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ABSTRACT

Geomycology is the study of the roles of fungi in geological processes. The biogeochemical importance of fungi is significant in several areas, including nutrient and element cycling, rock, mineral and metal transformations, bioweathering and mycogenic biomineral formation. Such processes can occur in aquatic and terrestrial habitats, but it is 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 many properties that effect changes in metal speciation, toxicity and mobility, as well as mineral formation or mineral dissolution or deterioration. Some fungal transformations have potential applications in environmental biotechnology, e.g. 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), biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment.

INTRODUCTION

Fungi are chemoorganotrophic (heterotrophic) eukaryotic organisms and are ubiquitous in natural and synthetic environments, occurring as unicellular yeasts, polymorphic and filamentous fungi, both free-living and symbiotic (Gadd 1993a; 1999). The most obvious environmental roles of fungi are in organic matter decomposition, plant pathogenicity, phototrophic symbioses (mycorrhizas, lichens), and in the maintenance of soil structure due to their filamentous branching growth habit and exopolymer production (Ritz and Young 2004). The filamentous branching growth pattern enables efficient exploration and colonisation of the substrate, as well as translocation of materials through the colony, and the expression of physical and chemical effects on their surroundings (Boswell *et al.* 2002; Jacobs *et al.* 2002). It is within the terrestrial aerobic ecosystem that fungi exert a significant influence on biogeochemical processes, especially in soil, rock and mineral surfaces, and the plant root–soil interface. For example, mycorrhizal fungi are associated

with approximately 80% of plant species and are responsible for major mineral transformations and redistributions of inorganic nutrients, including metals and phosphate as well as carbon flow, while free-living fungi have major roles in decomposition of organic substances, including xenobiotics, as well as mineral transformations (Fomina *et al.* 2005a; 2007a; 2007b; 2007c; Finlay *et al.* 2009). Fungi are often dominant in the soil, especially in acidic environments, and may operate over a wider pH range than many heterotrophic bacteria. Fungi are also major biodeterioration agents of stone, wood, plaster, cement and other building materials, and important components of rock-inhabiting microbial communities, with roles in mineral dissolution and secondary mineral formation (Gadd 2007a; 2011). The ubiquity and significance of lichens, a fungal growth form, as pioneer organisms in the early stages of mineral soil formation has also a major impact (Haas and Purvis 2006).

Despite the obvious environmental significance of fungi, a broad perception of fungi as agents of biogeochemical change is lacking, and apart from obvious connections with the carbon and nitrogen cycle because of their degradative abilities, they are frequently neglected in contrast to prokaryotes (Gadd 2007a; 2008a; 2008b; 2011). Obviously, much wider metabolic versatility is

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found throughout the prokaryotes, chemoautotrophy and anaerobiosis being particularly obvious examples, but it must be emphasised that fungi are of great importance in aerobic environments (Gadd 2008a; 2008b). Fungal populations are also found in deep subsurface and anaerobic environments, and more information about the biogeochemical transformations they may mediate in such locations will surely arise with further research (Reitner *et al.* 2006; Edgcomb *et al.* 2011; Gadd *et al.* 2012). This review will outline some important roles of fungi as biogeochemical agents, concentrating on metals and minerals, and the significance of these processes for the cycling of elements on global and local scales.

TRANSFORMATIONS OF ROCKS AND MINERALS

Rocks and minerals represent a vast reservoir of elements, many essential to life, and these must be released in forms that can be assimilated by the biota (Burford *et al.* 2003). These include essential metals as well as nutrients like sulfate and phosphate. The most common minerals are the silicates, with non-silicates constituting less than 10% of the Earth's crust, the most abundant of these being carbonates, oxides, sulfides and phosphates. Fungi are involved in the formation and deterioration of minerals, including those produced biogenically. The majority of such interactions are accompanied by changes in metal speciation and mobility.

Mineral formation

Biomining refers to the processes by which organisms form minerals, and it is usually categorised into biologically-induced mineralisation (BIM) and biologically-controlled mineralisation (BCM). Biologically-induced mineralisation is where an organism modifies its local microenvironment, creating conditions that favour extracellular precipitation of mineral phases. Whereas the organism does not appear to control the biomining process in BIM, a great degree of control is exerted in BCM, e.g. in the formation of complex cellular biomining structures found in certain eukaryotes (Gadd and Raven 2010). Fungal biomining therefore usually refers to biologically-induced mineralisation. This can result from oxidation or reduction of a metal species, and metabolite excretion, e.g. CO₂, oxalate. 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 formation of mineral precipitates (Lloyd *et al.* 2008; Gadd 2009a; 2010). This process may be important

in the soil because precipitation of carbonates, phosphates and hydroxides increases soil aggregation. Cations like Si⁴⁺, Fe³⁺, Al³⁺ and Ca²⁺ (which may be released through dissolution mechanisms) stimulate precipitation of compounds that may act as bonding agents for soil particles (Bronick and Lal 2005).

Mineral biodeterioration

Direct and indirect physical, chemical and biochemical mechanisms are involved in rock and mineral biodeterioration (Sand 1997; Edwards *et al.* 2005; Lian *et al.* 2008; Bonneville *et al.* 2009, 2011; McMaster 2012). Bioweathering is another term that can be used to refer to the erosion, decay or transformation of rocks and minerals mediated by living organisms and their activities (Hoffland *et al.* 2004; McMaster 2012). Biomechanical deterioration 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, and they can occur through excretion of, e.g. H⁺, CO₂, 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 biodeterioration of uranium oxides and depleted uranium (Fomina *et al.* 2007a; 2007b; 2008; Gadd and Fomina 2010). 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 by the excretion of protons and organic acids, while respiratory CO₂ 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). The origin of fungal tunnels within soil minerals has been explained as a result of dissolution and 'burrowing' 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 that 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 colonisation

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 Breeman *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 fossil signatures of previous biogeochemical fungal activity (Fomina *et al.* 2010).

COMMON FUNGAL MINERAL AND BIOMINERAL TRANSFORMATIONS

Fungi can be involved in many different kinds of mineral transformations (Gleeson *et al.* 2007; Rosling *et al.* 2009; Smits 2009; Wei *et al.* 2013), especially when considering their capacity for the production of mineral-transforming metabolites, their symbiotic associations, and their significant roles in organic matter decomposition. It should be noted that 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 microbial colonisation and biofilm formation, and for the ecology of microbial populations associated with mineral substrates including fungi (Vaughan *et al.* 2002; Gleeson *et al.* 2005; 2007; 2010; Bowen *et al.* 2007; Brown *et al.* 2008; Hutchens 2009).

Carbonates

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 a result of acid formation, but may also involve physical processes (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 limestones (Golubic *et al.* 2005; Cockell and Herrera 2008). Fungal attack on carbonates (dolomites and limestones) can result in diagenesis of these substrates to dolomite ($\text{Ca Mg}(\text{CO}_3)_2$, glushinskite ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 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 possibly struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), as well as intense substrate 'de-micritisation' and 'micritisation' (micritisation is a process by which the original grain structure in a carbonate sediment is transformed into a fine-grained or cryptocrystalline carbonate)

with oxalates, grain bridging and cementation, open space filling, formation of intergranular and intragranular porosity, and permeability enhancement. Advanced stages of diagenesis may be characterised by dissolution and replacement of original minerals by the new substrates produced by fungal biomineralisation activities (Kolo *et al.* 2007). Other metals may also be associated with carbonate precipitation. In *Paecilomyces marquandii*, for example, efficient Zn^{2+} and Pb^{2+} uptake was associated with the presence of the metal hydrocarbonates on the mycelium surface (Slaba and Dlugonski 2011).

Oxalates

Calcium oxalate is the most common environmental form of oxalate, occurring as the dihydrate (weddellite) or the more stable monohydrate (whewellite) (Gadd 1999). Calcium oxalate crystals can be associated with free-living, pathogenic and plant symbiotic fungi and with lichens, and are formed by precipitation of solubilised calcium as the oxalate (Lapeyrie *et al.* 1990; Gharieb *et al.* 1998; 1999; Gadd 1999; Adamo and Violante 2000; Adamo *et al.* 2002; Guggiari *et al.* 2011; Pinzari *et al.* 2010; 2013). The initial precipitation phase is the trihydrate, which loses water of crystallization to form either the dihydrate or monohydrate, depending on conditions. Fungal calcium oxalate exhibits 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 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). The precipitation of toxic metals as insoluble oxalates may contribute to fungal metal tolerance (Dutton and Evans 1986; Gadd 1993a; Jarosz-Wilkolazka and Gadd 2003). Many fungi are also capable of oxalate degradation, especially wood-rotting species (Guggiari *et al.* 2011).

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 biomineralised fungal filaments 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 glushinskite ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (Burford *et al.* 2003a, 2003b,

2006; Gadd 2007a). Fungal attack on dolomitic and seawater substrates resulted in the formation of Ca-oxalates (weddelite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and glushinskite ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (Kolo and Claeys 2005).

Oxides

Several fungi can promote Mn(II) oxidation to Mn(IV) O_2 including *Acremonium* spp. (Miyata *et al.* 2004, 2007; Saratovsky *et al.* 2009). 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, e.g. reactive moieties in the cell wall (Ehrlich and Newman 2009) although the involvement of laccase and/or multicopper oxidases have been shown in ascomycetes (Miyata *et al.* 2004, 2007). The MnO_x material produced by *Acremonium* KR21-2 has a todorokite-like tunnel structure, which is in contrast to previously reported microbial MnO_x materials, which adopt layered birnessite-type structures (todorokite and birnessite are two types of manganese oxide minerals) (Saratovsky *et al.* 2009). Non-enzymatic microbial Mn^{2+} oxidation may be effected through production of metabolites, e.g. hydroxycarboxylic acids such as citrate, lactate, malate, gluconate or tartrate. Some fungi can oxidise Mn(II) and Fe(II) in metal-bearing minerals such as siderite (FeCO_3) and rhodochrosite (MnCO_3) and precipitate them as oxides (Grote and Krumbein 1992). Manganese and iron oxides are major components (20%–30%) along with clay (approximately 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 mobilise oxidised or fixed manganese, releasing it into the aqueous phase. Most of those fungi that reduce Mn(IV) oxides such as MnO_2 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; Wei *et al.* 2012a).

PHOSPHATES

Phosphorus occurs primarily as organic phosphate esters and inorganic forms, e.g. calcium, aluminium, and iron phosphates. Organic phosphates are hydrolyzed by phosphatases that 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-solubilising activity is very important in the plant mycorrhizosphere for plant nutrition (Whitelaw *et al.* 1999).

Microbes can also play a role in the formation of phosphate minerals such as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$). The orthophosphate may arise from organic phosphate degradation, while Fe or Al may arise from microbial solubilisation 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 ($\text{NH}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$) and/or chernikovite ($\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (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 free-living and symbiotic fungi as well as 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; Banfield *et al.* 1999; Adamo and Violante 2000; Arocena *et al.* 1999; 2003; Tazaki 2006; Theng and Yuan 2008; Bonneville *et al.* 2009; Gleeson *et al.* 2010; Wei *et al.* 2012b; 2013). 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 (the type of mycorrhiza where the mycobiont forms a sheath around plant root tips so that the bulk of biomass is outside the root) (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 substances with chelating properties, e.g. organic acids, other acids (mineral or organic) and metabolites, together with biomechanical effects (Cromack *et al.* 1979; De la Torre *et al.* 1993; Mandal *et al.* 2002; Wei *et al.* 2013). Metabolic agents may be excreted into the bulk phase but may also involve adhering

organisms and biofilms on surfaces of silica or silicates that result in etching (Bennett *et al.* 2001; Wei *et al.* 2012b). After colonisation of muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH}_2)$ (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.* 2012b). Such mechanisms of silicate dissolution may be instrumental in releasing limiting nutrients like bound P and Fe. The bioweathering process may be initiated by biomechanical distortion of the lattice structure in biotite ($\text{K}(\text{Mg}, \text{Fe}(\text{II}))_3\text{AlSi}_3\text{O}_{10}(\text{OH}, \text{O}, \text{F})_2$), which subsequently becomes altered through dissolution and oxidation mechanisms that lead to mineral neoformation (Bonneville *et al.* 2009, 2011).

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 ($(\text{Mg}, \text{Fe}(\text{II}), \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_{2.4}\text{H}_2\text{O}$) (Barker and Banfield 1996). The fungal partner has also been reported to be involved in formation of secondary silicates, such as opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and forsterite (Mg_2SiO_4), in lichen thalli (Gorbushina *et al.* 2001). The transformation rate of mica (the general formula for minerals of the mica group is $\text{XY}_{2-3}\text{Z}_4\text{O}_{10}(\text{OH}, \text{F})_2$ with $X = \text{K}, \text{Na}, \text{Ba}, \text{Ca}, \text{Cs}, (\text{H}_3\text{O}), (\text{NH}_4)$; $Y = \text{Al}, \text{Mg}, \text{Fe}^{2+}, \text{Li}, \text{Cr}, \text{Mn}, \text{V}, \text{Zn}$; and $Z = \text{Si}, \text{Al}, \text{Fe}^{3+}, \text{Be}, \text{Ti}$) and chlorite ($(\text{Mg}, \text{Fe}, \text{Li})_6\text{AlSi}_3\text{O}_{10}(\text{OH})_8$) to 2:1 expandable clays was pronounced in ectomycorrhizosphere soil and probably a result of 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 stabilisation (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 2002a; 2002b).

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 $[\text{Se}(\text{VI})]$ and selenite $[\text{Se}(\text{IV})]$ to elemental selenium $[\text{Se}(0)]$; tellurite $[\text{Te}(\text{IV})]$ to elemental tellurium $[\text{Te}(0)]$ (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* species was able to grow at arsenate concentrations of 0.2M, and it was suggested that increased arsenate reduction contributed to tolerance (Canovas *et al.* 2003a; 2003b). An enhanced H_3AsO_3 efflux system was found to operate in an As-mine site isolate of *Hymenoscyphus ericae* as a mechanism for H_2AsO_4^- resistance (Sharples *et al.* 2000). 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 ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), iron gluconate, calcium formate, forsterite, goethite ($\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$), halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) (Grote and Krumbein 1992; Hirsch *et al.* 1995; Verrecchia 2000; Gorbushina *et al.* 2001; Burford *et al.* 2003b; Arocena *et al.* 2003). *Lichenothelia* spp can oxidise 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 certain fungi can lead to the formation of dark patinas on glass surfaces (Erkhardt 1985).

METAL, METALLOID, RADIONUCLIDE AND ORGANOMETAL TRANSFORMATIONS

Metals and their compounds interact with fungi in various ways depending on the metal species, organism and environment, while fungal metabolism also influences metal speciation and mobility (Gadd and Griffiths 1978; Gadd *et al.* 1984; Gadd 1992; 1993a; 2004a; 2004b; 2005; 2007a; 2007b; 2008a; 2008b; 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, Ag, Hg and Pb, have no known biological function, but can all be accumulated by fungi. Despite apparent toxicity, many fungi survive in metal-polluted locations, and a variety of mechanisms, both active and incidental,

contribute to tolerance (Gadd 1984; 1993a; Ramsay and Gadd 1997; Blaudez *et al.* 2000a; Perotto and Martino 2001; Baldrian 2003; Meharg 2003; Gadd *et al.* 2005; Jarosz-Wilkolazka *et al.* 2006).

Fungi have many properties that influence metal mobility and toxicity, including the production of metal-binding proteins, organic and inorganic precipitation, active transport and intracellular compartmentalisation, while major constituents of cell walls, e.g. chitin and melanin, have significant metal binding abilities (Gharieb and Gadd 1998; Gadd 2004a; 2004b; 2005; 2006; 2008c). Other properties such as excretion of extracellular enzymes, organic acids, H^+ and siderophores can lead to metal solubilisation/mobilisation from organic and inorganic sources (Gadd 2007a; 2007b). 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; 2004b). 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 considered in terms of metal mobilisation or immobilisation mechanisms.

METAL MOBILISATION

Metal mobilisation 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 and other excreted metabolites (e.g. amino acids, phenolic compounds, and organic acids) and methylation, which can result in volatilisation. 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). Oxalic acid can act as a leaching agent for metals that form soluble oxalate complexes, including Al and Fe (Strasser *et al.* 1994). Solubilisation mechanisms can also have consequences for mobilisation 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; 2005c). Fungi may also mobilise metals and attack mineral 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 to prokaryotic processes.

Reduction of Hg(II) to volatile elemental Hg(0) can also be mediated by fungi (Gadd 1993b).

METAL IMMOBILISATION

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 including minerals onto and/or around hyphae (Mowll and Gadd 1984; Gadd and Mowll 1985; Gadd 1993a; 2000a; 2000b; 2001a; 2001b; 2001c; 2007a; Baldrian 2003; Fomina *et al.* 2007b, 2007c). Metals can also be translocated and/or accumulated by fruiting bodies (e.g. Borovicka *et al.* 2010). 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). A variety of functional groups can be involved in biosorption and also metal association with other cellular components and macromolecules. Fungal activities in generating lignin-derived soil organic matter with cation-binding properties through wood decay are also significant in an environmental context (Northup *et al.* 1995). 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).

MINERAL TRANSFORMATIONS MEDIATED BY FUNGAL SYMBIOSES

Fungi form extremely important mutualistic partnerships with plant roots (mycorrhizas) and algae or cyanobacteria (lichens). Symbiotic fungi are provided with carbon by the photosynthetic partners (photobionts), while the fungi may protect the host plant from harsh environmental conditions (e.g., desiccation, metal toxicity), increase the absorptive area and provide increased access to mineral nutrients.

LICHENS

Lichens, e.g. *Xanthoria parietina*, are fungi that exist in facultative or obligate symbioses with one or more photosynthesising partners (e.g. the green alga *Trebouxia*, found in the majority of lichen species, and the cyanobacterium *Nostoc*, found in about 10% of lichen species) and found in almost all surface

terrestrial environments: an estimated 6%–8% of the Earth's land surface is dominated by lichens (Haas and Purvis 2006). Lichens play an important role in many biogeochemical processes, and are pioneer colonisers 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 in rock weathering (Lisci *et al.* 2003). Alteration of bedrock minerals and biomineralisation 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; Chen *et al.* 2000; Adamo and Violante 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; 2008; Wang and Qui 2006). Two main types include endomycorrhizas, where the fungus colonises 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 solubilisation, proton-promoted and ligand-promoted metal mobilisation from mineral sources, metal immobilisation within biomass, and extracellular precipitation of mycogenic metal oxalates (Lapeyrie *et al.* 1991; Blaudez *et al.* 2000a, 2000b; Christie *et al.* 2004; Fomina *et al.* 2004, 2005b; Bellion *et al.* 2006; Fomina *et al.* 2006; Finlay *et al.* 2009; McMaster 2012; Smits *et al.* 2012). Biogeochemical activities of mycorrhizal fungi lead to changes in the physico-chemical characteristics of the root environment and enhanced weathering of soil minerals (Bonneville *et al.* 2009; McMaster 2012). Furthermore, 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. colonisation, carbon allocation and substrate acidification (Roslind *et al.* 2004a; 2004b).

During growth, mycorrhizal fungi often excrete carboxylic acids, proteins and siderophores (Renshaw *et al.* 2002; Martino *et al.* 2003; Fomina *et al.* 2004; Gonzalez-Chavez *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; Perotto *et al.* 2002; Martino *et al.* 2003; Fomina *et al.* 2004, 2005b). Mobilisation of phosphorus from inorganic and organic phosphorus sources is generally regarded as one of the most important functions of mycorrhizal fungi (Smits *et al.* 2012), and this will also result in movement and redistribution of associated metals, and the formation of other secondary minerals including other metal phosphates.

ORGANIC MATTER DEGRADATION AND BIOGEOCHEMICAL CYCLING OF THE ELEMENTS

Organic matter decomposition is one of the most important microbial activities in the biosphere, and the ability of microbes, mainly bacteria and fungi, to use a wide spectrum of organic compounds is well-known. These range from simple compounds such as sugars, organic acids and amino acids to more complex molecules, which may be broken down by extracellular enzymes before cellular uptake and metabolism. These latter compounds include cellulose, pectin, lignin, lignocellulose, chitin and starch, and also hydrocarbons, pesticides, and other xenobiotics that may be anthropogenically produced. Degradation of such substances results in redistribution of component elements between organisms and environmental compartments. The vast majority of elements in plant, animal and microbial biomass (> 95%) comprise carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur, and, as well as these, several other elements are typically found in living organisms, mostly in essential biochemical and structural functions, e.g. K, Ca, Mg, B, Cl, Fe, Mn, Zn, Cu, Mo, Ni, Co, Se, Na, and Si. However, all 90 or so naturally occurring elements may be found in plants, animals and microbes, including Au, Ag, As, Hg, Pb, Cd and U (e.g. Borovicka *et al.* 2010). Some of these elements will be taken up as contaminants in food and from the environment.

Therefore, it should be stressed that all decomposition, degradative and pathogenic microbial activities are linked to cycling of these constituent elements, many of which are metals and some of which may be radionuclides accumulated from anthropogenic sources. This simple perspective on organic matter decomposition illustrates the global involvement of microbes in elemental cycling.

ENVIRONMENTAL AND APPLIED SIGNIFICANCE OF GEOMYCOLOGICAL PROCESSES

The mechanisms of metal and mineral transformations described previously are of considerable environmental and applied significance (Mapelli *et al.* 2012). In an adverse context, fungi may be involved in biocorrosion of metals and the bio-leaching of metals from contaminated soils or other wastes, which may contribute to redistribution of toxic metals via acidic leachates (Burgstaller and Schinner 1993; Beech and Sunner 2004; Gu 2009). This process may also be considered to have potential for biorecovery of metals from wastes, scrap metal, and electronic waste (Burgstaller and Schinner 1993; Gadd 2000a; Gadd and Sayer 2000; Brandl 2001; Santhiya and Ting 2005; Kartal *et al.* 2006; Brandl and Faramarzi 2006). Fungal bio-weathering activities are intimately involved not only in soil formation and development, but also in the decay of stone and mineral-based building materials, concrete, and cultural heritage (Gorbushina *et al.* 1993; Gu *et al.* 1998; Sterflinger 2000; Verrecchia 2000; Gaylarde and Morton 2002; Seaward 2003; Burford *et al.* 2003a; 2003b; Gadd 2007a; Fomina *et al.* 2007c; Gorbushina and Broughton 2009; Scheerer *et al.* 2009; Sverdrup 2009; Cutler and Viles 2010; Pinzari *et al.* 2010; 2013; Sterflinger 2010). In a bioremediation context, fungi, like other microbial groups, have been explored in areas of bioleaching, biosorption and bioaccumulation (Mowll and Gadd 1984; Gadd and Mowll 1985; Burgstaller and Schinner 1993; Gadd and White 1993; Wang and Chen 2006; 2009; Volesky 2007; Gadd 2009a), although the greatest successes have resulted from *in situ* bioremediation approaches for selenium-contaminated soils and sediments, and in composting and soil bioremediation treatments for organic substances (Thomson-Eagle and Frankenberger 1992). It should be emphasised that any contaminated soil management processes, including revegetation, are likely to involve fungi, both free-living and mycorrhizal, with the mycorrhizosphere being a particularly geoactive environment (Rufiyikiri *et al.* 2004; Adriaensen *et al.* 2005; Chen *et al.* 2005a, 2005b; Koele *et al.* 2009; Turnau *et al.* 2012). Mycoremediation is a term that has been used to specifically

describe bioremediation approaches using fungi (Krupa and Kozdroj 2004; Rosen *et al.* 2005; Daghighi *et al.* 2006; Gohre and Paszkowski 2006; Gadd *et al.* 2007). The use of fungi for the production or deposition of biominerals or metallic elements with catalytic or other properties, e.g. nanosilver, has also received attention (Dameron *et al.* 1989; Miyata *et al.* 2004; 2007; Hennebel *et al.* 2009).

CONCLUSIONS

Geomycological roles of fungi are often neglected in wider geomicrobiological contexts but are of importance 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 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, where their importance may be underestimated. Mutualistic relationships of fungi with phototrophic organisms, lichens (algae, cyanobacteria) and mycorrhizas (plants) are of special significance as geoactive agents. Metal and mineral transformations are central to many geomycological processes, and fungi possess many properties that 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 biosphere processes, metal and mineral transformations can have beneficial or detrimental consequences in a human context. Beneficial applications in environmental biotechnology include metal and radionuclide leaching, recovery, detoxification, and bioremediation, and the production or deposition of biominerals or metallic elements with catalytic or other properties in nanoparticle, crystalline or colloidal forms. Metal and mineral transformations may also cause adverse effects when these processes result in spoilage and destruction of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete); acidic leachates 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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