Gadd and Mowll, 1985; Gadd *et al.*, 1987; Gadd and De Rome, 1988). In rhizomorphs of an *Armillaria* sp., the highest concentrations of metals were located on the melanized outer surface (Rizzo *et al.*, 1992).

Fungi can also show morphological responses to substrate topography, which is known as thigmotropism or contact sensing. Thigmotropism has been reported in many different fungi, ranging from the opportunistic human pathogen *Candida albicans*, the barley brown rust fungus *Puccinia hordei*, the ectomycorrhizal fungus *Heboloma velutipes* and soil-dwelling *Aspergillus niger* (Read *et al.*, 1997; Bowen *et al.*, 2007a,b; Brand *et al.* 2007; Rosling *et al.*, 2009). *Heboloma velutipes* responded to the topography of the surface of potassium feldspar by re-orientating its growth direction along the surface contours (Rosling *et al.*, 2009). *Candida albicans* showed a Ca²⁺-dependent response to surface topography (Brand

et al. 2007). Bowen and colleagues (2007a,b) found that thigmotropism in *A. niger* can be a stress response when nutrient levels were low. A thigmotropic response appears to be important for exploration of substrates and colonization of soil, rocks, and minerals, perhaps to enable the fungus to locate nutrients or essential ions in cracks or grooves in the substrate.

Fungal morphology can be altered by toxic metals, and changes in mycelial density and morphology have often been observed (Darlington and Rauser, 1988; Lilly *et al.*, 1992; Jones and Muehlchen, 1994; Gabriel *et al.*, 1996; Baldrian and Gabriel, 1997; Gardea-Torresdey *et al.*, 1997; Ramsay *et al.*, 1999; Fomina *et al.*, 2005b). It was found that biomass distribution within *Trichoderma viride* colonies was altered by toxic metals, with biomass concentrated in the periphery of the colonies in the presence of Cu and towards the interior of the colonies in the presence of Cd (Ramsay *et al.*, 1999; Gadd *et al.*, 2001).

During growth of fungi in metal-containing agar tiles simulating a spatially heterogeneous distribution of metal concentrations and available nutritional resources, a wide range of morphological changes and growth responses occurred including negative chemotropism, cessation of growth, swelling and lysis of hyphal tips (Fomina *et al.*, 2003). Penetration of hyphae into metal-containing domains was often followed by formation of very dense mycelia or mycelial 'bushes' (Fomina *et al.*, 2003). Such hyphal aggregation could facilitate the colonization of a substrate, and the production of high local concentrations of extracellular metabolites such as complexing agents (e.g. organic acids, siderophores, polyphenolic compounds), metal precipitating agents (e.g. oxalate), and polysaccharides and pigments with metal-binding abilities (Gadd, 1993a; Dutton and Evans, 1996; Baldrian, 2003). Under poor-nutritional conditions, fungi often produced long sparsely branched or branchless hyphae in toxic metal-containing domains representing an explorative growth strategy (Fomina *et al.*, 2003). Some fungi also exhibited multiple repeated 'phase shifts' with a mixture of mycelial 'bushes' and long branchless explorative hyphae (Fomina *et al.*, 2003). Further, microfungi penetrating metal-contaminated domains may form mycelial cords and synnema, which may be atypical for these fungi under normal conditions. The production of synnema results in a wider separation between the conidia and the substrate than in non-synnematal colonies, and this may aid dispersal as well as ensuring conidia formation away from substrate toxicants (Newby and Gadd, 1987).

Mechanisms of metal resistance and tolerance

Fungi possess many properties, which influence metal toxicity and bioavailability. All mechanisms are dependent

on the metabolic and nutritional status of the organism, since this will affect expression of energy-dependent resistance mechanisms as well as synthesis of structural components, pigments and metabolites, which can affect metal availability and influence organism response (Gadd and Griffiths, 1978; Gadd, 1992; 1993a; Ramsay *et al.*, 1999). Fungi can restrict cellular entry of toxic metal species by: (i) reduced metal uptake and/or increased metal efflux; (ii) metal immobilization, e.g. cell wall adsorption, extracellular precipitation of secondary neoformed minerals (e.g. oxalates); and (iii) extracellular metal sequestration by, e.g. exopolysaccharides and other extracellular metabolites (Gadd, 1993a; 2001a,b,c; Macreadie *et al.*, 1994; Zhdanova *et al.*, 2000; Blaudez *et al.*, 2000b; Perotto and Martino, 2001; Baldrian, 2003) (Fig. 1). Metal tolerant fungi can survive due to their abilities of intracellular chelation by, for example low-molecular-weight cysteine-rich proteins (metallothioneins) and peptides derived from glutathione (PCs), and metal localization/sequestration within vacuoles (White and Gadd, 1986; Gadd 1993a; Gharieb and Gadd, 1998; Liu and Culotta, 1999). Metals preferentially sequestered by the vacuole include Mn^{2+} (Okorokov *et al.*, 1985; Gadd and Laurence, 1996), Fe^{2+} (Bode *et al.*, 1995), Zn^{2+} (White and Gadd, 1987), Co^{2+} (White and Gadd, 1986), Ca^{2+} and Sr^{2+} (Okorokov *et al.*, 1985; Borst-Pauwels, 1989; Gadd, 1993a; Okorokov, 1994), Ni^{2+} (Joho *et al.*, 1995) and the monovalent cations K^+ , Li^+ and Cs^+ (Okorokov *et al.*, 1980; Perkins and Gadd, 1993a,b). The absence of a vacuole or a functional vacuolar H^+ -ATPase in *Saccharomyces cerevisiae* was associated with increased sensitivity and a largely decreased capacity of the cells to accumulate Zn, Mn, Co and Ni (Ramsay and Gadd, 1997), metals known to be mainly detoxified in the vacuole (Gadd, 1993a; Joho *et al.*, 1995). The formation of toxic metal response indicators, such as thiols, oxalate and laccase, was investigated in the white-rot fungi *Cerrena unicolor* and *Abortiporus biennis*. Oxalate and laccase were produced by both fungi, and their extracellular levels were elevated on Cd exposure. Both responded to increasing Cd concentrations by increasing the intracellular amounts of thiol compounds (cysteine, γ -glutamylcysteine, and glutathione in both reduced and oxidized forms) (Jarosz-Wilkolazka *et al.*, 2006). Free-radical scavenging capacities through the activity of superoxide dismutase or production of glutathione are another defence mechanism against toxic metals (Bellion *et al.*, 2006).

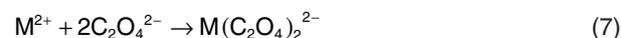
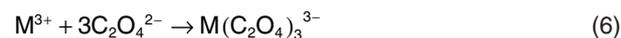
Metal, metalloid, radionuclide and organometal transformations

Fungi have many properties which influence metal mobility and toxicity including the production of metal-binding proteins, organic and inorganic precipitation, active trans-

port and intracellular compartmentalization, while major constituents of cell walls, e.g. chitin and melanin, have significant metal binding abilities (Gadd, 2004a,b; 2005; 2006; 2008c). Other properties lead to metal solubilization from organic and inorganic sources (Gadd, 2007a,b). Fungi can also transform certain metals, metalloids (elements with properties intermediate between those of metals and non-metals, e.g. arsenic, selenium and tellurium), organometallic compounds and metal radionuclides by, e.g. oxidation, reduction, methylation and dealkylation (Gadd, 1993b; 2004a,b). Such transformations alter chemical speciation and may affect mobility and toxicity. For example, methylated selenium derivatives are volatile and less toxic than inorganic forms while reduction of metalloid oxyanions, such as selenite or tellurite to amorphous elemental selenium or tellurium respectively, results in immobilization and detoxification. All the mechanisms by which fungi (and other microorganisms) effect changes in metal speciation and mobility are survival determinants but also components of biogeochemical cycles for metals, and many other associated elements including carbon, nitrogen, sulfur and phosphorus (Gadd, 2004a; 2006; 2007a; 2008a). These may be simply considered in terms of metal mobilization or immobilization mechanisms.

Metal mobilization

Metal mobilization from rocks, minerals, soil and other substrates can be achieved by protonolysis, carbonic acid formation from respiratory CO_2 , complexation by Fe(III)-binding siderophores (Fig. 6) and other excreted metabolites, e.g. amino acids, phenolic compounds and organic acids, and methylation which can result in volatilization (Fig. 1). Fungal-derived carboxylic acids can attack mineral surfaces (see previously) and these provide protons as well as a metal-chelating anion (Burgstaller and Schinner, 1993). A metal (M), which normally forms octahedral six-coordinate complexes (e.g. Al^{3+} , Cr^{3+} , Fe^{3+}), can bind three oxalates to form an anionic complex (Eq. 6), metals which form square planar four-coordinate complexes (e.g. Cu^{2+} , Zn^{2+}) can complex two oxalates (Eq. 7):



Oxalic acid can therefore act as a leaching agent for metals that form soluble oxalate complexes, including Al and Fe (Strasser *et al.*, 1994) (Fig. 7). Solubilization mechanisms can also have consequences for mobilization of metals from toxic metal containing minerals, e.g. pyromorphite [$Pb_5(PO_4)_3Cl$], contaminated soil and other solid wastes (Sayer *et al.*, 1999; Fomina *et al.*, 2004; 2005b,c). Fungi may also mobilize metals and attack mineral

Poly-carboxylate type Siderophore	
Rhizoferrin	
Hydroxamate type Siderophores	
Fusarinines	<p>Linear n = 1 cis-fusarinine n = 2 fusarinine A n = 3 fusarinine B</p>
	<p>Cyclic n = 3, R=H : fusarinine C n = 3, R=COCH₃ : triacetylfulsigen</p>
Coprogens	<p>R₁, R₂ = A, B or CH₃ R₃ = COCH₃, H or CH₃ R₄ = C, H or CH₃ e.g. Coprogen: R₁=A, R₂=A, R₃=COCH₃ and R₄=H</p>
Ferrichromes	<p>R₁ = H or CH₂OH R₂ = H, CH₂OH or CH₃ R₃ = A, D, E, F, G, J or CH₃ R₄ = A, D, E, F, G, J or CH₃ R₅ = A, D, E, F, G, J or CH₃ e.g. Ferrichrome: R₁=H, R₂=H R₃=CH₃, R₄=CH₃, R₅=CH₃</p>
	Des(diserylglycyl)ferrirhodin
<p>A: </p> <p>B: </p> <p>C: </p> <p>D: </p> <p>E: </p> <p>F: </p> <p>G: </p> <p>J: </p>	

Fig. 6. Examples of fungal siderophores, characterized as hydroxamate type, with the exception of the poly-carboxylate rhizoferrin. Hydroxamate-type siderophores can be classified into three major groups: fusarinines, coprogens and ferrichromes. The substituent alkyl groups in the acyl moieties and amino groups shown at the bottom of the figures are used to specify coprogen or ferrichrome siderophores. Siderophores are used for iron(III) capture but also have non-specific activities for other metal ions and radionuclides (adapted from Renshaw *et al.*, 2002).

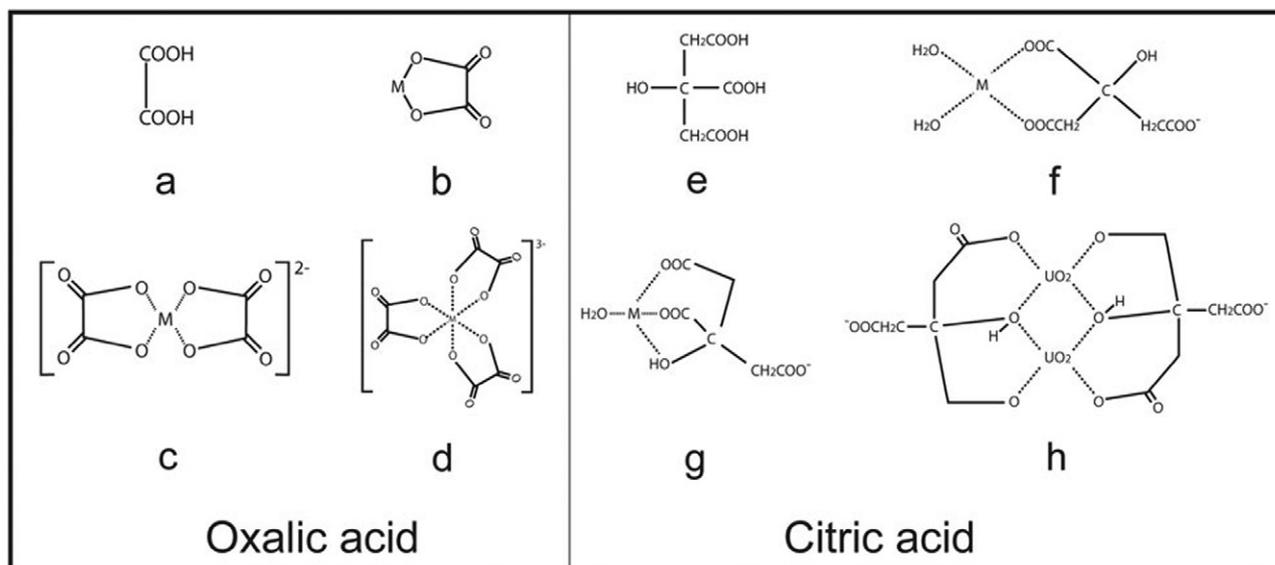


Fig. 7. Metal complex formation by oxalic acid and citric acid. (a) oxalic acid; (b) bidentate metal (M) complex formation; (c) complex anion formation with a metal which forms square planar four-coordinate complexes, e.g. Cu^{2+} (Cu oxal) $^{2-}$; (d) complex anion formation with metals which form octahedral six-coordinate complexes, e.g. Al^{3+} , Fe^{3+} , Cr^{3+} ; (e) citric acid; (f) bidentate complex, e.g. $(\text{Ca cit})^-$, $(\text{Ni cit})^-$, $(\text{Fe}(\text{OH})_2\text{cit})^{2-}$; (g) tridentate complex, e.g. $(\text{Cd cit})^-$, $(\text{Fe cit})^-$, $(\text{FeOH cit})^{2-}$, $(\text{Pb cit})^-$; (h) binuclear complex, e.g. $(\text{UO}_2)_2\text{cit}_2^{2-}$ (adapted from Francis *et al.*, 1992; Gadd, 1999).

surfaces by redox processes: Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II) respectively, although the environmental significance of fungi in these processes is likely to be low compared with relevant bacterial genera. Reduction of Hg(II) to volatile elemental Hg(0) can also be mediated by fungi (Gadd, 1993b).

Metal immobilization

Fungal biomass provides a metal sink, either by biosorption to biomass (cell walls, pigments and extracellular

polysaccharides), intracellular accumulation and sequestration, or precipitation of metal compounds onto and/or around hyphae (Gadd, 1993a; 2000a,b; 2001a,b,c; 2007a; Baldrian, 2003; Fomina *et al.*, 2007b,c) (Fig. 1). Fungi are effective biosorbents for a variety of metals including Ni, Zn, Ag, Cu, Cd and Pb, and this can be an important passive process in both living and dead biomass (Gadd, 1990; 1993a; Sterflinger, 2000). The presence of chitin, and pigments like melanin, strongly influences the ability of fungi to act as sorbents. A variety of functional groups can be involved in biosorption and

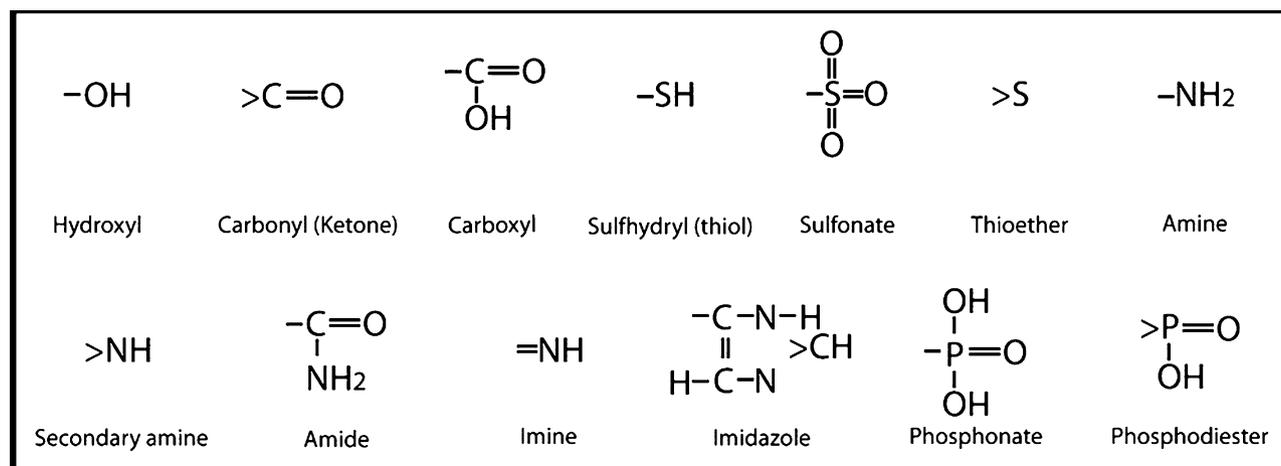


Fig. 8. Major metal-binding groups involved in fungal biosorption of metals and metal radionuclides, as well as non-specific intracellular binding or association with structural components and macromolecules (adapted from Hunt, 1986; Volesky, 1990; 2007; Gadd, 1992).

also metal association with other cellular components and macromolecules (Fig. 8). In a biotechnological context, fungi and their by-products have received considerable attention as biosorbent materials for metals and radionuclides (de Rome and Gadd, 1987; Gadd and White, 1989; 1990; 1992; White *et al.*, 1995). Fungi can also precipitate several inorganic and organic compounds, e.g. oxalates, phosphates, oxides and carbonates, and this can lead to formation of biogenic minerals (mycogenic precipitates) as described previously (Gadd, 2007a) (Figs 2–4).

Fungal symbioses in mineral transformations

Many fungi form remarkable partnerships with plants (mycorrhizas) and algae or cyanobacteria (lichens) that are of great significance in the terrestrial environment. In general terms, the mycobiont is provided with carbon by the photobionts, while the mycobiont may protect the symbiosis from harsh environmental conditions (e.g., desiccation, metal toxicity), and provide increased access to inorganic nutrients.

Lichens

Lichens are fungi that exist in facultative or obligate symbioses with one or more photosynthesizing partners and found in almost all surface terrestrial environments: an estimated 6–8% of the Earth's land surface is dominated by lichen covering (Haas and Purvis, 2006). Lichens play an important role in many biogeochemical processes, and are pioneer colonizers of fresh rock outcrops. Globally, lichens play important roles in retention and distribution of nutrient (e.g. C, N) and trace elements, in soil formation and rock weathering. Alteration of bedrock minerals and biomineralization processes in the proximity of lichens results in differing chemical microenvironments and underpins their participation in mineral transformations and element cycling (Banfield *et al.*, 1999; Adamo and Violante, 2000; Chen *et al.*, 2000). Lichens accumulate metals such as lead (Pb) and copper (Cu), and many other elements, including radionuclides, to high levels (Purvis and Pawlik-Skowronska, 2008). They also form a variety of metal-organic biominerals, e.g. oxalates, especially during growth on metal-rich substrates (Chen *et al.*, 2000; Adamo *et al.*, 2002). On copper-sulfide bearing rocks, precipitation of copper oxalate (moolooite) can occur within lichen thalli (Purvis, 1996; Purvis and Halls, 1996).

Mycorrhizas

Almost all land plants depend on symbiotic mycorrhizal fungi (Smith and Read, 1997; Wang and Qiu, 2006). Two main types include endomycorrhizas where the fungus colonizes the interior of host plant root cells (e.g. ericoid and arbuscular mycorrhizas) and ectomycorrhizas where

the fungus is located outside plant root cells. Mycorrhizal fungi are involved in phosphate solubilization, proton-promoted and ligand-promoted metal mobilization from mineral sources, metal immobilization within biomass, and extracellular precipitation of mycogenic metal oxalates (Fomina *et al.*, 2004; 2005b; Finlay *et al.*, 2009). Biogeochemical activities of mycorrhizal fungi lead to changes in the physicochemical characteristics of the root environment and enhanced weathering of soil minerals. Ectomycorrhizal mycelia may respond to the presence of different soil silicate and phosphate minerals (apatite, quartz, potassium feldspar) by regulating growth and activity, e.g. colonization, carbon allocation and substrate acidification (Rosling *et al.*, 2004a,b).

During growth, mycorrhizal fungi often excrete low-molecular-weight carboxylic acids and siderophores (Martino *et al.*, 2003; Fomina *et al.*, 2004). The weathering of hornblendes, feldspars and granitic bedrock in certain soils has been attributed to oxalic, citric, succinic, formic and malic acid excretion by ectomycorrhizal hyphae, which can produce micro- to millimolar concentrations of these organic acids in their microenvironments. Ectomycorrhizal fungi can form narrow cylindrical pores in weatherable minerals in podzol E horizons, probably by exuding low-molecular weight organic acids and/or siderophores at their hyphal tips, causing local dissolution of Al silicates (Jongmans *et al.*, 1997; Van Breemen *et al.*, 2000). Ectomycorrhizal fungi (*Suillus granulatus* and *Paxillus involutus*) can also release elements from apatite and wood ash (K, Ca, Ti, Mn, Pb) (Wallander *et al.*, 2003). Ericoid mycorrhizal and ectomycorrhizal fungi can dissolve a variety of cadmium, copper, zinc and lead-bearing minerals including metal phosphates (Leyval and Joner, 2001; Martino *et al.*, 2003; Fomina *et al.*, 2004; 2005b). Mobilization of phosphorus from inorganic and organic phosphorus sources is generally regarded as one of the most important functions of mycorrhizal fungi, and this will also result in movement and redistribution of associated metals, and also the formation of other secondary minerals including other metal phosphates.

Environmental and applied significance of geomycological processes

Biocorrosion of metals

The deterioration of metal due to microbial activity is termed biocorrosion or microbially influenced corrosion (MIC) (Beech and Sunner, 2004). While several groups of bacteria are more commonly associated with biocorrosion, e.g. sulfate-reducing bacteria (SRB), various fungi may colonize and/or be present within complex biofilm communities on metal surfaces (Beech and Sunner, 2004; Gu, 2009). Mechanisms of corrosion are complicated and

include depolarization of metals, biomineral formation, complexation by exopolymeric materials, H₂ embrittlement, acidic attack and electron shuttling (Gu, 2009) (Fig. 3).

Bioremediation of metals from ores

Solubilization mechanisms provide a means for removal of metals from industrial wastes and by-products, low-grade ores and metal-bearing minerals, which is relevant to bioremediation of soil matrices and solid wastes, metal recovery and recycling (Burgstaller and Schinner, 1993; Gadd and Sayer, 2000; Gadd, 2000a; Brandl, 2001; Kartal *et al.*, 2006). Extracellular ligands excreted by fungi, e.g. *Aspergillus* and *Penicillium* spp., have been used to leach metals such as Zn, Cu, Ni and Co from a variety of materials, including low grade ores (Brandl, 2001; Santhiya and Ting, 2005). Of the several mechanisms involved in chemoorganotrophic (= heterotrophic) leaching, the production of low-molecular-weight organic acids is probably of most significance (Burgstaller and Schinner, 1993; Gadd, 1999; 2007a; Brandl, 2001).

Bioweathering of rocks and minerals: soil formation

Weathering is a process in which rock is eroded or broken down into smaller particles and finally to constituent minerals, ultimately leading to mineral soil formation (Tazaki, 2006; Ehrlich and Newman, 2009). Physical, chemical and biological processes are involved: bioweathering can be defined as the erosion and decay of rocks and minerals mediated by living organisms, and in microbes is mediated by the direct and indirect physical and chemical mechanisms detailed previously. Many fungi are effective biological weathering agents and many can tolerate extremes of light, salinity, pH and water potential, as well as adopting a variety of growth, metabolic and morphological strategies (Gorbushina *et al.*, 1993; Sterflinger, 2000; Verrecchia, 2000; Burford *et al.*, 2003a,b; Gadd, 2007a; Gorbushina and Broughton, 2009; Sverdrup, 2009). Many organisms can scavenge nutrients from the atmosphere and rainwater, and also use organic and inorganic residues on surfaces or within cracks and fissures, waste products of other microbes, decaying plants and insects, dust particles, aerosols and animal faeces as nutrient sources (Sterflinger, 2000; Gorbushina and Broughton, 2009). Many organisms receive protection from the presence of pigments in their cell walls, e.g. melanins, and by the production of extracellular polymeric substances (EPS) during adhesion with biofilm formation providing extra protection (Gadd, 1993a; Gorbushina, 2007). Fungi are probably associated with all rocks and minerals, building stone and concrete (Burford *et al.*, 2003a,b; Gleeson *et al.*, 2005; 2006; 2010; Gorbushina, 2007; Gorbushina and

Broughton, 2009). Such ubiquitous endolithic rock ecosystems offer an ideal model system for studying complex interactions between microbes and minerals that drive the biosphere, and provide model systems for microbial ecology, geobiology and astrobiology, and form biosignatures that can be preserved in the geological record (Walker and Pace, 2007; Gorbushina and Broughton, 2009). As mentioned previously, lichens, a fungal growth form, are highly significant bioweathering agents (Adamo and Violante, 2000; Adamo *et al.*, 2002). Lithobiotic biofilm communities can interact with mineral substrates both geophysically and geochemically: as well as deterioration this can also result in the formation of patinas, films, varnishes, crusts and stromatolites (Gorbushina, 2007; Gadd, 2007a; Fomina *et al.*, 2010). Elements found in soil therefore largely reflect the composition of the Earth's crust, though some modification occurs by further weathering, biogenic and anthropogenic activities: chemical changes include mineral dissolution while biological activity causes enrichment of C, N and S. Elements and minerals that remain can reform as secondary minerals. Mycorrhizal fungi are also very important in mineral weathering and dissolution of insoluble metal compounds in the soil. Bioweathering is a primary source of essential elements for organisms, except nitrogen and carbon (Hoffland *et al.*, 2004). Acidification is an important fungal bioweathering mechanism with low-molecular-weight organic acid anions being especially significant (Gadd, 1999; Hoffland *et al.*, 2004). Because production of these substances has a carbon cost, symbiotic mycorrhizal fungi that are provided with organic carbon compounds by the plant host may have an advantage over free-living saprotrophs (Hoffland *et al.*, 2004).

Many microbes can attack silicates, therefore playing a role in the genesis of clay minerals, and in soil and sediment formation. Microbe–clay mineral interactions therefore play an important role in soil evolution, as well as aggregation and stabilization (Burford *et al.*, 2003a; Tazaki, 2006; Theng and Yuan, 2008). Fungi can entangle soil particles in their hyphae forming stable microaggregates and also take part in polysaccharide aggregation (Lunsdorf *et al.*, 2000). Direct biophysical effects have been shown where fungal hyphae attract and orient clay platelets because of surface charge phenomena, and act as nucleation zones for the formation of narrow clay-lined channels (Ritz and Young, 2004). Interactions between clay minerals and microbes alter adsorptive properties of both clays and biomass (Fomina and Gadd, 2002b). As well as being important in stages of mineral soil and sediment formation and development, bioweathering mechanisms also effect structural decay of rock and mineral-based building materials, monuments and other structures. It should be stressed that the activities of all groups of microbes and interactions between them should

be considered in bioweathering, and indeed other geomicrobiological, studies. Fungal–bacterial interactions in the root environment are likely to be significant in mineral weathering and plant nutrition for example (Balogh-Brunstad *et al.*, 2008; Koele *et al.*, 2009).

Bioweathering of rocks and minerals: structural decay of stone

Deterioration of stone monuments represents a permanent loss of cultural heritage (Scheerer *et al.*, 2009; Cutler and Viles, 2010). The most common stone types affected are marble, limestone, sandstone and granite, with many overlaps between calcareous and siliceous rocks. Materials used to stabilize building blocks (mortar) and to coat surfaces prior to painting (plaster or stucco) are also susceptible to degradation. External stone surfaces are a complex ecosystem, including cyanobacteria, bacteria, fungi, protists and also ‘higher’ organisms such as small animals, and plants (Scheerer *et al.*, 2009). Microbial colonization generally initiates with phototrophic cyanobacteria and algae, usually in a biofilm, probably followed by lichens, and then general heterotrophs although establishment of heterotrophic rock communities is possible without initial phototroph involvement (Roeselers *et al.*, 2007). Highly deteriorated stone surfaces provide appropriate conditions (a ‘proto-soil’) for colonization by mosses, ferns and higher plants.

Mechanisms of stone deterioration are complex and include most direct and indirect mechanisms previously discussed for mineral decay (Sand, 1997; Scheerer *et al.*, 2009). The weathering of sandstone monuments by fungi has been attributed to the production of, e.g., acetic, oxalic, citric, formic, fumaric, glyoxylic, gluconic, succinic and tartaric acids. The common formation of biofilms is significant, aiding colonization and survival, with the EPS also capable of metal complexation and weakening of the mineral lattice through wetting and drying cycles. The production of efflorescences (‘salting’) involves secondary minerals produced through reaction of anions from excreted acids with cations from the stone. Such secondary minerals can cause physical damage leading to blistering, flaking, scaling, and granular disintegration, which may often be the main mechanism of stone decay (Wright, 2002). Physical damage may be caused by penetration of fungal hyphae (Hirsch *et al.*, 1995; Cockell and Herrera, 2008). Weakened areas of the stone will be affected first. Lichens cause mechanical damage due to penetration of their rhizines, composed of fungal filaments, and the expansion/contraction of the thallus on wetting/drying, which can lift grains of stone from the surface (Gaylarde and Morton, 2002; De los Rios *et al.*, 2004). ‘Lichen acids’, principally oxalic acid, cause damage at the stone/lichen interface,

and lichen thalli may accumulate 1–50% calcium oxalate, depending on the substrate (Lisci *et al.*, 2003; Seaward, 2003). In addition, carbonic acid formed in the lichen thallus can solubilize calcium and magnesium carbonates in calcareous stone (Tiano, 2002).

Concrete biodeterioration

All types of building and ceramic materials, concrete and cement can be deteriorated by microbes and in some environments, fungi dominate the concrete-deteriorating microbiota (Gu *et al.*, 1998; Nica *et al.*, 2000; Gu, 2009; Scheerer *et al.*, 2009; Cutler and Viles, 2010). Apart from structural uses, cement and concrete are used as barriers in all kinds of nuclear waste repositories. Despite the theoretical service life of such concrete materials reaching up to one million years, biocorrosion is an important factor to take into account over such time periods. Microbial attack on concrete is mediated by protons, inorganic and organic acids and the production of hydrophilic slimes leading to biochemical and biophysical/biomechanical deterioration (Sand, 1997; Fomina *et al.*, 2007c; Scheerer *et al.*, 2009). Fungal degradation may proceed more rapidly than bacterial degradation with complexation suggested as the main mechanism of calcium mobilization. Microfungi from the genera *Aspergillus*, *Alternaria* and *Cladosporium* were able to colonize samples of the concrete used as radioactive waste barrier in the Chernobyl reactor and leached iron, aluminium, silicon and calcium, and re-precipitated silicon and calcium oxalate in their microenvironment (Fomina *et al.*, 2007c). Fungi are also important members of the microbial communities (including lichens) that colonize and deteriorate ‘normal’ concrete and cement used in buildings and other structures.

Bioremediation, biotechnology and bioprocessing

Several fungal metal and mineral transformations have potential for the treatment of environmental pollution (Pumpel and Paknikar, 2001; Gadd, 2004a; 2005). While several fungal-based systems have received interest and commercial development in the context of bioremediation of organic pollutants, there has not been so much attention given to metals. However, it should be stressed that fungi will be components of the microbiota in any metal-polluted sites where their activities may contribute to natural attenuation of the pollutants, and will also be involved in many soil and waste treatment processes, revegetation strategies and effluent treatments. Fungi were clearly important in remediation of selenium-contaminated soils (Thomson-Eagle and Frankenberger, 1992). In addition, fungal mineral-solubilizing properties are important in plant nutrition and soil fertility especially regarding phosphates: their application as biofertilizers is

an accepted concept. In addition to bioremediation, metal- and mineral transformations have applications in other areas of biotechnology and bioprocessing, including biosensors, biocatalysis, electricity generation and nanotechnology.

Bioleaching

Fungal solubilization of metals from solid minerals, metal and mineral wastes, including contaminated soil, for metal recovery, recycling and bioremediation purposes, have all been investigated, although fungal systems cannot compare with established bacterial bioleaching processes and may be more suited to bioreactor applications. Metals can be solubilized from fly ash (originating from municipal solid waste incineration), contaminated soil, electronic scrap and other waste materials by fungal activity (Brandl, 2001; Brandl and Faramarzi, 2006).

Biosorption and bioaccumulation

Biosorption is a physicochemical process, simply defined as 'the removal of substances from solution by biological material'. It is a property of both living and dead organisms (and their components), and has been proposed as a promising biotechnology for removal (and/or recovery) of metals, radionuclides, organic pollutants for many years because of its simplicity, analogous operation to conventional ion exchange technology, and apparent efficiency (Gadd, 1986; 2001a,b; 2009a; Gadd and White, 1990; 1993; Volesky, 1990; Garnham *et al.*, 1992; Wang and Chen, 2006, 2009). The term is now applied to all manner of organic and inorganic pollutants and biosorption can describe 'any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a biosorbent (i.e. a solid surface of a biological matrix) resulting in an accumulation at the sorbate-biosorbent interface, and therefore a reduction in the solution sorbate concentration' (Gadd, 2009a). However, despite dramatic increases in published research on biosorption there has been little or no exploitation in an industrial context. In recent years, modification of biomass has been attempted to improve efficiency or selectivity of microbial biosorbents. Fungal-clay biomineral sorbents combined the sorptive advantages of the individual counterparts, i.e. the high density of metal binding sites per unit area and high sorption capacity of fungal biomass, high sorption affinity, and the high surface area per unit weight mechanical strength and efficient sorption at high metal concentrations of the clay minerals (Fomina and Gadd, 2002b). *Saccharomyces cerevisiae* mutants (*pmr1*Δ) hypersensitive to heavy metals due to increased metal uptake have been investigated for the ability to remove Mn²⁺, Cu²⁺, Co²⁺ or Cd²⁺ from synthetic effluents by a combination of biosorption and intracellular

uptake (Ruta *et al.*, 2009). Phytochelatins are metal-binding cysteine-rich peptides, enzymatically synthesized in plants and certain fungi from glutathione in response to heavy metal stress. Overexpression of PC synthase in bacteria could be a means of improving the metal content of organisms for bioremediation (Valls *et al.*, 2000).

Metalloid bioremediation

Microbial responses to arsenic of bioremediation potential include chelation, compartmentalization, exclusion and immobilization. Attempts to engineer an arsenic accumulating microbe have involved modification of natural resistance mechanisms and development of novel or hybrid pathways into an easily manipulated organism. Thus, PC synthase from *S. pombe* (SpPCS) has been expressed in *E. coli*, resulting in higher As accumulation, these steps being combined in an arsenic efflux deletion *E. coli* strain to achieve the highest reported arsenic accumulation in *E. coli* of 16.8 μmol/g cells (Tsai *et al.*, 2009). A yeast strain coexpressing AtPCS and cysteine desulfhydrase, an aminotransferase that converts cysteine into hydrogen sulfide under aerobic conditions, was used to elevate As accumulation by formation of PC-metal-sulfide complexes (Tsai *et al.*, 2009). The ability of fungi, along with bacteria, to transform metalloids has been utilized successfully in the bioremediation of contaminated land and water. Selenium methylation results in volatilization, a process that has been used to remove selenium from the San Joaquin Valley and Kesterson Reservoir, California, using evaporation pond management and primary pond operation (Thomson-Eagle and Frankenberger, 1992).

Mycoremediation and the mycorrhizosphere

Mycorrhizal associations may have application in the general area of phytoremediation (Rosen *et al.*, 2005; Gohre and Paszkowski, 2006): phytoremediation is the use of plants to remove or detoxify environmental pollutants (Salt *et al.*, 1998). Mycorrhizas may enhance phytoextraction by increasing plant biomass, and some studies have shown increased plant accumulation of metals, especially when inoculated with mycorrhizal fungi isolated from metalliferous environments. However, the potential impact of mycorrhizal fungi on bioremediation may be dependent on many factors including their metal tolerance, and the nutritional status of contaminated soils (Meharg, 2003). In addition, some studies have shown mycorrhizas can reduce plant metal uptake (Tullio *et al.*, 2003). Arbuscular mycorrhizas depressed translocation of zinc to shoots of host plants by binding of metals in mycorrhizal structures and immobilization of metals in the mycorrhizosphere (Christie *et al.*, 2004). It is generally concluded that local conditions in metal-contaminated

sites may determine the relationship between the plant and the arbuscular mycorrhizal fungus, since detrimental, neutral or beneficial interactions have all been documented (Meharg and Cairney, 2000). A protective metal-binding effect of ectomycorrhizal fungi (EcM) has been postulated (e.g. Leyval *et al.*, 1997). A Cu-adapted *Suillus luteus* isolate provided protection against Cu toxicity in pine seedlings exposed to elevated Cu. Such a metal-adapted *Suillus-Pinus* combination might be suitable for large-scale land reclamation at phytotoxic metalliferous and industrial sites (Adriaensen *et al.*, 2005). Ectomycorrhizal fungi persistently fixed Cd(II) and Pb(II), and formed an efficient biological barrier that reduced movement of these metals in birch tissues (Krupa and Kozdroj, 2004). Such mycorrhizal metal immobilization around plant roots, including biomineral formation, may also assist soil remediation and revegetation. Naturally occurring soil organic compounds can stabilize potentially toxic metals like Cu, Cd, Pb and Mn. The insoluble glycoprotein, glomalin, produced in copious amounts on hyphae of arbuscular mycorrhizal fungi can sequester such metals, and could be considered a useful stabilization phenomenon (Gonzalez-Chavez *et al.*, 2004). Phytostabilization strategies may reduce the dispersion of uranium (U) and the environmental risks of U-contaminated soils. *Glomus intraradices* increased root U concentration and content, but decreased shoot U concentrations. Arbuscular mycorrhizal fungi and root hairs improved not only P acquisition but also root uptake of U, and the mycorrhiza generally decreased U translocation from plant root to shoot (Rufy-kiri *et al.*, 2004; Chen *et al.*, 2005a,b).

For ericaceous mycorrhizas, clear host protection has been observed in, e.g. *Calluna*, *Erica* and *Vaccinium* spp. growing on Cu- and Zn-polluted and/or naturally metalliferous soils, the fungus preventing metal translocation to plant shoots (Bradley *et al.*, 1981; 1982). Further, ericaceous plants are generally found on nutrient-deficient soils and it is likely the mycorrhiza could additionally benefit the plants by enhanced nutrient uptake (Smith and Read, 1997). The development of stress-tolerant plant-mycorrhizal associations may therefore be a promising strategy for phytoremediation and soil amelioration (Schutzendubel and Polle, 2002). Ericoid mycorrhizal fungal endophytes, and sometimes their plant hosts, can evolve toxic metal resistance, which enables ericoid mycorrhizal plants to colonize polluted soil (Perotto *et al.*, 2002; Martino *et al.*, 2003). This seems to be a major factor in the success of ericoid mycorrhizal taxa in a range of harsh environments (Cairney and Meharg, 2003).

The importance of mycorrhizas in plant phosphorus nutrition has been appreciated for a long time and their ability to dissolve and transform calcium-containing insoluble compounds and minerals (calcium phosphates, carbonate and sulfate) has been widely studied (Callot

et al., 1985a,b; Lapeyrie *et al.*, 1990; 1991; Gharieb and Gadd, 1999). However, toxic metal mineral solubilization has received little attention, though this should be considered in any revegetation, natural attenuation or phytoremediation strategies. The ectomycorrhizal fungi *Suillus granulatus* and *Pisolithus tinctorius* can promote release of cadmium and phosphorus from rock phosphate (Leyval and Joner, 2001), while the ericoid mycorrhizal fungus *Oidiodendron maius* can solubilize zinc oxide and phosphate (Martino *et al.*, 2003). Many ericoid mycorrhizal and ectomycorrhizal fungi are able to solubilize zinc, cadmium, copper phosphates and lead chlorophosphate (pyromorphite) releasing phosphate and metals (Fomina *et al.*, 2004). Both non-mycorrhizal *Pinus sylvestris* and pines infected with the ectomycorrhizal *Paxillus involutus* were able to enhance zinc phosphate dissolution, withstand metal toxicity and acquire the mobilized phosphorus, increasing the phosphorus amount in shoots when zinc phosphate was present in the growth matrix (Fomina *et al.*, 2006).

Nanoparticle formation and nano-biotechnology

Metal-containing micro-/nano-particles have applications as new ceramic-metal (cermet) or organic-metal (orgmet) composites or structured materials for a variety of applications (Hennebel *et al.*, 2009). The use of metal-accumulating microbes for the production of nanoparticles, and their assembly, may allow control over size, morphology, composition and crystallographic orientation. The production of such biomimetic materials is relevant to the production of new advanced materials, with applications in metal and radionuclide bioremediation, antimicrobial treatments (e.g. nano-silver), solar energy and electrical battery applications, and microelectronics (Dameron *et al.*, 1989; Klaus-Joerger *et al.*, 2001). Because of their high specific surface area and high catalytic properties, biogenic metal products also offer potential for sorption and degradation of organic contaminants, as well as a variety of other applications, e.g. electricity generation in fuel cells, novel catalysts and sensors. Biogenic Mn oxides can sequester metals like Pb, Zn, Co, Ni, As and Cr and also oxidize certain organic pollutants (Hennebel *et al.*, 2009). In contrast to bacteria, rather less attention has been given to fungal systems in this context although fungal reductive transformations of metalloids, Ag and Au species to nano- or colloidal forms are well known, as well as metal-containing reactive crystallites (Dameron *et al.*, 1989) and Mn oxides (Miyata *et al.*, 2004, 2007).

Soil treatment processes and microbial influence

Application to soils of certain amendments that immobilize metals, e.g. lime or phosphate treatment, has demon-

strated enhanced natural remediation resulting in improved vegetation growth, increased microbial activity and diversity, and reduced offsite metal transport. However, while long-term stability of certain metal complexes and compounds has been shown in model systems (Adriano *et al.*, 2004), the influence of plant roots and its microbial and mycorrhizal associations on such stability has often been neglected. For example, pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$], which can form in urban and industrially contaminated soils, can be solubilized by phosphate-solubilizing fungi, with concomitant production of lead oxalate (Sayer *et al.*, 1999; Fomina *et al.*, 2004). The ability of free-living and mycorrhizal fungi to transform pyromorphite (and other toxic metal-containing minerals) should be taken into account in risk assessments of the long-term environmental consequences of *in situ* chemical remediation techniques, revegetation strategies or natural attenuation of contaminated sites. The bioweathering potential of fungi has been envisaged as a possible means for the bioremediation of asbestos rich soils. Several fungi could extract iron from asbestos mineral fibres (e.g. 7.3% from crocidolite and 33.6% from chrysotile by a *Verticillium* sp.), thereby removing the reactive iron ions responsible for DNA damage (Daghino *et al.*, 2006).

Conclusions

Geomycological roles of fungi have often been neglected in wider geomicrobiological contexts but they are of significant importance of in several key areas. These include organic and inorganic transformations, nutrient and element cycling, rock and mineral transformations, bioweathering, mycogenic biomineral formation, fungal–clay interactions, and metal–fungal interactions. It is probably within the terrestrial environment where fungi probably have the greatest geochemical influence especially when considering soil, rock and mineral surfaces, and the plant root–soil interface. However, they are also important in aquatic habitats and since they are now recognized as significant components of aquatic sediments, their importance here may be underestimated. Mutualistic relationships of fungi with phototrophic organisms, lichens (algae, cyanobacteria) and mycorrhizas (plants) are of special significance as geoactive agents. Transformations of metals and minerals are central to many geomycological processes, and fungi possess many properties that can effect changes in metal speciation, toxicity and mobility, as well as mineral formation or mineral dissolution. Such mechanisms are important in natural biogeochemical cycles for metals as well as associated elements in biomass, soil, rocks and minerals, e.g. sulfur and phosphorus, and metalloids, actinides and metal radionuclides. Apart from being important in natural bio-

sphere processes, metal and mineral transformations can have beneficial or detrimental consequences in a human context. Some fungal transformations have beneficial applications in environmental biotechnology, e.g. in metal and radionuclide leaching, recovery, detoxification and bioremediation, and in the production or deposition of biominerals or metallic elements with catalytic or other properties in nanoparticle, crystalline or colloidal forms. Such substances may be relevant to the development of novel biomaterials for technological and antimicrobial purposes. Metal and mineral transformations may also result in adverse effects when these processes result in spoilage and destruction of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), acid mine drainage and associated metal pollution, biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment. The ubiquity and importance of fungi in biosphere processes underline the importance of geomycology as an interdisciplinary subject area within microbiology and mycology and areas of Earth Sciences and mineralogy concerned with abiotic and biotic interfaces.

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