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Geomycology: biogeochemical transformations of rocks, minerals, metals and radionuclides by fungi, bioweathering and bioremediation

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ABSTRACT

The study of the role that fungi have played and are playing in fundamental geological processes can be termed 'geomycology' and this article seeks to emphasize the fundamental importance of fungi in several key areas. These include organic and inorganic transformations and element cycling, rock and mineral transformations, bioweathering, mycogenic mineral formation, fungal–clay interactions, metal–fungal interactions, and the significance of such processes in the environment and their relevance to areas of environmental biotechnology such as bioremediation. Fungi are intimately involved in biogeochemical transformations at local and global scales, and although such transformations occur in both aquatic and terrestrial habitats, it is the latter environment where fungi probably have the greatest influence. Within terrestrial aerobic ecosystems, fungi may exert an especially profound influence on biogeochemical processes, particularly when considering soil, rock and mineral surfaces, and the plant root–soil interface. The geochemical transformations that take place can influence plant productivity and the mobility of toxic elements and substances, and are therefore of considerable socioeconomic relevance, including human health. Of special significance are the mutualistic symbioses, lichens and mycorrhizas. Some of the fungal transformations discussed have beneficial applications in environmental biotechnology, e.g. in metal leaching, recovery and detoxification, and xenobiotic and organic pollutant degradation. They may also result in adverse effects when these processes are associated with the degradation of foodstuffs, natural products, and building materials, including wood, stone and concrete. It is clear that a multidisciplinary approach is essential to understand fully all the phenomena encompassed within geomycology, and it is hoped that this review will serve to catalyse further research, as well as stimulate interest in an area of mycology of global significance.

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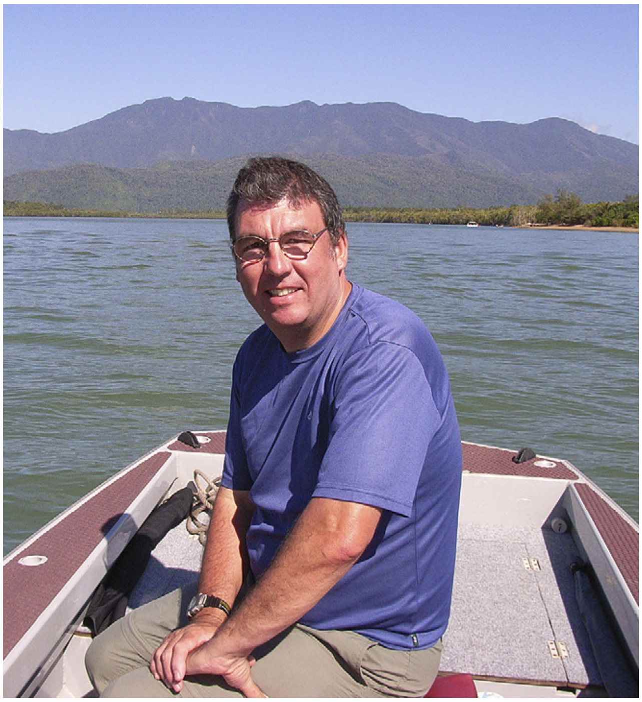

Fig 1 – Geoffrey Michael Gadd (President, British Mycological Society 2004–2006).

Introduction

Fungi are chemoheterotrophic organisms, ubiquitous in subaerial and subsoil environments, and important as decomposers, animal and plant mutualistic symbionts and pathogens, and spoilage organisms of natural and manufactured materials (Gadd 1993a, 1999, 2006; Burford *et al.* 2003a). They also have a role in the maintenance of soil structure, due to their filamentous branching growth habit and frequent exopolymer production. A fungal role in biogeochemical cycling of the elements (e.g. carbon, nitrogen, phosphorus, sulphur, metals) is obvious and interlinked with the ability to adopt a variety of growth, metabolic and morphological strategies, their adaptive capabilities to environmental extremes and, their mutualistic associations with animals, plants, algae and cyanobacteria (Burford *et al.* 2003a; Gadd 2004; Braissant *et al.* 2004; Fomina *et al.* 2005a). Fungal polymorphism and reproduction by spores underpin successful colonization of many different environments. Most fungi exhibit a filamentous growth habit, which provides the ability to adopt both explorative or exploitative growth strategies, and the formation of linear organs of aggregated hyphae for protected fungal translocation (Fomina *et al.* 2005a, 2005b). Some fungi are polymorphic, occurring as both filamentous mycelium and unicellular yeasts or yeast-like cells, as in black meristematic or microcolonial fungi colonizing rocks (Sterflinger 2000; Gorbushina *et al.* 2002a, 2002b, 2003). Fungi can also grow inside their own parental hyphae, utilizing dead parts of the colony under the protection of parental cell walls (Gorbushina *et al.* 2003). The ability of fungi to translocate nutrients through the mycelial network is another important feature for exploring heterogeneous environments (Lindahl & Olsson 2004; Jacobs *et al.* 2002a, 2002b, 2004; Boswell *et al.* 2002, 2003, 2006).

However, a broader appreciation of fungi as agents of biogeochemical change is lacking, and apart from obvious connections with the carbon cycle, they are frequently neglected within broader microbiological and geochemical research contexts. While the profound geochemical activities of bacteria and archaea receive considerable attention, especially in relation to carbon-limited and/or anaerobic environments (Gadd *et al.* 2005a), in aerobic environments fungi are of great importance, especially when considering rock surfaces, soil and the plant root–soil interface (Fig 2, Table 1) (Gadd 2005, 2006; Fomina *et al.* 2005a, 2005b; Gadd *et al.* 2005a, 2005b, 2006). For example, mycorrhizal fungi are associated with ~80 % of plant species, and are involved in major mineral transformations and redistributions of inorganic nutrients, e.g. essential metals and phosphate, as well as carbon flow (Paris *et al.* 1995; Hoffland *et al.* 2002; Fomina *et al.* 2004, 2005b). Free-living fungi have major roles in the decomposition of plant and other organic materials, including xenobiotics, as well as mineral solubilization (Gadd 2004). Lichens (a fungal growth form comprising a mutualistic symbiosis between an alga and/or cyanobacterium and a fungus) are one of the commonest members of the microbial consortia, inhabiting exposed rock substrates, and play fundamental roles in early stages of rock colonization and mineral soil formation. Fungi are also major biodeterioration agents of stone, wood, plaster, cement and other building materials, and it is now realized that they are important components of rock-inhabiting microbial communities with significant roles in mineral dissolution and secondary mineral formation (Hughes and Lawley 2003; Burford *et al.* 2003a, 2003b, 2006; Fomina *et al.* 2005a, 2005b). There is even some evidence that several fungi can dissolve minerals and mobilize metals at higher pH values, and over a wider redox range,

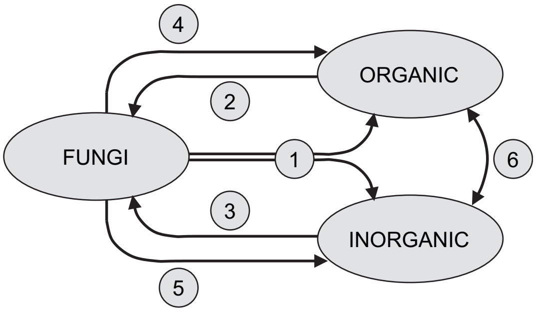

Fig 2 – Simple model of fungal action on naturally-occurring and/or anthropogenically-derived organic and inorganic substrates. (1) Organic and inorganic transformations mediated by enzymes and metabolites, e.g. protons (H^+), carbon dioxide (CO_2), and organic acids, and physicochemical changes occurring as a result of metabolism; (2) uptake, metabolism or degradation of organic substrates; (3) uptake, accumulation, sorption, metabolism of inorganic substrates; (4) production of organic metabolites, exopolymers, and biomass; (5) production of inorganic metabolites, secondary minerals and transformed metal(loid)s; and (6) chemical interactions between organic and inorganic substances, e.g. complexation and chelation (from Gadd 2004).

Table 1 – Some important roles and activities of fungi in biogeochemical processes

Fungal role and/or activity	Biogeochemical consequences
Growth	
Growth and mycelium development	Stabilization of soil structure; soil particulate aggregation; penetration of pores, fissures, and grain boundaries in rocks and minerals; mineral tunnelling; biomechanical disruption of solid substrates; plant colonization and/or infection (mycorrhizas, pathogens, parasites); animal colonization and/or infection (symbiotic, pathogens, parasites); translocation of inorganic and organic nutrients; assisted redistribution of bacteria; production of exopolymeric substances (serve as nutrient resource for other organisms); water retention and translocation; surfaces for bacterial growth, transport and migration; cord formation (enhanced nutrient translocation); mycelium acting as a reservoir of nitrogen and/or other elements (e.g. wood decay fungi)
Metabolism	
Carbon and energy metabolism	Organic matter decomposition; cycling and/or transformations of component elements of organic compounds and biomass: carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur, metals, metalloids, radionuclides (natural and accumulated from anthropogenic sources); breakdown of polymers; altered geochemistry of local environment, e.g. changes in redox, oxygen, pH; production of inorganic and organic metabolites, e.g. protons, carbon dioxide, organic acids, with resultant effects on the substrate; extracellular enzyme production; fossil fuel degradation; oxalate formation; metalloid methylation (e.g. arsenic, selenium); xenobiotic degradation (e.g. polynuclear aromatic hydrocarbons); organometal formation and/or degradation (note: lack of fungal decomposition in anaerobic conditions caused by water logging can lead to organic soil formation, e.g. peat)
Inorganic nutrition	Altered distribution and cycling of inorganic nutrient species, e.g. nitrogen, sulphur, phosphorus, essential and inessential metals, by transport and accumulation; transformation and incorporation of inorganic elements into macromolecules; alterations in oxidation state; metal(loid) oxido-reductions; heterotrophic nitrification; siderophore production for iron(III) capture; translocation of nitrogen, phosphorus, calcium, magnesium, sodium, potassium through mycelium and/or to plant hosts; water transport to and from plant hosts; metalloid oxyanion transport and accumulation; degradation of organic and inorganic sulphur compounds
Mineral dissolution	Rock and mineral deterioration and bioweathering including carbonates, silicates, phosphates and sulphides; bioleaching of metals and other components; manganese dioxide (MnO_2) reduction; element redistributions including transfer from terrestrial to aquatic systems; altered bioavailability of, e.g. metals, phosphorus, sulphur, silicon, aluminium; altered plant and microbial nutrition or toxicity; early stages of mineral soil formation; deterioration of building stone, cement, plaster, concrete etc.
Mineral formation	Element immobilization including metals, radionuclides, carbon, phosphorus, and sulphur; mycogenic carbonate formation; limestone calcrete cementation; mycogenic metal oxalate formation; metal detoxification; contribution to patinas on rocks (e.g. 'desert varnish'); soil storage of carbon and other elements
Physico-chemical properties	
Sorption of soluble and particulate metal species	Altered metal distribution and bioavailability; metal detoxification; metal-loaded food source for invertebrates; prelude to secondary mineral formation
Exopolysaccharide production	Complexation of cations; provision of hydrated matrix for mineral formation; enhanced adherence to substrate; clay mineral binding; stabilization of soil aggregates; matrix for bacterial growth; chemical interactions of exopolysaccharide with mineral substrates
Mutualistic symbiotic associations	
Mycorrhizas	Altered mobility and bioavailability of nutrient and inessential metals, nitrogen, phosphorus, sulphur, etc; altered carbon flow and transfer between plant, fungus and rhizosphere organisms; altered plant productivity; mineral dissolution and metal and nutrient release from bound and mineral sources; altered biogeochemistry in soil–plant root region; altered microbial activity in plant root region; altered metal distributions between plant and fungus; water transport to and from the plant
Lichens	Pioneer colonization of rocks and minerals; bioweathering; mineral dissolution and/or formation; metal accumulation and redistribution; metal accumulation by dry or wet deposition, particulate entrapment; metal sorption; enrichment of carbon, nitrogen, etc; early stages of mineral soil formation; development of geochemically-active microbial populations; mineral dissolution by metabolites including 'lichen acids'; biophysical disruption of substrate
Insects and other invertebrates	Fungal populations in gut aid degradation of plant material; invertebrates mechanically render plant residues more amenable for decomposition; cultivation of fungal gardens by certain insects (organic matter decomposition and recycling); transfer of fungi between plant hosts by insects (aiding infection and disease)

(*continued on next page*)

Table 1 (*continued*)

Fungal role and/or activity	Biogeochemical consequences
Pathogenic effects	
Plant and animal pathogenicity	Plant infection and colonization; animal predation (e.g. nematodes) and infection (e.g. insects, etc); redistribution of elements and nutrients; increased supply of organic material for decomposition; stimulation of other geochemically-active microbial populations

Such activities take place in aquatic and terrestrial ecosystems, as well as in artificial and man-made systems, their relative importance depending on the species present and physico-chemical factors that affect activity. The terrestrial environment is the main locale of fungal-mediated biogeochemical change, especially in mineral soils and the plant root zone, and on exposed rocks and mineral surfaces. There is rather a limited amount of knowledge on fungal biogeochemistry in freshwater and marine systems, sediments, and the deep subsurface. Fungal roles have been arbitrarily split into categories based on growth, organic and inorganic metabolism, physicochemical attributes, and symbiotic relationships. However, it should be noted that many if not all of these are inter-linked, and almost all directly or indirectly depend on the mode of fungal growth (including symbiotic relationships) and accompanying heterotrophic metabolism, in turn dependent on a utilizable carbon source for biosynthesis and energy, and other essential elements, such as nitrogen, oxygen, phosphorus, sulphur and many metals, for structural and cellular components. Mineral dissolution and formation are outlined separately although these processes clearly depend on metabolic activity and growth form (from Gadd 2007a).

faster and more efficiently than bacteria (Gu *et al.* 1998; Castro *et al.* 2000; Burford *et al.* 2003a).

The earliest fossil filamentous fungal remains appear to be from the mid- to late Precambrian (1430–1542 M years ago; Butterfield 2005), and they were extremely diverse by Devonian, times, when forms belonging to major groups and even some genera present today are found (Taylor & Osborn 1996; Taylor *et al.* 1994, 1997, 2005; Heckman *et al.* 2001). Since that time fungi have been ubiquitous components of the microbial communities of any terrestrial environment (Hawksworth 2001), including such hostile habitats as the arctic and Antarctic, hot deserts, and metal-rich and hypersaline soils (Burford *et al.* 2003a). The ability of many fungi to grow oligotrophically by scavenging nutrients from the air and rainwater helps them survive on stone and rock surfaces, which are usually considered to be an inhospitable environment (Wainwright *et al.* 1993). In addition, organic and inorganic residues on mineral surfaces or within cracks and fissures, waste products of other microorganisms, decaying plants and animals, dust particles, aerosols and animal faeces can also act as nutrient sources in the subaerial rock environment (Sterflinger 2000). Inhabitants of subaerial surfaces include poikilotrophic fungi, which are able to deal with varying extremes in microclimatic conditions, including irradiation, salinity, pH, and water potential, and which protect themselves by producing antioxidant protectors, such as melanins and mycosporines in their in cell walls, and by embedding colonies in mucilaginous polysaccharides that often contains clay particles (Gorbushina *et al.* 2003; Volkmann *et al.* 2003). One of the most successful means enabling fungi to survive in the extreme subaerial environment is by means of forming mutualistic symbioses with algae and cyanobacteria as lichens, where the phototrophs provide a source of carbon and are protected to some degree from light and irradiation (Gorbushina *et al.* 1993; Sterflinger 2000). As discussed later in this review, fungi are able to weather a wide range of rocks (Burford *et al.* 2003a). In subpolar areas, notably Iceland, the bioweathering of basaltic outcrops by fungal communities is believed to be chronologically the first process of weathering and followed by subsequent cryogenic processes (Etienne & Dupont 2002). The majority of fungi inhabit soil environments, which are seemingly much more hospitable than bare rock surfaces. Fungal communities in soil are diverse and include free-living and symbiotic fungi, as well as plant and animal pathogens, and unicellular yeasts.

Fungi encounter metals as normal components of the natural environment, as well as those introduced or redistributed by human activities. Like other organisms, fungi possess a variety of properties that can influence interactions with metals, while ‘normal’ growth and metabolism is dependent on metal and metal–mineral interactions to satisfy trace metal and associated nutrient requirements. Nevertheless, at potentially toxic metal concentrations, a variety of resistance mechanisms may be expressed: sensitive organisms may be vulnerable and population changes can result. Although metal toxicity can be influenced by the physico-chemical attributes of the environment, fungi possess a variety of intrinsic and inducible properties that can ensure survival. It seems fungi can be isolated from any habitats polluted by toxic metals.

The objective of this review is to outline important fungal roles and functions in rock, mineral, metal and soil transformations, and to emphasize the importance of fungi as agents of geochemical change. It also outlines the effects toxic metals may have on fungal communities, the physiological and morphological strategies employed to combat metal stress, mechanisms of resistance, fungal-mediated metal transformations, and the role of fungi in the geochemistry of metal cycling, as well as the applied significance of these processes in environmental biotechnology. Such roles can be included under the term ‘geomycology’, defined as ‘the study of the role fungi have played and are playing in fundamental geological processes’. Although the majority of processes discussed here 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 influenced strongly by spatial and environmental factors (Gadd 2006). Geochemical activities of fungi in the latter habitats have not been widely studied to date.

Organic matter degradation and biogeochemical cycling

Most attention has probably been given to the roles of fungi in carbon and nitrogen cycles, and their ability to utilize a wide spectrum of organic compounds for nutrition and energy generation is well known. These range from simple compounds (sugars, organic acids, and amino acids) which can easily be transported into the cell, to more complex molecules, which are first broken down by extracellular enzymes before entering the cell. These latter compounds include natural substances such as cellulose, pectin, lignin, lignocellulose, chitin and starch, and anthropogenic products such as hydrocarbons, pesticides, and other xenobiotics. Utilization of these substances results in redistribution of component elements, primarily carbon, hydrogen and oxygen, but also nitrogen, phosphorus, sulphur and others, in more complex molecules (see later). Here the significance of organic matter degradation in element recycling is emphasized using natural and certain anthropogenically derived xenobiotics as examples.

Some fungi have remarkable degradative properties, and lignin-degrading white-rot fungi, like *Phanerochaete chrysosporium*, can degrade several xenobiotics, including aromatic hydrocarbons, chlorinated organics, polychlorinated biphenyls, nitrogen-containing aromatics, and many other pesticides, dyes and xenobiotics (Harvey & Thurston 2001). Such activities are of potential in bioremediation where appropriate ligninolytic fungi have been used to treat soil contaminated with substances like pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs), the latter are constituents of creosote. Treatment generally involves inoculation of the contaminated soil, followed by nutrient addition, irrigation and aeration, and maintenance by general land farming procedures (Singleton 2001). In many cases, xenobiotic-transforming fungi need additional utilizable carbon sources because, although capable of degradation, they cannot utilize these substrates as an energy source for growth. Therefore, inexpensive utilizable lignocellulosic wastes, such as corncobs, straw and sawdust are used as nutrients to obtain enhanced pollutant degradation. Wood-rotting and other fungi are also receiving attention for the bleaching of dyes and industrial effluents, and the biotreatment of agricultural wastes, such as forestry, pulp and paper by-products, sugar cane bagasse, coffee pulp, sugar beet pulp, apple and tomato pulp, and cyanide (Knapp *et al.* 2001; Barclay & Knowles 2001; Cohen & Hadar 2001).

PAHs enter the environment *via* many routes, including fossil-fuel combustion, vehicle exhaust emissions, gas and coal tar manufacture, wood-preservation processes, and waste incineration (Harvey 1997; Cerniglia & Sutherland 2001, 2006). Aerobic biodegradation of PAHs by soil microorganisms uses the monooxygenase, peroxidase, and dioxygenase pathways; the first and third of these pathways are used by bacteria, while the first and second are found in fungi. Many fungi can metabolize PAHs (Cerniglia & Sutherland 2001, 2006; Sutherland 2004; Verdin *et al.* 2004). As fungi cannot generally use PAHs as their sole carbon and energy source (Cerniglia & Sutherland 2001), they must be supplied with nutrients to allow co-metabolism. The transformation of PAHs by ligninolytic wood-decaying fungi involves different enzymes. Those produced by white-rot fungi that are involved in PAH degradation include lignin peroxidase, manganese peroxidase, laccase, cytochrome P450, and epoxide hydrolase (Haemmerli *et al.* 1986; Bezalel *et al.* 1996; Cerniglia & Sutherland 2006). Ligninolytic fungi metabolize PAHs *via* reactions involving reactive oxygen species to phenols and quinones (Pickard *et al.* 1999; Steffen *et al.* 2003), and these may be further degraded by ring-fission enzymes (Cerniglia & Sutherland 2006). Several wood-decaying fungi (e.g. *Bjerkandera*, *Coriolopsis*, *Irpex*, *Phanerochaete*, *Pleurotus*, and *Trametes* spp.), have been investigated for bioremediation of PAH-contaminated soils (Baldrian *et al.* 2000; Novotný *et al.* 2000; Cerniglia & Sutherland 2006). Non-ligninolytic fungi, including *Cunninghamella*, *Mucor*, *Fusarium*, and *Penicillium* spp., have also been considered for PAH bioremediation (Colombo *et al.* 1996; Pinto & Moore 2000; Saraswathy & Hallberg 2002). Biodegradation may require the presence of mixed bacterial and fungal communities, although less is known about the pathways of PAH degradation by co-cultures (Juhasz & Naidu 2000).

Fungi are also important in the degradation of naturally occurring complex molecules in the soil, an environment where the hyphal mode of growth provides several advantages, and also in aquatic habitats. As 95 % of plant tissue is composed of carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur, the decomposition activities of fungi are clearly important in relation to the redistribution of these elements between organisms and environmental compartments. As well as those elements listed above, another 15 elements are typically found in living plant tissues: potassium, calcium, magnesium, boron, chlorine, iron, manganese, zinc, copper, molybdenum, nickel, cobalt, selenium, sodium, and silicon. However, all 90 or so naturally occurring elements may be found in plants, most at low concentrations, although this may be highly dependent on environmental conditions. These include gold, arsenic, mercury, lead and uranium, and there are even plants that accumulate relatively high concentrations of nickel and cadmium. Plant metal concentrations may reflect environmental conditions and provide an indication of toxic metal pollution or metalliferous ores. Such plants are also receiving attention in bioremediation contexts (i.e. phytoremediation). Animals likewise contain a plethora of elements in varying amounts. For example, the human body is mostly water, and 99 % of the mass comprises oxygen, carbon, hydrogen, nitrogen, calcium and phosphorus. However, many other elements are present in lower amounts including substances taken up as contaminants in food and water. A similar situation occurs throughout the plant, animal and microbial worlds. Consequently, any decomposition, degradative and pathogenic activities of fungi is linked to the redistribution and cycling of all these constituent elements, both on local and global scales (Fig 3). This simple perspective on organic matter decomposition illustrates the global significance of fungi in geochemical cycling of the elements.

Organometals (compounds with at least one metal–carbon bond) can also be attacked by fungi with the organic moieties being degraded and the metal compound undergoing changes in speciation (Gadd 1993b). Degradation of organometallic compounds (which are still widely used in agriculture and industry) can be carried out by fungi, either by direct biotic action (enzymes), or by facilitating abiotic degradation, for instance by alteration of pH and excretion of metabolites. Organotin compounds, such as tributyltin oxide and tributyltin naphthenate, may be degraded to mono- and dibutyltins by fungal action, inorganic tin(II) being the ultimate degradation product (Gadd 2000a). Organomercury compounds may be detoxified by conversion to mercury(II) by fungal organomercury

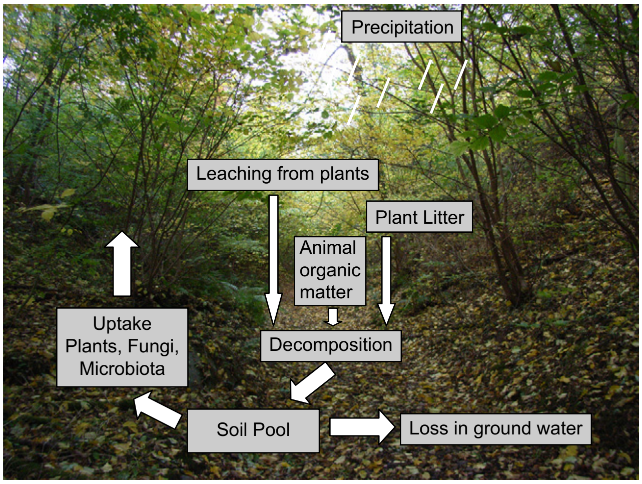

Fig 3 – Simple elemental biogeochemical cycle in a forest or other vegetated soil ecosystem where decomposition, and therefore a prime fungal role, leads to cycling of many other elements besides carbon. The cycle depicted could be of calcium or potassium for example (from Gadd 2004: see also Schlesinger 1997).

lyase, the mercury(II) being subsequently reduced to less toxic, diffusible and volatile mercury(0) by mercuric reductase, a system broadly analogous to that found in mercury-resistant bacteria (Gadd 1993b). Degradation of persistent carbon sources, such as charcoal and black shale, is accelerated by fungal activity, which in turn may accelerate the release of toxic metals. The main products of such degradation processes are organic metal complexes (Wengel *et al.* 2006).

Weathering processes

The composition of the Earth's lithosphere, biosphere, hydrosphere, and atmosphere is influenced by weathering processes (Ferris *et al.* 1994; Banfield *et al.* 1999; Vaughan *et al.* 2002). A mineral is a naturally occurring, homogeneous solid with a definite, but generally not fixed, chemical composition and an ordered atomic arrangement (i.e. it is crystalline). Although usually assumed to be formed by inorganic processes, some can be formed biotically. The latter may be termed biominerals, and their process of formation biomineralization; some show no chemical difference to inorganically derived minerals (e.g. carbonates). A rock is a solid substance composed of a mixture of one or several minerals in varying proportions, though a rock may also include organic remains. Rocks and their mineral constituents are weathered through physical (mechanical), chemical and biological mechanisms; the relative significance of each process depending on environmental and other conditions (Ferris *et al.* 1994; Banfield *et al.* 1999; Vaughan *et al.* 2002). Near-surface weathering of rocks and minerals, which occurs in subaerial (i.e. situated, formed, or occurring on or immediately adjacent to the surface of the earth) and subsoil (i.e. not exposed to the open air) environments often involves all three mechanisms (White *et al.* 1992). At or near the Earth's surface, interaction between minerals, metals and non-metallic species in an aqueous fluid nearly always involves the presence of microbes and/or their metabolites (Banfield & Nealson 1998). Mineral replacement reactions in rocks mainly occur by dissolution–re-precipitation processes (e.g. cation exchange, chemical weathering, leaching, diagenesis), where one mineral or mineral assemblage is replaced by a more stable one (Putnis 2002). Microorganisms can influence this by mineral dissolution, biomineralization, and alteration of mineral surface chemistry and reactivity (Hochella 2002). Mineral dissolution can also be inhibited by extracellular microbial polysaccharides that block reactive centres on minerals (Welch & Vandevivere 1994; Welch *et al.* 1999). In contrast, mineral dissolution may be accelerated by microbially mediated pH changes and other changes in solution chemistry. The production of extracellular organic ligands and siderophores not only enhances nutrient acquisition by microorganisms, but also can markedly affect mineral composition and dissolution reactions (Grote & Krumbein 1992; Maurice *et al.* 1995; Hersman *et al.* 1995; Stone 1997; Gadd 1999; Kraemer *et al.* 1999; Liermann *et al.* 2000; Sayer & Gadd 2001). In addition, the formation of secondary minerals (biogenic crystalline precipitates) can occur through both metabolism-independent and metabolism-dependent processes, and this is influenced by both abiotic and biotic factors (Ferris *et al.* 1987; Gadd 1993a; Arnott 1995; Thompson & Ferris 1990; Douglas & Beveridge 1998; Fortin *et al.* 1998; Sterflinger 2000; Verrecchia 2000). Biomineralization is biologically induced mineralization, where an organism modifies the local microenvironment creating conditions that promote the chemical precipitation of extracellular mineral phases (Hamilton 2003). Secondary minerals can form by direct nucleation on cellular macromolecules, e.g. melanin and chitin in fungal cell walls (Gadd 1990, 1993a; Fortin & Beveridge 1997; Beveridge *et al.* 1997). However, indirect precipitation of secondary minerals also frequently occurs through microbially mediated changes in solution conditions (Fortin & Beveridge 1997; Banfield *et al.* 2000). Regardless of the mechanism, weathering of rocks and minerals can result in the mobilization and redistribution of essential nutrients (e.g. phosphorus, sulphur) and metals (e.g. sodium, potassium, magnesium, calcium, manganese, iron, copper, zinc, cobalt, nickel) required for plant and microbial growth. In addition, non-essential and potentially toxic metals (e.g. caesium, aluminium, cadmium, mercury, lead) may also be mobilized from rock, mineral, and soil pools (Gadd 1993a, 2001a, 2001b; Morley *et al.* 1996).

Bioweathering is the erosion, decay and decomposition, of rocks and minerals mediated by living organisms. Microorganisms, as well as animals and plants, can weather rock aggregates through biomechanical and biochemical attack on minerals (Goudie 1996; Adeyemi & Gadd 2005). Filamentous microorganisms, plant roots, and burrowing animals can physically affect rocks and enhance splitting and fractionation: the disruptive (hydraulic) pressure of growing roots and hyphae is also important (Sterflinger 2000; Money 2001). However, biochemical actions of organisms are considered more significant processes than mechanical degradation (Sterflinger 2000; Etienne 2002). Microbes (e.g. bacteria, algae, fungi, protists) and also plants can mediate chemical weathering of rocks and minerals through excretion of, for example, organic acids and other metabolites, while released respiratory carbon dioxide (CO_2) can lead to carbonic acid attack on mineral surfaces (Johnstone & Vestal 1993; Ehrlich 1998; Sterflinger 2000; Gadd & Sayer 2000). Biochemical weathering of rocks can result in changes in the microtopography of minerals through pitting and etching, mineral displacement reactions and even complete dissolution (Ehrlich 1998; Kumar & Kumar 1999; Adeyemi & Gadd 2005).

Fungi in rock and mineral habitats

Microorganisms occur in and on rocks and building stone in a variety of microhabitats, and may be epilithic, hypolithic, endolithic, chasmolithic, cryptoendolithic or euendolithic (Gerrath *et al.* 1995, 2000; May 2003; Burford *et al.* 2003a, 2003b). Epiliths occur on the surface of rocks and building stone; hypoliths are found under and attached to pebbles, particularly in hot and cold deserts; and endoliths inhabit the rock subsurface, sometimes forming distinct masses or brightly coloured layers. Endolithic microorganisms can occur as chasmoliths that grow in pre-existing cracks and fissures within rock, often being visible from the rock surface; cryptoendoliths grow inside cavities and among crystal grains and cannot be observed from the rock surface; and euendolithic microbes are a specialized group of cryptoendoliths that can actively penetrate (bore) into rock (Ehrlich 1998; Gerrath *et al.* 1995).

Microorganisms play a fundamental role in mineral transformations in the natural environment, most notably in the formation of mineral soils from rock and the cycling of elements (May 2003; Gadd *et al.* 2005a; Gadd 2006). Therefore, it is not surprising that a wide variety of microorganisms including, bacteria, algae and fungi, inhabit rocks and stonework of buildings and historic monuments (Ehrlich 2002; Burford *et al.* 2003a; Gleeson *et al.* 2005, 2006). Exposed surfaces are not necessarily conducive to microbial growth as a result of moisture deficit, exposure to solar radiation, and limited availability of nutrients. However, complex interactions between microorganisms and the mineral substrate are frequently observed, often to some distance into the mineral (May 2003). The rock micro-environment is subject to diurnal and seasonal changes in, for example temperature, moisture, and available nutrients (Gorbushina & Krumbein 2000; Roldan *et al.* 2002). Nutrients may accumulate as a result of water interactions, wind-blown dust particles, animal faeces, or the death and degradation of living organisms, and be utilized by microbes. Mineral grains within the host rock may also serve as a source of metals essential for microbial growth. The transfer of biological material (e.g. fungal spores and other reproductive structures) from external sources may also play a role in the colonization of subaerial environments by microbes. Physical properties (e.g. porosity) and elemental composition of the host rock (e.g. carbon, phosphorus, potassium, sulphur, metal content) may govern initial establishment, growth and survival of microbial communities (Gleeson *et al.* 2005, 2006). Thus, colonization of rock substrates by microorganisms and the development of a microbial consortium is likely to be influenced by physical and chemical properties, and interactions based on environmental (e.g. macro/micro-climate) and biological factors, resulting in and influencing ecological succession at the micro-scale.

Microbial processes influenced by minerals

Many important microbial processes can be influenced by minerals including energy generation, nutrient acquisition, cell adhesion and biofilm formation (Hochella 2002). Microorganisms can also acquire essential nutrients from mineral surfaces, which effectively concentrate these vital substances above surrounding environmental levels (e.g. carbon, nitrogen, phosphorus, iron, various organic compounds; Vaughan *et al.* 2002). Environmental contaminants may also be concentrated on mineral surfaces by various sorption reactions, and these can be displaced by similar microbial processes (Kraemar *et al.* 1999). Furthermore, it is likely that potentially toxic metals released from minerals, as a result of physico-chemical and biological processes, will affect microbial communities (Gadd 2005). The properties of mineral surfaces (e.g. microtopography, surface composition, surface charge, hydrophobicity) also play an integral role in microbial attachment and detachment. Minerals and their surfaces are therefore critical in colonization and biofilm formation, and the ecology of proximal microbial populations in, on, and around, mineral substrates (Wolfaardt *et al.* 1994; Fredrickson *et al.* 1995; Bennett *et al.* 1996; Rogers *et al.* 1998).

Fungi in the terrestrial environment

Fungi are ubiquitous components of terrestrial microbial communities, with soil usually being regarded as their most characteristic habitat. Subaerial rock surfaces can be considered to be an inhospitable habitat for fungal (and other microbial) growth due to such factors as desiccation and limited availability of nutrients (Gorbushina & Krumbein 2000). Microorganisms that thrive under these extreme conditions have been termed 'poikilotrophic', i.e. able to deal with varying microclimatic conditions such as light, salinity, pH, and moisture, and many successful species are known. Microbial communities on and in rocks are believed to be major factors in rock decay, and also contribute to the formation of various patinas, films, varnishes, crusts and stromatolites in rock substrates (Gorbushina & Krumbein 2000).

Fungi have been recorded from a wide range of rock types including limestone, soapstone, marble, granite, sandstone, andesite, basalt, gneiss, dolerite, amphibolite and quartz, from a variety of environments (Table 2, Staley *et al.* 1982; Gorbushina *et al.* 1993; Sterflinger 2000; Verrecchia 2000; Burford *et al.* 2003a, 2003b). It is likely that they are ubiquitous inhabitants of all rocks and building stone, throughout a wide range of geographical and climatic zones. Despite the apparent inhospitality of the rock environment, the presence of organic and inorganic residues on mineral surfaces or within cracks can encourage the proliferation of fungi and other microorganisms. Waste products of algae and bacteria, dead cells, decaying plant material, dust particles, aerosols, and animal faeces can all act as nutrient sources (Sterflinger 2000). Some extremophilic fungi are especially adapted to exploit microhabitats on and within mineral substrata, occurring within

Table 2 – Some fungal genera encountered in rock substrates (see Burford *et al.* 2003a, 2003b; adapted from Hirsch *et al.* 1995; Kumar & Kumar 1999; Sterflinger 2000; Verrecchia 2000)

Fungal genera	Rock substrates							
	Limestone	Granite	Marble	Sandstone	Andesite	Basalt	Gneiss	Quartz
Absidia							*	*
Acremonium	*						*	*
Acremoniella			*					
Acrodyctis			*					
Alternaria	*	*	*	*			*	*
Alysidium			*					
Aphanocladium		*	*	*				
Aposphaeria			*					
Arthrinium							*	*
Aspergillus	*	*	*	*	*		*	*
Aureobasidium	*	*	*	*			*	*
Botrytis		*	*	*				
Camarosporium			*					
Candida				*		*		
Chaetocladium							*	*
Cephalotrichum	*							
Chaetomium				*				
Chloridium			*					
Ciliciopodium			*					
Cladosporium		*	*	*	*		*	*
Clonostachys					*			
Coniosporium		*	*					
Coniothyrium		*	*	*				
Cunninghamella					*			
Curvularia			*	*	*			
Drechslera			*					
Engydodontium	*	*	*	*				
Epicoccum		*	*	*				
Exophiala		*	*	*			*	*
Fusarium	*	*	*	*	*		*	*
Gilmaniella			*					
Gliomastix			*				*	*
Hormiscium			*					
Hormonema		*	*	*			*	*
Hortaea		*	*	*				
Humicola			*	*				
Lecythophora		*	*	*				
Lichenothelia		*	*	*				
Lipomyces				*				
Macrophoma			*	*				
Melanospora							*	*
Memnoniella			*					
Moniliella							*	*
Monillia	*							
Monodictys			*					
Mucor			*				*	*
Paecilomyces		*	*	*				
Papulospora							*	*
Penicillium	*	*	*	*	*		*	*
Pestalotia			*					
Phaeococcomyces		*	*	*				
Phaeosclera			*					
Phaeotheca		*	*	*				
Phialophora			*				*	*
Phoma		*	*	*				
Phyllosticta			*					
Pithomyces			*					
Polyscytalum							*	*
Pseudobotrytis			*					
Rhinocladium			*					
Rhinocladiella			*					
Rhizoctonia							*	*

Table 2 (*continued*)

Fungal genera	Rock substrates							
	Limestone	Granite	Marble	Sandstone	Andesite	Basalt	Gneiss	Quartz
Rhizopus			*	*	*			*
Rhodotorula		*	*	*				
Sarcinomyces		*	*	*				
Sclerococcum			*					
Scopulariopsis			*				*	*
Scytalidium			*				*	*
Sordaria							*	*
Sporobolomyces				*				
Stachybotrys			*					
Staphylotrichum			*					
Stemphylium	*		*					
Taeniolella			*					
Tetracoccosporium			*					
Torula			*					
Trichocladium			*					
Trichoderma		*	*	*			*	*
Trichothecium							*	*
Trimmatostroma		*	*	*			*	*
Ulocladium		*	*	*			*	*
Verticillium		*	*	*				
Virgaria			*					

Note that the number of genera and incidence of occurrence on different rock substrates shown here is likely to be a considerable underestimate.

the lichen symbiosis or as free-living microcolonial fungi (Gorbushina *et al.* 1993; Bogomolova *et al.* 1998; Sterflinger 2000). Microcolonial fungi include those black fungi, also known as the black yeasts or yeast-like black meristematic fungi, which occur as spherical clusters of tightly packed thick-pigmented-walled cells or hyphae (Staley *et al.* 1982; Gorbushina *et al.* 1993; Wollenzien *et al.* 1995; Bogomolova *et al.* 1998; de Leo *et al.* 2003). Meristematic growth is characterized by the production of swollen isodiametric cells with thick-pigmented (melanin-containing) walls. In addition to meristematic growth, many of the black fungi can exhibit yeast-like growth (Gadd 1980; Gorbushina *et al.* 1993; Wollenzien *et al.* 1995; Bogomolova *et al.* 1998; Sterflinger 2000; de Leo *et al.* 2003). As well as these, other filamentous fungi, including zygomycetes, ascomycetes, and basidiomycetes, often occur on rock surfaces (epiliths), and in cracks, fissures and pores (endoliths). Certain fungi may also actively 'burrow' into rock substrates (cryptoendoliths). In addition, many other conidial fungi are commonly found in mineral substrates (Kumar & Kumar 1999; Sterflinger 2000; Verrecchia 2000)

In soil, fungi generally comprise the largest proportion of the biomass (including other microorganisms and invertebrates). This, combined with their filamentous habit, ensures that fungus–mineral interactions are an integral component of soil biogeochemistry (Gadd 1993a, 1999, 2001a, 2001b, 2004, 2005, 2006). They occur as free-living filamentous forms, plant symbionts, unicellular yeasts, and animal and plant pathogens, and play an important role in carbon, nitrogen, phosphorus, and other biogeochemical cycles (Gadd & Sayer 2000; Gadd 2005). Their ability to translocate nutrients through the mycelial network also provides significant environmental advantages (Fomina *et al.* 2003; Jacobs *et al.* 2004; Boswell *et al.* 2002, 2003, 2006). Mycorrhizal fungi, in particular, are one of the most important ecological groups of soil fungi in terms of mineral weathering processes (Paris *et al.* 1995; Jongmans *et al.* 1997; Lundstrom *et al.* 2000; Hoffland *et al.* 2002; Martino *et al.* 2003; Fomina *et al.* 2004, 2005b, 2006a). A detailed account of modern molecular approaches to characterize geoactive fungal populations is found in Gadd *et al.* (2006).

Mechanisms of rock weathering by fungi

Fungi grow in a microenvironment where the organism, associated extracellar mucilage, solid adsorbents, and organic and inorganic surfaces all interact with each other. All the processes that contribute to fungal weathering of rocks and minerals, such as dissolution, sorption, transport, diffusion and recrystallization of mobilized cations occur within that microenvironment (Fig 4) (Burgstaller & Schinner 1993; Banfield & Nealson 1998; Fomina *et al.* 2004, 2005a, 2006a). Two frequently synergistic actions by which fungi degrade mineral substrates are biomechanical and biochemical (Burford *et al.* 2003a).

Biomechanical deterioration

Biomechanical weathering of minerals by fungi can be direct and indirect. Direct biomechanical deterioration of rocks may occur through hyphal penetration (e.g. into decayed limestone), and by tunnelling into otherwise intact mineral material, for example along crystal planes in sandstone, calcitic, and dolomitic rocks (Kumar & Kumar 1999; Sterflinger 2000). Fungal hyphae can also penetrate grain boundaries, cleavages, and cracks to gain access to mineral surfaces (Adeyemi & Gadd 2005). In lichens, cleavage-bound mineral

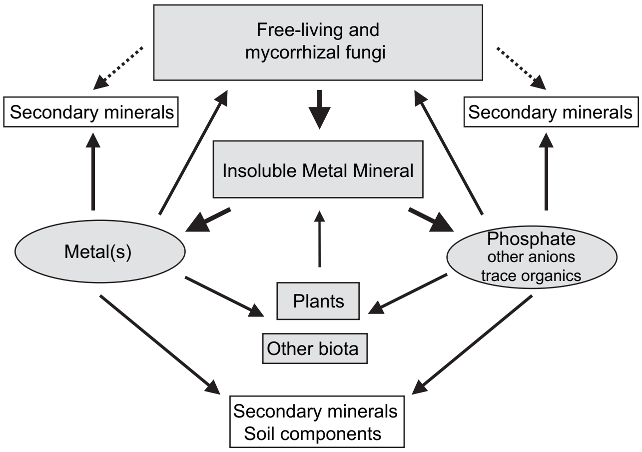

Fig 4 – Action of free-living and mycorrhizal fungi on insoluble metal minerals in the terrestrial environment resulting in release of mineral components: metal(s), anionic substances, trace organics and other impurities, which can be taken up by the biota, as well as forming secondary minerals with soil components or fungal metabolites/biomass, and also be sorbed or otherwise removed by organic and inorganic soil components. The dashed arrows imply secondary mineral formation from excreted metabolites, as well as fungal action on non-biogenic minerals. Losses to groundwater are not shown (from Gadd 2004).

fragments as small as 5 μm diam can accumulate within the lower thallus (Banfield *et al.* 1999). An important feature of hyphal growth is spatial exploration of the environment to locate and exploit new substrates (Boswell *et al.* 2002, 2003; Jacobs *et al.* 2002a). This may be facilitated by a range of tropic responses that determine the direction of hyphal growth. Among the tropisms that may occur, thigmotropism, contact guidance, is a well-known property of fungi that grow on and within solid substrates (Watts *et al.* 1998); this is directed fungal growth towards grooves, ridges and pores in solid material that enables hyphae to explore and exploit weaknesses in mineral surfaces (Watts *et al.* 1998). Chemotropism, and other nutritional responses, may also be important in stress avoidance, such as that caused by toxic metals (Fomina *et al.* 2000a; Gadd *et al.* 2001). It has been shown that the intensity of rock colonization by fungi and the space distribution of colonies depends both on the chemical composition of the rock or minerals, and also microtopography. A strong tendency to grow along surface cracks and junctions between crystals was observed (Bogomolova *et al.* 2003).

The process of invasive growth is facilitated by the turgor pressure inside hyphae and this allows fungi to acquire nutrients from many solid materials (Money 2001). Highly pressurized hyphae can penetrate tougher substrates than those with lower pressures, and fungi that naturally invade hard materials generate extremely high pressures (Money 1999, 2004; Money & Howard 1996), though some estimates may have been high (Goriely & Tabor 2006). Melanin has also been implicated in the penetrative ability of plant pathogenic fungi as this black pigment facilitates the development of infection structures (Wheeler & Bell 1988; Money & Howard 1996). Many rock-dwelling fungi are melanized (see Burford *et al.* 2003a), and the significance of melanin in fungal protection from metal toxicity has long been established (Gadd & Griffiths 1980a; Gadd 1984, 1993a; Gadd & Mowll 1985; Gadd *et al.* 1987).

Indirect biomechanical weathering is particularly associated with the action of extracellular mucilaginous substances produced by fungi, which underpin fungal biofilm formation and attachment to solid surfaces. Fungal-associated mucilaginous slime may also contain acidic and metal-chelating metabolites (Burford *et al.* 2003a). Shrinking and swelling of biofilms can result in mechanical pressure to the mineral unit, causing erosion or abrasion (Warscheid & Krumbein 1994). All the biomechanical processes involved in fungal weathering are connected with biochemical processes, and the latter are believed to be more important in biogeochemical cycling (Kumar & Kumar 1999; Burford *et al.* 2003a).

Biochemical deterioration

Biochemical weathering of rocks can result in changes in the microtopography of minerals through pitting and etching, mineral displacement reactions, and even complete dissolution of mineral grains (Leyval *et al.* 1993; Ehrlich 1998; Gharieb *et al.* 1998; Kumar & Kumar 1999; Adeyemi & Gadd 2005). The environmental significance of fungal solubilization processes includes the mobilization of metals, phosphates, and other nutrients from minerals, which also have biotechnological potential for leaching of primary or waste ores, and industrial wastes, such as fly ash, galvanic sludge, and electronic soap (Whitelaw *et al.* 1999; Brandl 2001; Gadd 1999, 2001a, 2001b; Hoffland *et al.* 2002).

Fungi can solubilize minerals and metal compounds (‘heterotrophic leaching’) through several mechanisms, including acidolysis, complexolysis, redoxolysis, and by metal accumulation in the biomass (Fig 4) (Burgstaller & Schinner 1993). The primary fungal impact on mineral dissolution appears to result from acidolysis and complexolysis, and occurs as a result of several processes including proton efflux *via* the plasma membrane H^+-ATPase and/or maintenance of charge balance during nutrient uptake, the production of siderophores [for iron(III) mobilization], or respiratory CO_2 production. However, in many fungi an important leaching mechanism occurs through the production of organic acids (e.g. oxalic acid, citric acid) (Adams *et al.* 1992; Francis *et al.* 1992; Devevre *et al.* 1996; Sayer *et al.* 1997; Gadd 1999, 2000b; Sayer & Gadd 2001; Jarosz-Wilkolazka & Gadd 2003; Fomina *et al.* 2005a). Organic acid excretion by fungi is inter- and intraspecific, and can be strongly influenced by the presence of toxic metal minerals (Sayer *et al.* 1995; Fomina *et al.* 2004, 2005c; Sayer & Gadd 2001). Fungal-derived carboxylic acids with strong chelating properties (e.g. oxalic acid, citric acid) can aggressively attack mineral surfaces (Sayer *et al.* 1997; Gharieb *et al.* 1998; Gadd 1999; Gharieb & Gadd 1999; Fomina *et al.* 2004). Oxalic acid can leach those metals that form soluble oxalate complexes, including aluminium and Fe (Strasser *et al.* 1994; Devevre *et al.* 1996). Moreover, the production of organic acids provides another source of protons. The significance of proton *versus* ligand-promoted dissolution may depend on the mineral, metabolic activity, and conditions of growth, including nutrient availability and carbon and nitrogen sources (Gharieb & Gadd 1999). For the majority of tested ericoid mycorrhizal and ectomycorrhizal fungi grown in the presence of ammonium as a nitrogen source, the main mechanism of dissolution of toxic metal phosphates was acidolysis (Fomina *et al.* 2004, 2005c). However, if the fungus was capable of excreting large amounts of a strong chelator such as oxalate, the mechanism switched to ligand-promoted dissolution and became much more efficient than acidolysis, as demonstrated for pyromorphite (Fomina *et al.* 2004, 2005a, 2005c). Notably, oxalic acid was the only tested agent to give a clear solubilization zone for pyromorphite (Fomina & Gadd 2007). The main compounds originating from the extramatrical mycelium of *Hebeloma crustuliniforme* (in association with *Pinus sylvestris* seedlings) were oxalate and ferricrocin. The exudation rate for oxalate was 19 ± 3 fmol per hyphal tip h^{-1} or 488 ± 95 fmol hyphal $mm^{-2} h^{-1}$. Such results clearly indicate that hyphal exudation may alter the chemical conditions of soil microsites and affect mineral dissolution (van Hees *et al.* 2006). Fungi excrete many other metabolites with metal-complexing properties, such as amino acids and phenolic compounds (Manley & Evans 1986; Muller *et al.* 1995).

Endolithic and epilithic microbial communities produce polyols as osmotic protectants (osmolytes) in response to desiccation. Low molecular weight polyols and polysaccharides bind to the siloxane layers within layered siliceous minerals, such as micas and soapstone, by hydrogen bonding. These interlaminar complexes cause expansion of the crystalline layer, weakening the structure, and may allow entry of chelating agents that mobilize the ions stabilizing the crystal structure. During periods of desiccation, the polyols become concentrated, forming non-aqueous systems. Basic catalysis in such water-deficient ecosystems favours the formation of water-soluble organosilicon compounds, principally organic siloxanes. Such ecosystems with low water activity are common in all dry environments. Polyols and complex organic acids can also attack siliceous minerals under alkaline conditions. Extracellular carbohydrate polymers released by fungi (and bacteria) can react with inorganic siloxanes to form water-soluble organic siloxanes. Extracellular polymer surfaces also prolong water residence time, increasing the duration of the chemical reactions causing silicate weathering. The result of these biochemical and biophysical activities, is the expansion of the rock or stone and spalling of the surface layers from the weakened material behind (Gaylarde & Gaylarde 2004).

Metal accumulation by fungal biomass can also play a role in rock and mineral solubilization, the mycelium functioning as a sink for mobilized metal cations, and thereby ‘pulling’ the equilibrium and increasing the efficiency and rate of dissolution (Gadd 1990, 1993a, 2000a, 2001c; Sterflinger 2000).

Fungal symbioses in mineral transformations

One of the most remarkable adaptations of fungi for exploitation of soil and rock environments is their formation of mutualistic partnerships with land plants (mycorrhizas) and algae or cyanobacteria (lichens). Symbiotic fungi are provided with carbon by the photosynthetic partners, while the fungi protect the symbiosis from harsh environmental conditions (e.g. desiccation, metal toxicity), increase the absorptive area of the symbiotic associations, and provide increased access to mineral nutrients (Bradley *et al.* 1982; Wilkins 1991; Hetrick *et al.* 1994; Wilkinson & Dickinson 1995; Smith & Read 1997; Meharg & Cairney 2000; Adriaensen *et al.* 2003; Meharg 2003; Colpaert *et al.* 2004).

Lichens

Lichen-forming fungi, fungi that exist in facultative or more usually obligate mutualistic symbioses with one or more photosynthetic algae or cyanobacteria, play an important role in many biogeochemical processes. In most cases the fungi and algae involved are not known outside the lichen symbiosis. The fungal partners belong to a wide range of classes and orders, and are not a systematic but an ecological group; most are ascomycetes, but some are basidiomycetes. Lichens are commonly thought of as pioneer colonizers of rocks, and were possibly one of the earliest life forms to colonize Earth’s land surfaces. The lichen is a mutualistic symbiosis formed between the fungal partner (mycobiont) and the photosynthesizing partner (algal or cyanobacterial photobiont) which enables lichens to grow in practically all surface terrestrial environments: an estimated 6 % of the Earth’s land surface is covered by lichen-dominated vegetation (Haas & Purvis 2006). Globally, lichens play an important biogeochemical role in the retention and distribution of nutrient (e.g. carbon, nitrogen) and trace elements, in soil-formation processes, and in rock weathering (Barker *et al.* 1997; Banfield *et al.* 1999). The alteration of bedrock minerals and synthesis of biominerals in the proximity of lichens gives rise to different chemical microenvironments and emphasizes their participation in mineral nutrient cycling (de Los Rios *et al.* 2002, 2004, 2005). Lichens can accumulate metals such as lead, copper, and many other elements of environmental concern, including radionuclides, to high levels (Purvis 1996). They can also form a variety of metal-organic biominerals, especially during growth on metal-rich substrates (Purvis & Halls 1996). A detailed account of lichen biogeochemistry is provided by Haas & Purvis (2006).

Mycorrhizas

Nearly all land plants depend in some way on mutualistic symbiotic mycorrhizal fungi (Smith & Read 1997). The two main types of mycorrhizas are endomycorrhizas where the fungus colonizes the interior of host plant root cells (e.g. ericoid and arbuscular mycorrhizas (AM)), and ectomycorrhizas where the fungus is located outside the root cells of the host plant. It has been demonstrated that mycorrhizal fungi are involved in proton-promoted and ligand-promoted metal mobilization from mineral sources and metal immobilization *via* biosorption and accumulation within biomass and extracellular precipitation of mycogenic toxic metal oxalates (Fomina *et al.* 2004, 2005a, 2005b). Further, the formation of mycorrhizas in weathered bedrock fractures, and hyphal extension into the matrix, may be crucial to the water balance of evergreen trees (in Mediterranean climates) by providing a link between matrix resources and the plant (Bornyasz *et al.* 2005).

Biogeochemical activities of mycorrhizal fungi lead to changes in the physico-chemical characteristics of the root environment and enhanced weathering of soil minerals resulting in metal cation release (Fig 5) (Olsson & Wallander 1998; Lundstrom *et al.* 2000; Whitelaw 2000; Leyval & Joner 2001; Habergerg *et al.* 2003). Dissolution of soil weatherable calcium-bearing minerals by ectomycorrhizal fungi has been well-documented (Callot *et al.* 1985a, 1985b; Lapeyrie *et al.* 1990, 1991). Ectomycorrhizal mycelia may respond to the presence of different soil silicate and phosphate minerals (apatite, quartz, potassium feldspar) by regulating their growth and activity, including colonization, carbon allocation, and substrate acidification (Habergerg *et al.* 2003; Rosling *et al.* 2004a, 2004b). Carbon allocation within the mycelium was significantly greater in *Hebeloma crustuliniforme*/*Pinus sylvestris* ectomycorrhizas colonizing potassium feldspar patches than to quartz patches (Rosling *et al.* 2004b). Ectomycorrhizal fungi growing in symbiosis with tree seedlings stimulated weathering and the uptake of nutrients from silicates. Such organisms take up measurable amounts of calcium and potassium from microcline and biotite (Wallander *et al.* 2006). When *P. sylvestris* seedlings were grown with or without ectomycorrhizal fungi, and with or without the mineral muscovite as the only potassium source or the mineral hornblende as the only magnesium source, *Paxillus involutus* increased weathering of muscovite but not of hornblende. The other ectomycorrhizal fungi tested, *Piloderma croceum* and *Suillus bovinus*, did not increase weathering of either muscovite or hornblende. The *Paxillus involutus*-mediated mobilization of potassium from muscovite resulted in an increased potassium content of the root plus adhering hyphae, but not of shoots. Ectomycorrhizal fungi may therefore increase weathering of minerals in response to nutrient deficiencies, but this response is species specific (van Scholl *et al.* 2006). Ectomycorrhizal fungi were stimulated by phosphorus-containing apatite in a forest with low phosphorus status, but not in a forest with adequate phosphorus, and dissolution of the apatite was more intense in the forests with low phosphorus. However, there was no indication that ectomycorrhizal mycelia interacted with potassium-containing biotite, whether in forests with deficient potassium or an adequate potassium supply (Wallander & Hagerberg 2004).

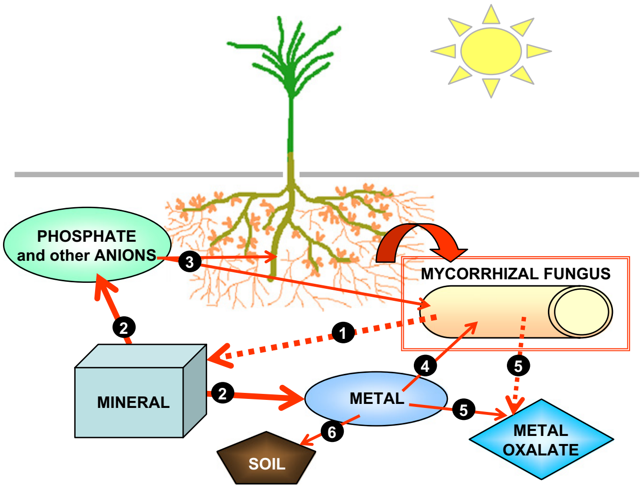

Fig 5 – Simple biogeochemical model for metal mineral transformations in the mycorhizosphere (the role of the plant and other microorganisms contributing to the overall process is not shown). (1) Proton-promoted (proton pump, cation–anion antiport, organic anion efflux, dissociation of organic acids) and ligand-promoted (organic acids) dissolution of metal minerals; (2) release of anionic (e.g. phosphate) nutrients and metal cations; (3) nutrient uptake; (4) intra- and extracellular sequestration of toxic metals: biosorption, transport, compartmentation, precipitation, etc; (5) immobilization of metals as oxalates; (6) binding of soluble metal species to soil constituents, e.g. clay minerals, metal oxides, humic substances. From Fomina *et al.* (2006a).

During their growth, mycorrhizal fungi often excrete low molecular weight carboxylic acids (e.g. malic, succinic, gluconic, oxalic) (Ahonen-Jonnarth *et al.* 2000; Martino *et al.* 2003; Fomina *et al.* 2004). In podzol E horizons under European coniferous forests, the weathering of hornblendes, feldspars and granitic bedrock has been attributed to the excretion of such acids by ectomycorrhizal hyphae (see below). The ectomycorrhizal fungus *Piloderma* was able to extract potassium and/or magnesium from biotite, microcline, and chlorite to satisfy nutritional requirements and precipitated calcium-oxalate crystals on the hyphae (Glowa *et al.* 2003). Ectomycorrhizal species can release elements (potassium, calcium, titanium, manganese, lead) from apatite and wood ash and accumulate them in the mycelia. Species capable of doing this included *P. involutus*, *Thelephora terrestris*, *S. granulatus* and *Tylospora fibillosa*. *S. granulatus* contained three to 15 times more potassium (3 mg g^{-1}) than the other species and had large calcium-rich crystals deposited on the surface of rhizomorphs when incubated with apatite. Wood ash addition to the soil system increased the amount of titanium, manganese and lead accumulated by the fungi (Wallander *et al.* 2003).

Ericoid mycorrhizal and ectomycorrhizal fungi can dissolve a variety of toxic metal-bearing (e.g. cadmium, copper, zinc, lead) minerals including phosphates (Leyval & Joner 2001; Martino *et al.* 2003; Fomina *et al.* 2004). Mobilization of phosphorus is generally regarded as one of the most important functions of mycorrhizal fungi (Lapeyrie *et al.* 1991; Wallander *et al.* 1997; Whitelaw 2000). Zinc phosphate solubilization is correlated with zinc tolerance for both ericoid mycorrhizal and ectomycorrhizal fungi. The relationship between toxic metal mineral solubilization and metal tolerance was confirmed by principal component analysis where copper-tolerant isolates of the ericoid mycorrhizal fungus *Hymescyphus ericae* (from the Devon Consol copper mine area) demonstrated a much higher ability to solubilize cadmium, copper and zinc phosphates than isolates from non-polluted areas (Fomina & Gadd 2007). Zinc-tolerant isolates of ectomycorrhizal fungi (*P. involutus*, *S. bovinus*, *S. luteus*) from a zinc smelter location (Lommel, Belgium) demonstrated a higher ability to dissolve zinc and cadmium phosphates than isolates from non-polluted soils (Fomina *et al.* 2004). In mesocosm experiments with ectomycorrhizal associations of *P. sylvestris* with *P. involutus* strains, zinc phosphate dissolution, and zinc accumulation by roots and whole plants depended on the strain of the mycobiont, its zinc tolerance, and the phosphorus status of the matrix (Fomina *et al.*

2006a). Under phosphorus-rich conditions, an ectomycorrhizal association with a zinc-tolerant fungal strain isolated from zinc-polluted soil showed the least zinc mobilization from zinc phosphate and the least zinc accumulation by the whole plant, whereas the highest zinc mobilization and accumulation was observed for non-mycorrhizal plants. In contrast, under phosphorus deficiency, the ectomycorrhizal association with the zinc-tolerant fungus demonstrated the highest zinc mobilization from zinc phosphate, and the highest zinc accumulation by the plant. In both phosphorus-deplete and -replete conditions, ectomycorrhizal mycobionts efficiently assisted phosphorus acquisition and much more phosphorus was accumulated in ectomycorrhizal roots than in non-mycorrhizal roots. This indicates that these biogeochemical activities of ectomycorrhizas were conditional and could be altered by additives, such as phosphates, and the physico-chemical conditions. The nutritional status of the metal-polluted environment could therefore shift toxic metal transformation processes from metal mobilization to immobilization and *vice versa*. Acidification or protonolysis may be the main mechanism of toxic metal mineral solubilization by the majority of mycorrhizal fungi: in one study, most strains examined were found not to excrete such strong chelating agents as oxalate and citrate (Fomina *et al.* 2004).

Some studies have revealed that in AM, system complexity may be increased by the presence of a third symbiont: a bacterium living inside the fungus. Molecular analysis has shown that the bacterium has genes involved in the acquisition of mineral nutrients. Such experimental data support the view that mycorrhizal symbioses are often tripartite associations (Bonfante 2003).

Fungal deterioration of minerals, rocks and building stone

Attacks on minerals may be specific and depend on the groups of microorganisms involved, for example hyphae from some lichens overgrew augite and mica but avoided quartz (Aristovskaya 1980). Substrate acidification can vary between species as well as in relation to different mineral substrates. *Mycena galopus* and *Cortinarius glaucopus* produced the highest substrate acidification during growth on tri-calcium phosphate (Rosling *et al.* 2004).

In podzols, quartz and kaolin are usually overgrown by fungi and algae, with abundant fungal hyphae also associated with apatite particles (Aristovskaya 1980). It seems that alkaline (basic) rocks are more susceptible to fungal attack than acidic ones (Eckhardt 1985a,b; Kumar & Kumar 1999). Along with other organisms, fungi are believed to contribute to the weathering of silicate-bearing rocks, including mica and orthoclase, and iron- and manganese-bearing minerals such as biotite, olivine, and pyroxene (Kumar & Kumar 1999). Callot *et al.* (1987) showed that siderophore-producing fungi were able to pit and etch samples of olivine and glasses under laboratory conditions. A polycarboxylate siderophore, rhizoferrin, showed the ability to bind chromium(III), iron(III) and aluminium(III) (Pillichshammer *et al.* 1995). Fungi can also deteriorate natural and manufactured antique and medieval glass (Krumbein *et al.* 1991). Degradation of aluminosilicates and silicates is believed to occur as a result of the production of organic acids, inorganic acids, alkalis and complexing agents (Rossi & Ehrlich 1990; Gomez-Alarcon *et al.* 1994; Hirsch *et al.* 1995; Sterflinger 2000). It is also likely that CO_2 released during fungal respiration can enhance silicate degradation by carbonic acid attack (Sterflinger 2000). *Aspergillus niger* can degrade olivine, dunite, serpentine, muscovite, feldspar, spodumene, kaolin and nepheline. *Penicillium expansum* can degrade basalt, while *P. simplicissimum* and *Scopulariopsis brevicaulis* both release aluminium from aluminosilicates (Mehta *et al.* 1979; Rossi 1979; Sterflinger 2000). *Piloderma* was able to extract potassium and/or magnesium from biotite, microcline, and chlorite to satisfy nutritional requirements. Energy dispersive X-ray analysis indicated that *Piloderma* extracted significantly more potassium from biotite than from microcline. The high calcium and oxygen content of hyphal ornamentation mainly resulted from calcium oxalate crystals (Glowa *et al.* 2003).

In podzol E horizons under European coniferous forests, the weathering of hornblendes, feldspars and granitic bedrock has been attributed to oxalic, citric, succinic, formic and malic acid excretion by saprotrophic and mycorrhizal fungi. Ectomycorrhizal fungi could form micropores (3–10 μm) in weatherable minerals, and hyphal tips could produce micro- to millimolar concentrations of these organic acids (Jongmans *et al.* 1997; van Breemen *et al.* 2000; van Hees *et al.* 2003). Tunnel formation in mineral grains was more intense in nutrient-poor sites, indicating a higher contribution of fungi to ecosystem influx of potassium and calcium. Ectomycorrhizal density was positively correlated with feldspar tunnel density in the upper 2 cm of the E horizon, which suggests that ectomycorrhizas were involved in mineral tunnelling (Hoffland *et al.* 2003). In order to quantify the contribution of mineral tunnelling to the weathering of feldspars and ecosystem influx of calcium and potassium, surface soils of 11 podzols were studied by Smits *et al.* (2005). Tunnels were observed only in soils older than 1650 y, with the contribution of tunnelling to mineral weathering in the upper mineral soil being less than 1 %. Feldspar tunnelling corresponded to an average ecosystem influx of 0.4 g ha^{-1} $year^{-1}$ for potassium and 0.2 g ha^{-1} $year^{-1}$ for calcium over 5000 y of soil development. These data indicate that the contribution of tunnelling to weathering is more important in older soils, but remains low (Smits *et al.* 2005).

Fungal weathering of limestone, sandstone and marble, also occurs (Kumar & Kumar 1999; Ehrlich 2002). Cavities in limestone provide a major habitat for fungi, particularly in extreme environments (Ehrlich 1998). In hot and cold deserts and semi-arid regions, clump-like colonies of epi- and endolithic darkly-pigmented microcolonial fungi are common inhabitants of limestone, sandstone, marble and granite, as well as other rock types (Staley *et al.* 1982; Sterflinger 2000; Gorbushina *et al.* 1993). Analysis of desert rock samples has shown colonies or single cells in connection with pitting and etching patterns suggesting organic- or carbonic acid attack of the mineral surface (Sterflinger 2000). Microcolonial fungi are common inhabitants of biogenic oxalate crusts on granitic rocks (Blazquez *et al.* 1997).

Acidolysis, complexolysis and metal accumulation were involved in solubilization of zinc phosphate and pyromorphite by a selection of soil fungi representing ericoid and ectomycorrhizal plant symbionts and an endophytic/entomopathogenic fungus, *Beauveria caledonica*. Acidolysis (protonation) was found to be the major mechanism of both zinc phosphate and pyromorphite dissolution for most of the fungi examined and, in general, the more metal tolerant fungal strains yielded more biomass, acidified the medium more and dissolved more of the metal mineral than less tolerant strains. However, *B. caledonica* excreted a substantial amount of oxalic acid (to 0.8 mM) in the presence of pyromorphite that coincided with a dramatic increase in lead mobilization providing a clear example of complexolysis (Fomina *et al.* 2004, 2005a). A strain of *Penicillium oxalicum* could solubilize different insoluble phosphates by producing organic acids, particularly malic acid, and improved the efficiency of rock phosphate applied to maize plants (Shin *et al.* 2005). Growth, proton and oxalate efflux, potassium ion absorption and mineral depletion by isolates of *Cenococcum geophilum*, *Pisolithus microcarpus* and by two isolates of *Pisolithus* sp. were compared using vermiculite or phlogopite as the sole potassium source. Protons produced by the fungi replaced interlayer potassium ions, while oxalate led to biological weathering of the minerals, especially under conditions of limited exchangeable potassium with phlogopite as a potassium source (Yuan *et al.* 2004).

Calcium carbonate ($CaCO_3$) and calcium magnesium carbonate [$CaMg(CO_3)_2$] occur extensively on the Earth's surface as limestone and dolomite and are an important reservoir of carbon (Ehrlich 2002; Goudie 1996). Numerous microorganisms, including bacteria and fungi, have been isolated from natural limestone, and cryptoendolithic (i.e. actively penetrating the rock matrix to several mm in depth) and chasmolithic or endolithic (i.e. living in hollows, cracks and fissures) fungal species are known. Homogeneous carbonates are predominantly colonized by endolithic species that actively penetrate the rock substratum independent of already existing pores or fissures. These organisms construct a system of ducts and cavities by active dissolution of the substratum. The production of organic acids is again believed to play a major role in degradation of limestone (Ehrlich 2002). A fresh, non-colonized surface is penetrated by algae and ascomycetes in the first and second year after exposure to the environment. The establishment of complex colonization patterns on and in the substratum by lichen-forming fungi takes several years. In spite of the primary deteriorative effect on their substratum by the organisms, long-term endolithic growth also involves mechanisms that stabilize and preserve the rock surface morphology. A tightly woven cellular network may strengthen colonized stone (Hoppert *et al.* 2004).

The chemical basis for carbonate weathering is the instability of carbonates in acid solution:

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \quad (1)$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2 \quad (3)$$

As $Ca(HCO_3)_2$ is very soluble compared with $CaCO_3$, $CaCO_3$ dissolves even in weakly acidic solutions. In strong acid solutions, $CaCO_3$ dissolves more rapidly as carbonate is lost from the solution as CO_2. Any organism capable of producing acidic metabolites extracellularly is capable of dissolving carbonates, and even the production of CO_2 during respiration can have the same effect:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (4)$$

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (5)$$

Fungi can also attack rock surfaces through redox attack of mineral constituents such as manganese and iron, where reduction to manganese(II) and iron(II) species can result in dissolution (Timonin *et al.* 1972; Grote & Krumbein 1992; de la Torre & Gomez-Alarcon 1994). Conversely, the oxidation of iron(II) and manganese(II), to iron(III) and manganese(IV) respectively, leads to the formation of dark patinas on glass surfaces (Erkhardt 1985). It is probable that most types of rock, stone and other mineral-based materials can be susceptible to fungal deterioration.

Concrete biodeterioration in radioactive waste disposal

Cement and concrete are used as barriers in all kinds of nuclear waste repositories. Despite the theoretical service life of concrete reaching up to 1 M years, biological corrosion is an important factor to take into account. All types of building and ceramic materials, concrete and cement can be deteriorated by microorganisms (Diercks *et al.* 1991; Gaylarde & Morton 1999; Kikuchi & Sreekumari 2002; Roberts *et al.* 2002). In some environments, fungi may dominate the microbiota and play an important role in the deterioration of concrete (Perfettini *et al.* 1991; Nica *et al.* 2000; Fomina *et al.* 2005d) with complexolysis suggested as the main mechanism of calcium mobilization (Gu *et al.* 1998). The potential mycocorrosion problem for metal containers selected for storage of nuclear waste in terrestrial environments has been stressed (Geesey 1993). Further, endolithic, indigenous microorganisms are capable of surviving gamma irradiation doses simulating the near-field environment surrounding waste canisters (Pitonzo *et al.* 1999). Fungal attack on concrete can be strongly and mildly aggressive caused by protons and organic acids and production of hydrophilic slimes leading to biochemical and biophysical/biomechanical deterioration (Sand & Bock 1991a, 1991b). Fungi include desiccant-resistant species and many can grow on traces of nutrients. *Fusarium*, *Penicillium* and *Amorphotheca* (anam. *Hormoconis*) species can degrade hydrocarbon-based lubricants and produce organic acids that cause localized corrosion of post-tension structures used in buildings, bridges, and nuclear power plants (Little & Staehle 2001). Many studies have indicated that fungi play an important role in the deterioration of concrete (Perfettini *et al.* 1991; Gu *et al.* 1998; Nica *et al.* 2000). Fungal degradation proceeded more rapidly than bacterium-mediated degradation with complexolysis suggested as the main mechanism of calcium mobilization (Gu *et al.* 1998). Several fungi exhibit very high levels of radiation-resistance and can survive and colonize concrete barriers even under the severe radioactive contamination which occurred after the Chernobyl accident in 1986 (Zhdanova *et al.* 2000). It was discovered that low-level gamma radiation did not affect spore germination, but apparently led to directed growth of fungal tips towards the radiation source (so-called positive radiotropism) (Zhdanova *et al.*

2001). The high radiation selection pressure inside Reactor No. 4 of the Chernobyl nuclear power plant (radiation $\alpha = 500$ Bq cm^{-2}, $\beta = 20000$ Bq cm^{-2}, $\gamma = 700$ mR h^{-1}) led to genetic adaptation of fungal strains inhabiting the concrete surfaces (Mironenko *et al.* 2000). The most frequently isolated microfungi in the first years after the accident and later in the habitats with severe radiation were melanized species of *Alternaria*, *Cladosporium*, and *Aureobasidium* (Zhdanova *et al.* 2000). It was also shown that microfungi from the genera *Aspergillus*, *Alternaria* and *Cladosporium* were able to colonize the samples of the concrete used as the radioactive waste barrier and leached iron, aluminium, silicon and calcium, and reprecipitated silicon and calcium oxalate in their microenvironment (Fomina, unpubl.; Olishevskaya *et al.* 2004; Fomina *et al.* 2005d). Fungi are, of course, also important members of the microbial communities (including lichens) that colonize and deteriorate 'normal' concrete and cement used in buildings and other structures (Perfettini *et al.* 1991).

Mycogenic mineral formation

Free-living and symbiotic fungi play an important role in mineral formation through precipitation of organic and inorganic secondary minerals and through nucleation and deposition of crystalline material on and within cell walls, notably oxalates and carbonates (Table 3) (Arnott 1995; Ehrlich 1998; Gadd 1999; Burford *et al.* 2003a, 2003b, 2006; Urzi *et al.* 1999; Gorbushina *et al.* 2002a, 2002b). This process may be important in soil as precipitation of carbonates, phosphates and hydroxides increases soil aggregation. Cations like Si^{4+}, Fe^{3+}, Al^{3+} and Ca^{2+} (that may be released through weathering mechanisms) stimulate the precipitation of such compounds that act as bonding agents for soil particles. Roots and hyphae can enmesh particles together, alter alignment and release organic metabolites that assist aggregate stability (Bronick & Lal 2005)

Oxalates

Calcium oxalate is the most common form of oxalate associated with soils and leaf litter, occurring as the dihydrate (weddellite $CaC_2O_4 \cdot 2H_2O$) or the more stable monohydrate (whewellite, $CaC_2O_4 \cdot H_2O$; Fig 6). Calcium oxalate crystals are commonly associated with free-living, pathogenic and plant symbiotic fungi, and are formed by reprecipitation of solubilized calcium as calcium oxalate (Arnott 1995; Tait *et al.* 1999). Fungal-derived calcium oxalate can exhibit a variety of crystalline forms (tetragonal, bipyramidal, plate-like, rhombohedral or needles). The formation of calcium oxalate by fungi has a profound effect on geochemical processes in soils, acting as a reservoir for calcium, but also influencing phosphate availability (Gadd 1993a, 1999; Gadd & Sayer 2000; Jacobs *et al.* 2002a, 2002b).

Fungi can produce other metal oxalates with a variety of different metals and metal-bearing minerals, including cadmium, cobalt, copper, manganese, lead, strontium and zinc (Fig 6) (Sayer & Gadd 1997; Gadd 2000a; Jarosz-Wilkolazka & Gadd 2003; Burford *et al.* 2003b, 2006; Fomina *et al.* 2005a). *Beauveria caledonica* was able to solubilize cadmium, copper, lead and zinc minerals, converting them into oxalates in the local microenvironment, but also in association with the mycelium (Fomina *et al.* 2005a). When grown on copper phosphate-containing medium, this fungus accumulated approximately 100 mg copper (g dry wt^{-1}) with approximately 35 % comprising copper oxalate (moolooite) crystals. Oxalate excretion has been reported to be induced or enhanced by NO_3^- in contrast to NH_4^+, and also the presence of HCO_3^-, Ca^{2+}, and some toxic metals (copper, aluminium) or minerals (pyromorphite, zinc phosphate) (Lapeyrie *et al.* 1987, 1991; Wenzel *et al.* 1994; Gharieb & Gadd 1999; Whitelaw *et al.* 1999; Ahonen-Jonnarth *et al.* 2000; van Leerdam *et al.* 2001; Arvieu *et al.* 2003; Casarin *et al.* 2003; Clausen & Green 2003; Fomina *et al.* 2004). Calcium oxalate has commonly been associated with ectomycorrhizal fungi (Cromack *et al.* 1979; Lapeyrie *et al.* 1990). However, it has been observed that oxalate-excreting strains of ectomycorrhizal fungi (*Rhizopogon rubescens*, *R. roseolus* and *Suillus collimitus*) are able to precipitate zinc oxalate when grown on NO_3^--containing medium in the presence of zinc phosphate and copper oxalate (moolooite) in the presence of copper phosphate (Fomina & Gadd 2007). Moreover, zinc-containing crystalline precipitates, presumably zinc oxalate, have been found within the extraradical mycelium of the ectomycorrhizal *R. rubescens*/*Pinus sylvestris* association grown in mesocosms with zinc phosphate (Fomina & Gadd 2007). The formation of metal oxalates may provide a mechanism whereby fungi can tolerate environments containing potentially high concentrations of toxic metals. Similar features occur in lichens growing on copper sulphide bearing rocks, where precipitation of copper oxalate occurs within the thallus (Arnott 1995; Easton 1997). Oxalic acid was thought to be an important metabolite in the responses of wood-rotting fungi to toxic metal stress. The formation of oxalate crystals by white-rot fungi (*Bjerkandera fumosa*, *Phlebia radiata*, and *Trametes versicolor*) and the brown-rot fungus *Fomitopsis pinicola*, was observed during growth on media containing high levels of toxic metal ions (Jarosz-Wilkolazka & Gadd 2003). Brown-rot fungi were incubated in agar and agar-wood microcosms containing metallic or hydroxide forms of aluminium, copper, and iron. Metal dissolution was associated with elevated oxalate concentrations in agar, but metals translocated into wood did not affect oxalate accumulation, crystal production, or decay rate (Schilling & Jellison 2006).

One study investigated the *in vitro* formation of calcium oxalates and glushinskite through fungal interaction with carbonate substrates and seawater. Fungal interactions and attack on the dolomitic and seawater substrates resulted in the formation of calcium oxalates (weddellite, whewellite) and glushinskite ($MgC_2O_4 \cdot 2H_2O$) associated with the destruction of the original hard substrates and their replacement by the new minerals. Both calcium and magnesium were mobilized from the experimental substrates by fungi. Such biochemical and diagenetic products of the interaction strongly mark the attacked substrates with a biological fingerprint, which also has relevance as biomarkers for primitive life. The formation of glushinskite is of importance as a biomineral bearing recycled magnesium, as well as the possibility of its transformation into a magnesium carbonate (Kolo & Claeys 2005).

Lichens are probably the most common expression of fungal growth on exposed subaerial rock substrates and building stone. Oxalic acid excretion by lichen fungi can result in the

Table 3 – Some examples of biomineralization of fungal hyphae and lichen thalli with different secondary minerals (from Burford *et al.* 2003a, 2003b; Burford, Fomina & Gadd, unpubl; also adapted from a number of sources including Grote & Krumbein 1992; de la Torre & Gomez-Alarcon 1994; Easton 1997; Verrecchia 2000; Haas & Purvis 2006; Burford *et al.* 2006)

Mineral	Fungal hyphae	Lichen thalli	Organism(s)
Birnessite $[(Na,Ca,K)Mn_7O_{14}\cdot 3H_2O)]$	Fungi on siderite boulder and natraqualf soil		*Alternaria* spp. *Cladosporium* spp.
Cadmium oxalate (CdC_2O_4)	Fungi cultured with , e.g. cadmium phosphate, or other cadmium compounds and minerals		*Beauveria caledonica*
Calcite ($CaCO_3$)	Fungi on stalactites, quaternary eolianites and calcretes; fungi grown in limestone cement microcosms and laboratory media containing insoluble calcium compounds, e.g. calcite, or other calcium-containing compounds and minerals	Lichens on roofing tiles, andesite, volcaniclastite and exposed caliche plates in weathered basaltic and rhyolitic rocks	*Caloplaca aurantia* *Cephalotrichum* sp. *Penicillium coryliphilum* *Penicillium simplicissimum* *Verrucaria* spp.
Cobalt oxalate (CoC_2O_4)	Fungi cultured with cobalt compounds		*Aspergillus niger*
Desert varnish (MnO and FeO)	Fungal action on siderite and rhodochrosite in desert regions and sandstone limestone and granite monuments		*Alternaria alternata* *Cladosporium cladosporoides* *Lichenothelia* spp. *Penicillium frequentans* *P. steckii* *Phoma glomerata*
Ferrihydrite ($Fe_2HO_8\cdot H_2O$ or $5Fe_2O_3\cdot 9H_2O$)		Lichen on recent lava flow, on olovine of basalt, gabbro and augite	*Pertusaria corallina* *Stereocaulon vulcani*
Glushinskite ($MgC_2O_4\cdot 2H_2O$)	Fungi cultured with hydromagnesite	Lichen–rock interface on serpentinite	*Lecanora atra* *Penicillium simplicissimum*
Goethite $[FeO(OH)]$		Lichen on metamorphic rocks, feldspars, granite and gneiss	*Xanthoparmelia conspersa* *Parmelina tiliacea*
Halloysite $[Al_2Si_2O_5(OH)_4\cdot 2H_2O]$		Action of lichens on cave deposits and waters	*Lasallia* spp. *Mucor* spp. *Parmelia s. lot* spp. *Penicillium* spp. *Rhizocarpon* spp. *Rhizopus* spp.
Humboldtine ($FeC_2O_4\cdot 2H_2O$)		Lichens on iron rich crystalline limestone and cupriferous rocks	*Acarospora smargdula* *Aspicila alpina* *Lecidea lactea*
Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$)		Mycobiont of lichen in ruins of a lead smelting mill	*Sterocaulon vesuvianum*
Hydromagnesite $[Mg_5(CO_3)_4(OH)_{2.4}\cdot H_2O]$	Fungi cultured with hydromagnesite		*Penicillium simplicissimum*
Lead oxalate, lead oxalate dihydrate (PbC_2O_4, $PbC_2O_4\cdot 2H_2O$)	Fungi cultured with pyromorphite, or in laboratory media containing lead compounds		*Aspergillus niger* *Beauveria caledonica*
Manganese oxalate ($MnC_2O_4\cdot 2H_2O$)	Fungi cultured in laboratory media containing manganese compounds	Lichen on manganese ore	*A. niger* *Pertusaria corallina*
Montmorillonite $[X_{0.33}Al_2Si_2O_{10}(OH)_2\cdot nH_2O$ where $X = Na^+, K^+, Ca^{2+}, Mg^{2+}]$		Action of lichens on cave deposits and waters	*Lasallia* spp. *Mucor* spp. *Parmelia* spp. *Penicillium* spp. *Rhizocarpon* spp. *Rhizopus* spp.
Moolooite $[CuC_2O_4\cdot nH_2O\ (n < 1)]$	Fungi cultured with, e.g. copper phosphate, or other copper-containing compounds and minerals	Lichens on cupriferous rocks	*Acarospora rugulosa* *Aspergillus niger* *Beauveria caledonica* *Lecidea inops* *L. lactea* *Rhizopogon rubescens* *Serpula himantioides*

Table 3 (*continued*)

Mineral	Fungal hyphae	Lichen thalli	Organism(s)
Strontium oxalate hydrate ($SrC_2O_4 \cdot H_2O$; $SrC_2O_4 \cdot 2.5H_2O$)	Fungi cultured with strontianite ($SrCO_3$), or other strontium-containing compounds and minerals		*Penicillium simplicissimum* *Pseudallescheria boydii* *Serpula himantioides*
Todorokite [(Mn,Ca,Mg) $Mn_3O_7 \cdot H_2O$]	Fungi in cave deposits and waters		*Mucor* spp. *Penicillium* spp. *Rhizopus* spp.
Uramphite [$NH_4(UO_2)(PO_4) \cdot 3H_2O$] and Chernikovite [$(H_3O)_2(UO_2)_2(PO_4)_2\ 6H_2O$]	Fungi cultured with uranium oxides, metallic depleted uranium, or other uranium-containing compounds and minerals		*Beauveria caledonica* *Hymenoscyphus ericae* *Rhizopogon rubescens*, *Serpula himantioides*
Weddellite ($CaC_2O_4 \cdot 2H_2O$)	In leaf litter and soils; fungi grown on limestone cement microcosms, and laboratory media containing insoluble calcium compounds, e.g. calcite, or other calcium-containing compounds and minerals	On serpentinite, cupriferous rocks, andesite and volcaniclastite	*Acarospora rugulosa* '*Aphyllophorales*' spp. *Aspicilia calcarea* *Caloplaca aurantia* *C. flavescens* *Geastrum* spp. *Hypogymnia physodes* *Hysterangium crassum* *Lecanora atra* *L. rupicola* *Lecidea inops* *L. lactea* *Ochrolechia parella* *Penicillium coryliphilum* *P. simplicissimum* *Pseudallescheria boydii* *Serpula himantioides*
Whewellite ($CaC_2O_4 \cdot H_2O$)	In Nari Limecrusts, Quaternary calcretes, forest leaf litter and soils; fungi grown on limestone cement microcosms, and laboratory media containing insoluble calcium compounds, e.g. calcite, or other calcium-containing compounds and minerals	On basalt, serpentinite, cupriferous rocks, gabbro, dolerite, andesite and volcaniclastite	*Acarospora rugulosa* *A. smargdula* *Aspicila alpina* *Caloplaca flavescens* *Cephalotrichum* sp. *Hypogymnia physodes* *Lecanora atra* *Lecanora rupicola* *Lecidea inops* *L. lactea* *Lobothallia calcarea* *L. radiosa* *Ochrolechia parella* *Xanthoarmelia conspersa* *Punctelia subrudecta* *Penicillium coryliphilum* *P.simplicissimum* *Pertusaria corallina* *Pseudallescheria boydii* *Serpula himantioides* *Xanthoria aureola*
Zinc oxalate ($ZnC_2O_4 \cdot 2H_2O$)	Fungi exposed to, e.g. zinc oxide, zinc phosphate		*Aspergillus niger*, *Beauveria caledonica* *Rhizopogon rubescens*. *Suillus collimitus*

Note that the hydration state of some minerals is unclear: hydration state only stated when this was specifically identified. The list is not exhaustive and many other mycogenic minerals are possible, as well as the species capable of mediating their formation.

dissolution of insoluble carbonates and silicates and the formation of water-soluble and insoluble oxalates (Jones & Wilson 1985; May *et al.* 1993; Edwards *et al.* 1991; Verrecchia 2000). Powder X-ray diffraction (XRD) and extended X-ray absorption spectroscopy studies (EXAFS) of lichens grown in areas heavily contaminated with lead and zinc, revealed that lead and zinc were coordinated by oxalates within the biomass of *Diploschistes muscorum*, whereas in *Xanthoria parietina*, lead was complexed to carboxylic groups of a polyphenolic compound, parientinic acid, located in the walls of the fungal hyphae (Sarret *et al.* 1998). Oxalates can be formed with a variety of metal ions wherever lichens grow (Purvis

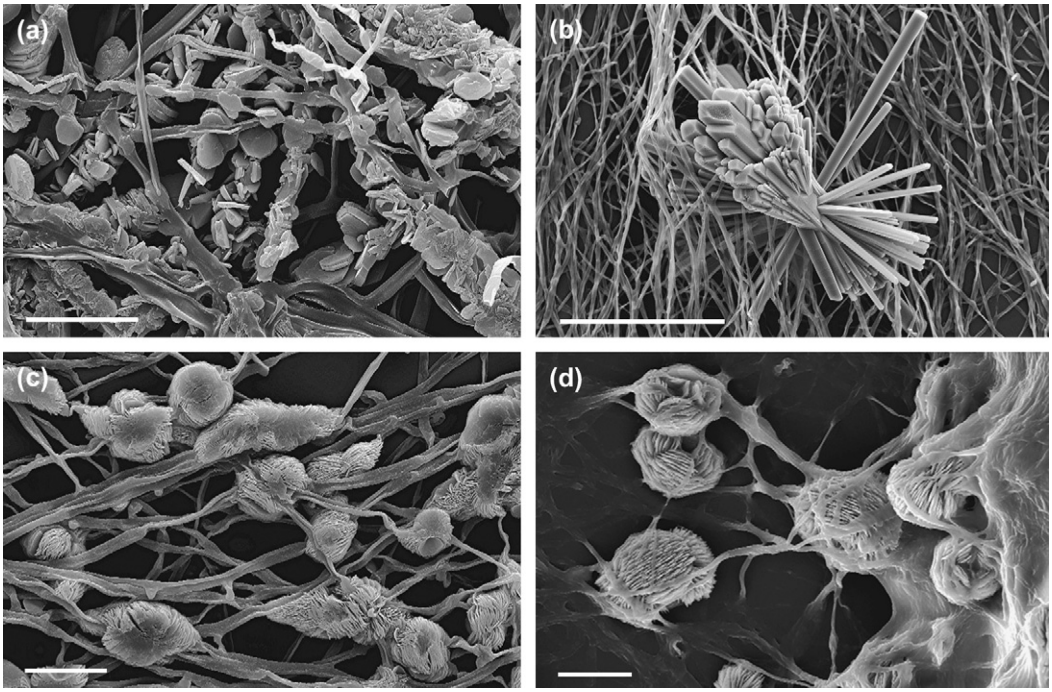

Fig 6 – Mycogenic oxalates. (A) Magnesium oxalate dihydrate ($MgC_2O_4 \cdot 2H_2O$, glushinskite) and hydromagnesite [$Mg_5(CO_3)_4(OH)_{2.4} \cdot H_2O$] precipitated on *Penicillium simplicissimum*; (B) strontium oxalate hydrate ($SrC_2O_4 \cdot H_2O$; $SrC_2O_4 \cdot 2.5H_2O$) on *Serpula himantioides*; (C) calcium oxalate monohydrate (whewellite) and calcium oxalate dihydrate (weddellite) on *S. himantioides*; and (D) copper oxalate hydrate [$CuC_2O_4 \cdot nH_2O$ ($n < 1$), moolooite] precipitation on *Beauveria caledonica*. Bars = (A) 20 μm; (B) 100 μm; (C,D) 20 μm [From Burford, Fomina & Gadd (unpubl.); see also Fomina *et al.* (2005a)].

1996). In particular, there has been concern over the deteriorative effects of biologically formed oxalic acid on architecturally important buildings, monuments and frescoes (Nimis et al. 1992). Conversely, several studies have suggested that lichen cover protects certain rock surfaces, acting as an 'umbrella', and reducing the erosion of, for instance slightly soluble calcium sulphates (Mottershead & Lucas 2000).

Carbonates

The precipitation of carbonates by microorganisms is widespread and significant in the biosphere (Rivadeneyra *et al.* 1993; Folk & Chafetz 2000; Fujita *et al.* 2000; von Knorre & Krumbein 2000; Mertz-Preiß 2000; Riding 2000; Warren *et al.* 2001; Hammes & Verstraete 2002). As mentioned earlier, free-living and lichen-forming fungi can be important agents of carbonate mineral deterioration. However, a less appreciated area of fungal action is their influence and roles in carbonate precipitation (Fig 7) (Goudie 1996; Sterflinger 2000). Many near-surface limestones (calcretes), calcic and petrocalcic horizons in soils are often secondarily cemented with calcite and whewellite (Verrecchia 2000). Although this phenomenon has partly been attributed to physicochemical processes, the presence of calcified fungal filaments in limestone and calcareous soils from a range of localities indicates that fungi may play a prominent role in secondary calcite precipitation. Fungal filaments mineralized with calcite, together with whewellite, have been reported in limestone and calcareous soils from a range of localities (Kahle 1977; Calvet 1982; Callot *et al.* 1985a, 1985b; Verrecchia *et al.* 1993; Monger & Adams 1996; Bruand & Duval 1999; Verrecchia 2000). It has been experimentally shown that fungi are able to reprecipitate secondary carbonates and biomineralize hyphae with both calcite and whewellite or with glushkinskite and hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] (Figs 6, 8; Burford *et al.* 2003b). Further, calcium oxalate can be degraded to $CaCO_3$ in the oxalate–carbonate cycle (Verrecchia *et al.* 2006). In semi-arid environments, this process may act in the cementation of pre-existing limestones (Verrecchia *et al.* 1990).

The formation of biogenic fabrics in limestone by two fungi, *Serpula himantioides* and a polymorphic fungal isolate from limestone identified as a *Cephalotrichum* sp., was investigated using laboratory microcosms containing carboniferous limestone (Fig 8) (Burford *et al.* 2006). After 21 d incubation at 25 °C, biomineralization of fungal filaments was observed and environmental electron scanning microscopy (ESEM) and X-ray micro-analysis (EDXA) of crystalline precipitates on the hyphae of *S. himantioides* demonstrated that the secondary crystals were similar in elemental composition to the original limestone. Powder X-ray diffraction (XRD) of crystalline precipitates showed they were composed of a mixture of calcite and whewellite. Analysis of crystals precipitated on the hyphae of the a *Cephalotrichum* sp. showed that they were composed solely of calcite or of calcite with some calcium oxalate dihydrate. These results provided direct experimental evidence for the precipitation of calcite on fungal hyphae in low nutrient calcareous environments, and suggest that fungi may play a wider role in the biogeochemical carbon cycle than has previously been appreciated.

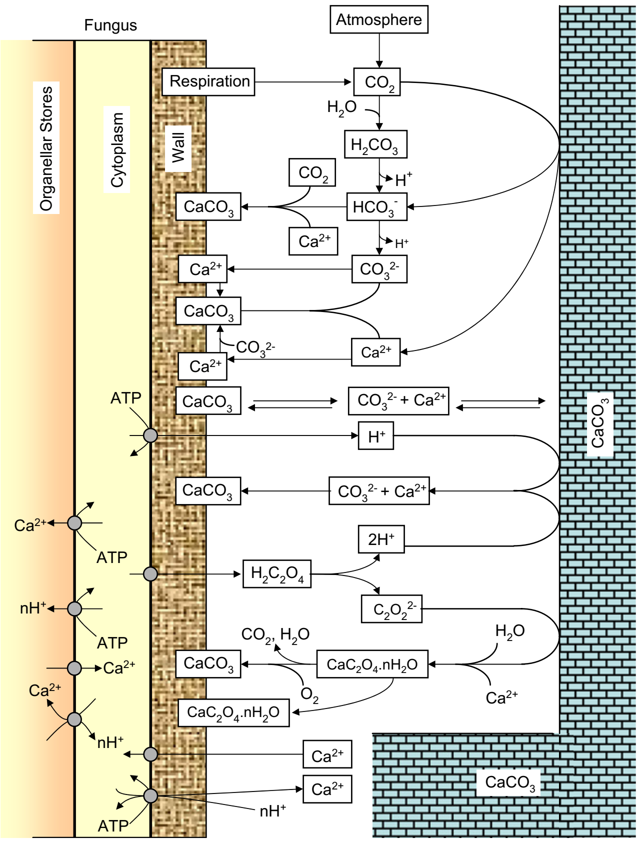

Fig 7 – Proposed mechanisms involved in the calcification of fungal hyphae in calcareous environments. Key biotic and abiotic mechanisms are shown that can influence Ca^{2+} and carbon dioxide (CO_2) mobility and production including cellular transport processes, respiratory activity, and solid, liquid and atmospheric CO_2 speciation. The scheme does not imply any quantification of the relative importance of the reactions shown, nor does it imply that all mechanisms shown may be operational under given physico-chemical and biological conditions. The fungal organellar stores could include the vacuole and endoplasmic reticulum. $H_2C_2O_4$, oxalic acid; $CaC_2O_4 \cdot nH_2O$, calcium oxalate; $C_2O_4^{2-}$, oxalate anion. From Burford *et al.* (2006).

Calcite formation by fungi may occur through other indirect processes *via* the fungal excretion of oxalic acid and the precipitation of calcium oxalate (Verrecchia *et al.* 1990, 2006; Gadd 1999; Verrecchia 2000). For example, oxalic acid excretion and the formation of calcium oxalate results in the dissolution of the internal pore walls of the limestone matrix so that the solution becomes enriched in free carbonate. During passage of the solution through the pore walls, $CaCO_3$ re-crystallizes as a result of a decrease in CO_2, and this contributes to hardening of the material. Biodegradation of oxalate as a result of microbial activity can also lead to transformation into carbonate, resulting in precipitation of calcite in the pore interior, leading to closure of the pore system and hardening of the chalky parent material. During decomposition of fungal hyphae, calcite crystals can act as sites of further secondary calcite precipitation (Verrecchia 2000). Manoli *et al.* (1997) demonstrated that chitin, the major component of fungal hyphal walls, is a substrate on which calcite will readily nucleate and grow. In the soil, oxalate oxidation by oxalotrophic bacteria results in CO_2 production and $CaCO_3$ precipitation. Verrecchia *et al.* (2006) propose that a large amount of the secondary $CaCO_3$ found in soils and surficial sediments originates by such a process, further emphasizing a key role of fungi in the oxalate–carbonate pathway, and its importance as a major global carbon sink.

Carnegiea gigantea is a columnar cactus that can weigh up to several tons, of which 85–90 % of the mass is water. Roughly 18 % of the dry mass consists of the biomineral weddellite, which is derived from atmospheric CO_2 *via* photosynthesis. A mature specimen can contain approximately 1×10^5 g weddellite, which occurs as aggregates up to 1 mm wide. After the death of the saguaro, a series of minerals crystallize in the decomposing plant. These minerals form from elements released from the decay of the cactus by microorganisms and is therefore a type of biologically induced mineralization. During the initial stages of decay, authigenic magnesium- and calcium-bearing minerals crystallize from elements released and include lansfordite ($MgCO_3 \cdot 5H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), several polymorphs of $MgC_2O_4 \cdot 2H_2O$ including glushinskite, monohydrocalcite ($CaCO_3 \cdot H_2O$), calcite, vaterite, and several unidentified magnesium-bearing phases. The common occurrence of fungal hyphae on the glushinskite suggests that it forms as a result of the reaction between oxalate released by fungi and the magnesium-rich solutions of the rotting saguaro. During the final stages of decay, the pith consists of a pale brown to tan-coloured sand of weddellite and its transformation product monohydrocalcite. This sand lithifies to porous sponge-like masses during the final stages of saguaro decay. This monohydrocalcite further alters to calcite. The calcite is subsequently solubilized and remobilized, precipitating as caliche in the desert soil, or redistributed by wind (Garvie 2003).

CO_2 and proteins released from a '*Verticillium* sp.' and an extremophilic actinomycete, *Thermomonospora* sp., may react with aqueous Ca^{2+} and Ba^{2+} to produce biogenic $CaCO_3$ and barium carbonate ($BaCO_3$) crystals. While extracellular synthesis of the highly unstable vaterite polymorph of $CaCO_3$ in a spherical morphology was observed with the fungus, both extra- and intracellular formation of $CaCO_3$ in the form of composites of flat plates and branched elongated flat plates, were observed with the actinomycete. Reaction of Ba^{2+} with '*Verticillium* sp.' and *Thermomonospora* sp. resulted in the extracellular synthesis of $BaCO_3$ crystals of spherical and flat, plate-like morphologies respectively. Specific proteins secreted by the microorganisms were significant in directing crystal structure and morphology (Rautaray *et al.* 2004).

Other mycogenic minerals

A wide range of minerals may be deposited under conditions that strongly deviate from 'normal' pressure/temperature diagrams of precipitation and stability, and these have been found in association with fungal communities on rock surfaces (Gorbushina *et al.* 2002a, b). Apart from $CaCO_3$ and oxalate, a variety of other mycogenic secondary minerals are associated with fungal hyphae and lichen thalli, including birnessite, desert varnish [manganese oxide (MnO) and iron oxide (FeO)], ferrihydrite, iron gluconate, calcium formate,

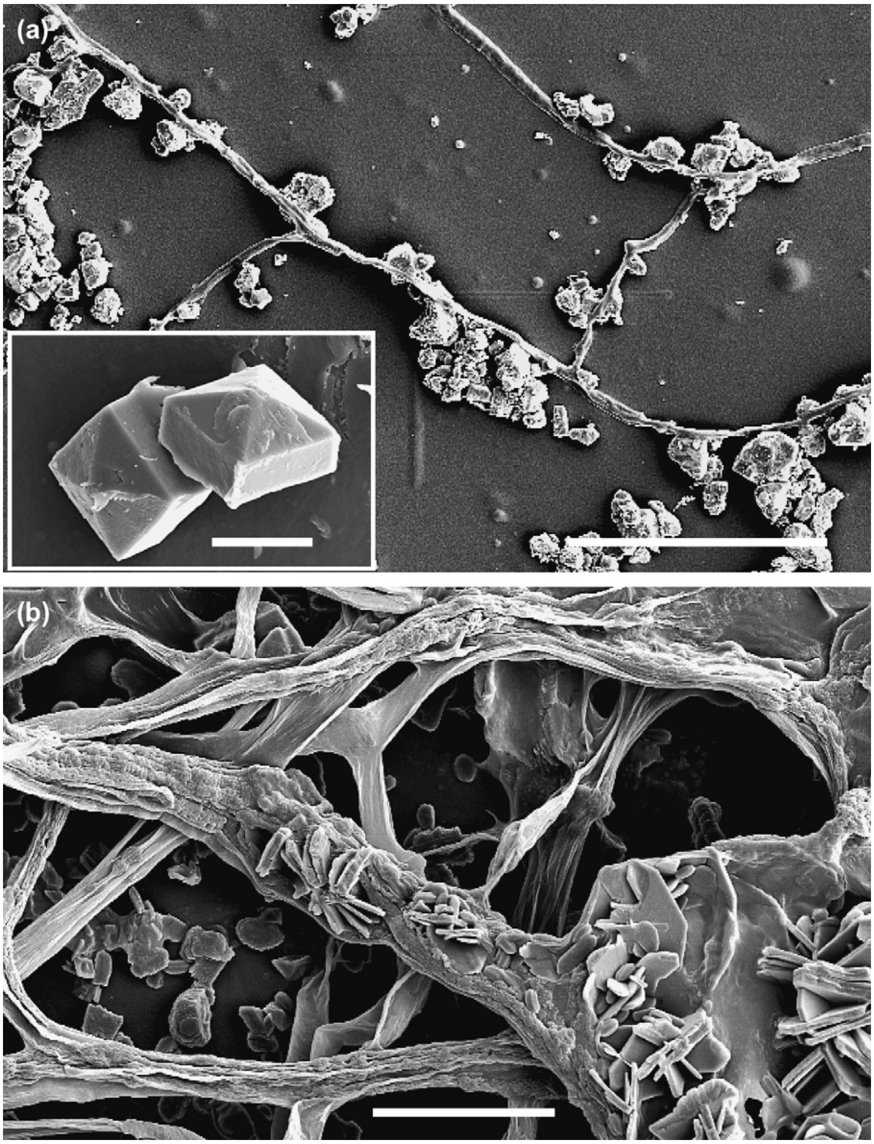

Fig 8 – Mycogenic carbonates. (A) Calcite crystals precipitated on a *Cephalotrichum* sp.; and (B) calcite and calcium oxalate monohydrate precipitated on *Serpula himantioides*. Inset: Calcite crystals precipitated in proximity to *Cephalotrichum* sp. Bars = (A) 20 μm; (B) 10 μm; inset = 20 μm. From Burford & Gadd (unpubl., see Burford *et al.* 2006).

forsterite, goethite, halloysite, hydroserussite, and todorokite (Grote & Krumbein 1992; Hirsch *et al.* 1995; Verrecchia 2000; Gorbushina *et al.* 2001; Burford *et al.* 2003b; Arocena *et al.* 2003). Precipitation, including crystallization, immobilizes metals and limits their bioavailability, as well as leading to the release of nutrients, such as sulphate and phosphate, if these are mineral components (Gadd 2000b). Small quantities of crystals were produced in the agar when *Rhizoctonia solani* was grown on calcium phosphate- and strontium hydrogen phosphate-amended media and these were identified as calcium or strontium sulphates, respectively (Jacobs *et al.* 2002a, 2002b). Fungi can also precipitate a variety of uranium-containing minerals after growth on uranium oxides or metallic-depleted uranium (Fig 9).

Some evaporate minerals, gypsum ($CaSO_4 \cdot 2H_2O$) and iron oxides (magnetite, Fe_3O_4), also display distinctive morphologies indicative of the presence of microbial communities (Gorbushina *et al.* 2002a). Another biogenic mineral (tepius) has been identified in association with a lichen carpet that covers high mountain ranges in Venezuela (Gorbushina *et al.* 2001). Forsterite (Mg_2SiO_4), the magnesium member of the olivine $[(Mg,Fe)_2\ SiO_4]$ mineral solid solution series, is known to occur only in volcanic rocks, meteorites and metamorphosized carbonates (e.g. skarn deposits). The presence of forsterite in surficial deposits on rock surfaces can therefore be considered a possible biosignature for former or extant life (Gorbushina *et al.* 2002a).

Reduction or oxidation of metals and metalloids

Many fungi precipitate reduced forms of metals and metalloids in and around fungal hyphae. For example, silver(I) reduction

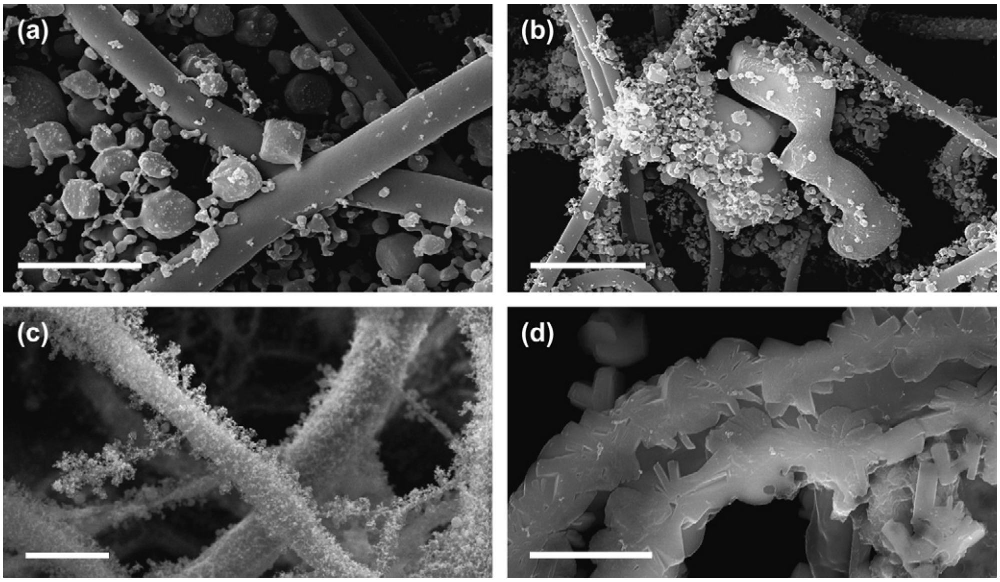

Fig 9 – Formation of uranium-containing mycogenic biominerals. (A–B) Uranium biomineralization on *Beauveria caledonica* mycelium grown on uranium oxide (U_3O_8)-containing agar showing hyphal encrustation with tabular uranium precipitates; (C) the ericoid mycorrhizal fungus *Hymenoscyphus ericae* grown in the presence of metallic depleted uranium (DU) showing encrustation of hyphae with secondary mycogenic uranium minerals; (D) the ectomycorrhizal fungus *Rhizopogon rubescens* grown in the presence of DU showing encrustation with secondary mycogenic uranium minerals. Bars = (A) 2μm (B) 5 μm (C) 20 μm (D) 5 μm. From Fomina & Gadd (unpubl.).

to elemental silver [silver(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 mercury(II) to volatile mercury(0) can also be mediated by fungi (Gadd 1993b, 2000b, 2000c). An *Aspergillus* sp. was able to grow at arsenate concentrations of 0.2 M (more than 20-fold higher than that withstood by *Escherichia coli*, *Saccharomyces cerevisiae* and *A. nidulans*), and it was suggested that increased arsenate reduction contributed to the hyper-tolerant phenotype (Canovas *et al.* 2003a, 2003b).

Desert varnish, an oxidized metal layer (patina) a few millimetres thick found on rocks and in soils of arid and semi-arid regions, is believed to be of fungal and bacterial origin. *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 & Krumbein 1992). Similar oxidation of iron(II) and manganese(II) by fungi leads to the formation of dark patinas on glass surfaces (Erkhardt 1985). A manganese-depositing fungus, identified as an *Acremonium*-like hyphomycete, was isolated from a variety of laboratory and natural locations including manganese(III,IV) oxide-coated stream-bed pebbles. A proposed role for a laccase-like multicopper oxidase was postulated, analogous to the manganese(II)-oxidizing factors found in certain bacteria (Miyata *et al.* 2004).

Fungi–clay interactions

Clay mineral formation and impact on soil properties

Silicon dioxide, when combined with oxides of magnesium, aluminium, calcium and iron, forms the silicate minerals in rocks and soil (Bergna 1994). Silicates are the largest class of minerals comprising 30 % of all minerals and making up 90 % of the Earth's crust (Ehrlich 1998). These high-temperature minerals are unstable in the biosphere and break down readily to form clays. Microorganisms, including fungi, play a fundamental role in the dissolution of silicates in rock weathering, and therefore in the genesis of clay minerals, and soil and sediment formation (Banfield *et al.* 1999; Bennett *et al.* 2001). Indeed, the presence of clay minerals can be a typical symptom of biogeochemically weathered rocks, and this has been observed for symbiotic fungi (lichens and ectomycorrhizas) (Barker & Banfield 1996, 1998; Rodriguez Navarro *et al.* 1997; Arocena *et al.* 1999, 2003). The fungal partner is also reported to be involved in the formation of secondary silicates, such as opal and forsterite, in lichen thalli (Gorbushina *et al.* 2001). In lichen weathering of silicate minerals, calcium, potassium, iron clay minerals and nanocrystalline aluminous iron oxyhydroxides were mixed with fungal organic polymers (Barker & Banfield 1998), while biotite was interpenetrated by fungal hyphae growing along cleavages and partially converted to vermiculite (Barker & Banfield 1996). Other studies have shown that the transformation rate of mica and chlorite to 2:1 expandable clays was predominant in the ectomycorrhizosphere compared with non-ectomycorrhizosphere soils, likely to be a result of the high production of organic acids and direct extraction of K^+ and Mg^{2+} by fungal hyphae (Arocena *et al.* 1999).

Soil, which can be considered to be a biologically active loose mass of weathered rock fragments mixed with organic matter, is the ultimate product of rock weathering, i.e. the interaction between the biota, climate, and rocks. Clay minerals are generally present in soil in larger amounts than organic matter and, because of their ion-exchange capacity, charge, and adsorption powers, they perform a significant buffering function in mineral soils (Ehrlich 2002) and are important reservoirs of cations and organic molecules (Wild 1993; Li & Li 2000; Dinelli & Tateo 2001; Dong *et al.* 2001; Krumhansl *et al.* 2001).

Biological effects of clay minerals

Fungi are in close proximity to clay minerals in soils and sediments. Numerous studies have shown that interactions of microorganisms with solid adsorbents leads to an increase in biomass, growth rate and the production of enzymes and metabolites (Stotzky 1966, 2000; Martin *et al.* 1976; Fletcher 1987; Marshall 1988; Clause & Filip 1990; Lee & Stotzky 1999; Lotareva & Prozorov 2000; Lunsdorf *et al.* 2000; Demaneche *et al.* 2001; Fomina & Gadd 2002a). Some clays may stimulate or inhibit fungal metabolism (Fomina *et al.* 2000b; Fomina & Gadd 2002a). Stimulatory effects may arise from the abilities of different clays to serve as: (1) pH buffers; (2) a source of metal cationic nutrients; (4) specific adsorbents of metabolic inhibitors, other nutrients and growth stimulators; and (4) modifiers of the microbial microenvironment because of their physico-chemical properties such as surface area and adsorptive capacity (Stotzky 1966; Babich & Stotzky 1977; Marshall 1988; Martin *et al.* 1976; Fletcher 1987; Garnham *et al.* 1991; Vettori *et al.* 2000). Further, clay minerals (bentonite, palygorskite and kaolinite) can markedly influence the size, shape and structure of mycelial pellets in liquid media (Fomina & Gadd 2002b).

Fungi–clay mineral interactions in soil aggregation

Fungi–clay mineral interactions play an important role in soil evolution, aggregation and stabilization (Dorioz *et al.* 1993; Burford *et al.* 2003a). Fungi entangle soil particles in their hyphae forming stable microaggregates and take part in polysaccharide aggregation (Tisdall *et al.* 1997; Chantigny *et al.* 1997; Puget *et al.* 1999). Interactions between hyphae and solid particles are subject to a complex of forces of both a physico-chemical (electrostatic, ionic, hydrophobic effects, etc) and biological nature (chemotropism, production of specific enzymes, polysaccharides, lectins and other adhesins, etc) (Lunsdorf *et al.* 2000). Direct biophysical effects were shown in the microscale whereby fungal hyphae attracted and oriented clay platelets because of surface charge phenomena, and acted as nucleation zones in the formation of narrow clay-lined channels (Ritz & Young 2004). Interactions between clay minerals and fungi alter the adsorptive properties of both clays and hyphae (Morley & Gadd 1995; Fomina & Gadd 2002b). Under certain conditions, sorption abilities of fungi–clay aggregates can be decreased due to blocking and masking of binding sites or increased due to modification of binding sites and emergence of new ones, and this may have further implications for the fate of toxic metals in soil (Fomina & Gadd 2002b).

Clay and silicate weathering by fungi

Fungi and bacteria play an important role in the mobilization of silica and silicates (Ehrlich 2002). Their action is mainly indirect, either through the production of chelates or the production of acids (mineral or organic), or as for certain bacteria, the production of ammonia or amines. Fungi isolated from weathered rock surfaces (*Botrytis*, *Mucor*, *Penicillium* and *Trichoderma* spp.) could solubilize calcium, magnesium and zinc silicates (Webley *et al.* 1963). Mobilization of silicate from clay minerals by *Aspergillus niger* was a result of oxalic acid excretion (Henderson & Duff 1963). The majority of fungal strains belonging to the genera *Aspergillus*, *Paecilomyces*, *Penicillium*, *Scopulariopsis* and *Trichoderma* can leach iron in submerged culture from a China clay sample (Mandal *et al.* 2002). Large amounts of oxalic, citric and gluconic acids were produced by *Penicillium frequentans* in liquid culture. This caused extensive deterioration of clay silicates, as well as micas and feldspars, from sandstone and granite as a result of organic salt formation such as calcium, magnesium and ferric oxalates and calcium citrates (De la Torre *et al.* 1993). The oxalate-excreting fungus *Hysterangium crassum* also weathered clay minerals *in situ* (Cromack *et al.* 1979).

Metal–fungi interactions

Approximately 75 % of the elements in the Periodic table are metals and all occur in the environment to varying extents, many as components of rocks and minerals as mentioned above (Fraústo da Silva & Williams 1993). Fungi encounter metals in their natural environment, and through anthropogenic influences such as the accidental or deliberate release of pollutant metals, industrial and agricultural applications and treatments, and colonization of human constructions. Although many metals are essential for fungal growth and metabolism (e.g. sodium, potassium, copper, zinc, cobalt, calcium, magnesium, manganese, iron), all can exert toxicity when present above certain threshold concentrations in bioavailable forms (Gadd 1993a). Metals that have no known biological function (e.g. cadmium, mercury, lead) can also be accumulated and exhibit toxicity (Gadd 1993a). Toxicity is greatly affected by the physicochemical nature of the environment and the chemical behaviour of the particular metal species in question. Metals exert toxic effects in many ways, they can inhibit enzymes, displace or substitute for essential metal ions, cause disruption of membranes, and interact with systems that normally protect against the harmful effects of free radicals (Gadd 1993a; Howlett & Avery 1997). Toxic metals can inhibit growth and spore germination of fungi, affect reproduction and metabolism, and reduce the ability of mycorrhizal fungi to colonize roots of host plants (Fomina *et al.* 2005). However, many fungi survive and grow in apparently metal-polluted locations and a variety of mechanisms, both active and incidental, contribute to tolerance. Several studies have reported a population shift from unicellular bacteria and streptomycetes to fungi in contaminated soils (Chander *et al.* 2001a,b; Khan & Scullion 2002). 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 as metallothioneins and phytochelatins, etc, vacuolar localization) (Gadd

1993a; Blaudez *et al.* 2000a; Perotto & Martino 2001; Baldrian 2003; Meharg 2003). In several mycorrhizal fungi, more metal-tolerant fungal strains solubilized toxic metal minerals more efficiently (Fomina *et al.* 2004, 2005c).

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

Fossil fuel combustion, mineral mining and processing, and the production of industrial effluents and sludges, biocides and preservatives, release a variety of toxic metal species into aquatic and terrestrial ecosystems and this can have significant effects on the biota (Gadd & Griffiths 1978; Gadd 1992a, 2000c, 2005, 2007b; Wainwright & Gadd 1997). Metal-rich habitats also occur due to natural localized ores and mineral deposits, and the weathering processes described earlier: rocks, minerals, soil and sediments are a vast reservoir of metals. Restoration of metal-contaminated environments requires a functional microbial community for plant community establishment, soil development, and biogeochemical cycling. Many studies have revealed that metal toxicity reduces microbial numbers and activity and greatly affects microbe-mediated processes in soil ecosystems, such as organic matter decomposition (Aoyama & Nagumo 1997a, 1997b; Chander & Brookes 1991; Brookes & McGrath 1984; Kuperman & Carreiro 1997; Khan & Scullion 2000; Olayinka & Babalola 2001). The frequency of tolerant microorganisms may increase with an increase in toxic metal levels (Olson & Thornton 1982; Huysman *et al.* 1994; Kunito *et al.* 1997). This can lead to a decrease in species diversity and therefore a shift in microbiota composition (Pennanen *et al.* 1996). In fungi, metal resistance is genetically inherited as species- or strain-specific characteristics, and adaptation to metal stress is thought to be of minor importance. Resistant fungal species are usually present at low frequencies in non-contaminated soils, but can become dominant under toxic metal stress (Kunito *et al.* 1998). However, fungi, including ectomycorrhizal fungi, show considerable interspecific responses to toxic metals, and the extent to which intraspecific (adaptive) resistance occurs remains unclear (Meharg & Cairney 2000). It should be emphasized that resistance and tolerance are arbitrarily defined, frequently interchangeable terms, and often based on whether particular strains can grow in the presence of selected toxic metal concentrations in laboratory media. It is more appropriate to use ‘resistance’ to describe a direct mechanism resulting from metal exposure, such as metallothionein synthesis. ‘Tolerance’ may rely on intrinsic biochemical and structural properties of the host, such as possession of impermeable cell walls, extracellular slime layers or polysaccharide, and metabolite excretion, as well as environmental modification of toxicity. However, distinctions are difficult in many cases because several direct and indirect mechanisms, both physico-chemical 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 speciations and toxicity, and the nature of any microbial resistance/tolerance mechanisms involved (Gadd 1992b).

Mycelial fungi can develop a significant biomass in soil and may sequester considerable 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 (Mineev *et al.* 1999; Chander *et al.* 2001a, 2001b; Kostov & van Cleemput 2001; Olayinka & Babalola 2001; Khan & Scullion 2002). The different responses of bacteria and fungi to toxic metals were reflected in an increase in the relative fungal:bacterial ratio (estimated using phospholipid fatty acid analysis) with increased metal loads (Rajapaksha *et al.* 2004). Fungal and bacterial activities in soil are also differentially affected by toxic metals. The population shift to fungi can lead to increased decomposition of organic matter and reduced assimilation of released N (Khan & Scullion 2002).

All nutritional groups of fungi (saprotrophs, biotrophs, and necrotrophs) can be affected by toxic metals. A relative decrease in an indicator fatty acid for AM fungi and an increase for other fungi has been reported in zinc-polluted soil (Kelly *et al.* 1999). Toxic metal (cadmium, chromium, copper, nickel, lead and zinc) contamination of soil led to a significant decrease in the number of AM fungi and low colonization of plant roots, and as a result, to changes in the species diversity of mycorrhizal fungi (Mozafar *et al.* 2002; Moynahan *et al.* 2002). Toxic metals also reduced plant root colonization by ectomycorrhizal fungi (Fay & Mitchell 1999). Multiple contamination of soil with cadmium, lead, zinc, antimony, and copper, as well as nickel deposition, had a toxic effect on ectomycorrhizal fungi associated with *Pinus sylvestris* seedlings and caused shifts in ectomycorrhizal species composition (Hartley *et al.* 1999; Markkola *et al.* 2002). The extent to which such changes in below-ground communities of mycorrhizal fungi are sustained in the longer term is unclear. The major limitation to predicting the consequences of pollution-mediated changes in mycorrhizal fungal communities is a limited understanding of the functional significance of mycorrhizal biodiversity (Cairney & Meharg 1999).

A variety of other population and species responses has been recorded. Non-keratinolytic fungi showed a higher tolerance to cadmium than keratinolytic fungi (Plaza *et al.* 1998). Zygomycetes were more tolerant to cadmium than ascomycetes and conidial fungi (Plaza *et al.* 1998). 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) and may also be dominant members of the mycobiota of metal-contaminated phylloplanes (Mowll & Gadd 1985). Dark septate endophytes were found to be the dominant fungi from healthy fine roots of *Erica herbacea* in lead, cadmium, and zinc-polluted soil (Cevnik et al. 2000). Strains of *Aspergillus* were more cadmium tolerant than strains of *Penicillium* (Plaza *et al.* 1998), but *Penicillium* species are often reported to be dominant in copper-contaminated environments. In Brazilian soils with copper concentrations 25–11 500 mg kg^{-1} the predominance of a *Penicillium* species tolerant to a copper concentration of 750 mg kg^{-1} in soil was found (Ribeiro *et al.* 1972). A very high predominance of *Penicillium* species (80 % of isolations) was observed in freshly excavated archeological soil, containing 500 mg kg^{-1} copper and 500 mg kg^{-1} lead, at the site of a Bronze Age ancient Greek copper-smelting furnace (Olviya , Ukraine) (Fomina *et al.* unpubl.). A useful bioindicator for soil contamination by toxic metals is the ratio of metal-tolerant to metal-sensitive microorganisms (Kunito *et al.* 1998). For example, the ratio of copper-tolerant to copper-sensitive fungal isolates was 50–92 % in different toxic metal polluted soils and only 2–19 % in non-polluted soils from southern Ukraine (Fomina *et al.* unpubl.). Fungal colony-forming units (CFUs) were ten-times lower in lead-enriched soils, the species composition was widely different from that in control soils, and the isolated fungi had a high lead tolerance. The most commonly isolated fungus in lead-enriched soils was *Tolypocladium inflatum*. Comparison of isolates from lead-enriched soil and isolates from unpolluted soils showed that *T. inflatum* was intrinsically lead-tolerant, and that the prolonged conditions with high lead had not selected for any increased tolerance (Baath *et al.* 2005).

Investigations on metal toxicity in mycorrhizal, especially ectomycorrhizal, fungi have revealed wide inter- and intraspecific variation in metal sensitivity (Colpaert & van Assche 1987; Jones & Muehlchen 1994; Hartley *et al.* 1997a,b; Vodnik *et al.* 1998; Blaudez *et al.* 2000b; Meharg & Cairney 2000; Sharples *et al.* 2001). For fungi growing on wood at metal-contaminated sites, natural selection for metal-tolerant strains was not observed (Baldrian 2003; Baldrian & Gabriel 2002). However, the situation may be different in soil where concentrations of toxic metals could be considerably higher, and the process of adaptation to metal stress is probably accompanied by the exclusion of metal-sensitive fungal strains (Baldrian 2003). Many studies have suggested that selection for resistant ecotypes occurs where the degree of toxic metal contamination and selection pressure is high (Colpaert & van Assche, 1987; Colpaert *et al.* 2000; Sharples *et al.* 2000, 2001). For example, isolates of the ericoid mycorrhizal fungus *Oidiodendron maius*, recovered from *Vaccinium myrtillus* growing in metal polluted areas, were generally less sensitive to metals than strains from non-polluted sites (Lacourt *et al.* 2000). *In vitro* zinc tolerance of isolates of the ectomycorrhizal *Suillus luteus* from a zinc-polluted habitat was significantly higher than isolates from a non-polluted site (Colpaert *et al.* 2000). An isolate of an ectomycorrhizal *Pisolithus* sp. from a chromium and nickel-contaminated site not only colonized a greater percentage of root tips *in vitro*, but was more effective in promoting *Eucalyptus urophylla* seedling total biomass in nickel-amended soils than other isolates (Aggangan *et al.* 1998). 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.

Physiological responses of fungi to toxic metals

Toxic metals can inhibit growth and spore germination of fungi, affect reproduction and metabolic activity, and reduce the ability of mycorrhizal fungi to colonize host plant roots (Gadd 1993a; Amir & Pineau 1998; Fay & Mitchell 1999; Hartley-Whitaker *et al.* 2000a,b; Jentschke & Godbold 2000; Mozafar *et al.* 2002; Moynahan *et al.* 2002; Baldrian 2003).

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). Nickel was reported to be more toxic to fungal growth and ectomycorrhiza formation than chromium (Aggangan *et al.* 1998). Copper was found to be toxic and cadmium very toxic to cultures of 15 decomposer basidiomycetes (Hoiland 1995). However, a similar toxicity of both metals was shown on a solid medium with cadmium and copper reducing radial growth of most strains of aquatic hyphomycetes by 50 % at concentrations between 150 and 400 μM (Miersch *et al.* 1997). Radial extension rates of *Trichoderma virens* did not significantly differ during growth on tap water agar containing glucose and 0.1 mM copper or cadmium (Ramsay *et al.* 1999). 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 considerably with increasing concentrations of copper and cadmium (Fomina *et al.* 2003).

A decrease in metal toxicity is correlated with an increase in available carbon source (Ramsay *et al.* 1999; Fomina *et al.* 2003). For *Stereum hirsutum* and *Trametes versicolor*, cadmium and mercury toxicity was lower in rich, complex media (Baldrian & Gabriel 1997), although metal binding to medium constituents would contribute in this case (Gadd & Griffiths 1978). This was also reported for *T. virens* grown with copper, cadmium and zinc where radial extension rate was commensurate with the availability of carbon, revealing a decrease in metal toxicity with increasing levels of glucose (Ramsay *et al.* 1999). The tolerance of decomposer basidiomycetes to cadmium was higher in fungi from rich, basophilous soils than from poor, acidic soils, whereas resistance to aluminium was highest in fungi from poor, acidic soils (Hoiland 1995). A decrease in growth rate in the presence of toxic metals is sometimes accompanied by an increase in the lag phase (or growth delay) (Gadd & Griffiths 1980b; Baldrian & Gabriel 2002; Baldrian 2003). A considerable increase in the lag period was observed for *T. virens* and *C. rosea* grown with copper and cadmium (Fomina *et al.* 2003).

Toxic metal treatment was reported to reduce the sporulating ability of *Aspergillus niger* and AM fungi (Magyarosy *et al.* 2002; Liao *et al.* 2003). Spore germination was found to be more sensitive to Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+} and Mg^{2+} than mycelial growth (Amir & Pineau 1998). However, a proportion of the spores of metal-sensitive strains of *Curvularia* sp. and *Fusarium* sp. were able to germinate and grow moderately well in the presence of relatively high metal concentrations (Amir & Pineau 1998).

Toxic metals can be potent inhibitors of enzymatic reactions. Cadmium, copper, lead, manganese, nickel and cobalt decreased cellulase and amylase production by several fungi, with reduced enzyme activity correlating with increasing metal concentration (Falih 1998a, 1998b). It was also suggested that the lack of reactivity of purified laccases from *Pycnoporus cinnabarinus* towards hydrocarbons was due to metal interference (Mougin *et al.* 2002). However, other studies have shown that extracellular laccase activity was markedly stimulated by cadmium in white-rot basidiomycetes (Jarosz-Wilkolazka *et al.* 2002; Baldrian & Gabriel 2003). In lignocellulose degradation by *Pleurotus ostreatus*, a decrease in substrate dry weight and manganese-peroxidase activity decreased with increasing cadmium concentration, whereas activities of endo-1,4-β-glucanase, 1,4-β-glucosidase and laccase significantly increased in the presence of cadmium (Baldrian & Gabriel 2003). The addition of Zn^{2+} and Cd^{2+}, to levels below 1 mM, to purified polygalacturonase from a metal-tolerant ericoid mycorrhizal isolate of *Oidiodendrum maius* increased enzyme activity, but the same metal concentrations did not affect or only slightly inhibited extracellular enzyme activity in a non-tolerant isolate (Martino *et al.* 2000)

Several toxic metals can induce or accelerate melanin production in fungi, leading to blackening of colonies and chlamydospore development (Gadd & Griffiths 1980a). Chlamydospores and other melanized forms have high capacities for metal biosorption, with the majority of metal remaining within the wall (Gadd 1984; Gadd & Mowll 1985; Gadd *et al.* 1987; Gadd & 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). A significant proportion of fungal biomass in soils is melanic (Bell &Wheeler 1986) and such interactions may be of ecological significance in polluted soils (Gadd 1993a).

Morphological strategies in response to toxic metals

Fungal morphology can be altered by toxic metals, and changes in mycelial density have often been observed (Ramsay *et al.* 1999; Fomina *et al.* 2005b). For example, *Schizophyllum commune*, *Daedalea quercina* and *Paxillus involutus* exhibited increased hyphal branching in response to cadmium (Darlington & Rauser 1988; Lilly *et al.* 1992; Gabriel *et al.* 1996). *S. commune* also developed loops and connective filaments under cadmium stress (Lilly *et al.* 1992). Changes in mycelial morphology have also been observed in *Stereum hirsutum* and *Trametes versicolor* cultivated with cadmium and mercury (Baldrian & Gabriel 1997), in *Mucor rouxii* in the presence of a high copper concentration (Gardea-Torresdey *et al.* 1997), and in ectomycorrhizal fungi during growth in metal-containing (copper, aluminium, zinc) media (Jones & Muehlchen 1994). It was also 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 copper and towards the interior of the colonies in the presence of cadmium (Ramsay *et al.* 1999; Gadd *et al.* 2001).

Metal-contaminated soils usually contain a spatially heterogeneous distribution of metal concentrations and available nutritional resources, and an experimental system based upon tessellated agar tiles, simulating this heterogeneity, has been successfully used for the study of morphological changes of fungi colonizing spatially discrete metal-containing domains. During growth of fungi in metal-containing agar tiles, a wide range of morphological changes and growth responses occurred (Fomina *et al.* 2000, 2003). In the gap between metal-free and metal-containing tiles, the presence of copper or cadmium led to negative chemotropism in *Geotrichum candidum*, *Clonostachys rosea*, *Humicola grisea*, and *T. virens*, and cessation of growth, swelling and lysis of some hyphal tips of *T. virens* and *Cladosporium cladosporioides* (Fomina *et al.* 2000, 2003). Many strategies that fungi employ in physico-chemically hostile metal-polluted environments can be thought of as analogous to those adopted in human warfare and, applying this concept, negative tropisms and growth cessation can be viewed as a ‘retreat’ strategy aimed at avoiding toxic metal-contaminated areas. The concept also includes ‘guerrilla’ and ‘phalanx’ growth forms of mycelial systems as well as ‘re-allocation’ strategies by the formation of mycelial cords (aggregation of longitudinally aligned hyphae) (Lovett-Doust 1981; Boddy 1993; Carlile 1995). Changes in these strategies can be represented by changes in branching patterns or different degrees of commitment to radial (explorative) or tangential (exploitative) growth (Rayner *et al.* 1995). Penetration of hyphae into metal-containing domains was often followed by the formation of very dense mycelia or mycelial ‘bushes’ (Fomina *et al.* 2003). Such hyphal aggregation could be an example of the phalanx growth form with profusely branching hyphae facilitating the colonization of a substrate, and the production of high local concentrations of extracellular enzymes, antibiotics and other metabolites. In the case of a toxic metal-containing domain, aggregated mycelia could produce high local concentrations of extracellular products 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 & Evans 1996; Morley *et al.* 1996; Baldrian 2003). After fungi enter toxic metal-containing domains under poor-nutritional conditions, they often produced long sparsely-branched or branchless hyphae representing an explorative growth strategy with a large hyphal growth unit and infrequent branching (Fomina *et al.* 2003). It was also observed that fungi were able to exhibit multiple repeated ‘phase shifts’, e.g. when *T. virens* and *C. cladosporioides* growing on copper at low sucrose concentrations first formed mycelial ‘bushes’, then long branchless explorative hyphae and, then, ‘bushes’ on the tips of these exploring 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 (Fomina & Gadd, unpubl.). Metal cations are believed to be involved in the formation of synnema of penicillia (Tinnell *et al.* 1977). In *Sphaerostilbe repens*, both synnematal and rhizomorph development only occurred in the presence of calcium, with strontium (which can act as a calcium analogue) also capable of the induction of some morphological changes (Botton 1978). 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 toxicants in the substrate (Newby & Gadd 1987).

Mechanisms of metal resistance and tolerance

Metals and their compounds can interact with fungi in various ways depending on the metal species, organism and environment, while metabolic activity can also influence speciation and mobility. Many metals are essential for fungal growth and metabolism (e.g. sodium, potassium, copper, zinc, cobalt, calcium, magnesium, manganese, Fe), but all can exert toxicity when present above certain threshold concentrations (Gadd 1993a). Other metals (e.g. cadmium, Mercury , lead) have no known biological function but can still be accumulated by fungi (Gadd 1993a). Metal toxicity is greatly affected by the physicochemical nature of the environment and the chemical behaviour of the particular metal species in question. Metals exert toxic effects in many ways, for example they can block the functional groups of important biological molecules such as enzymes, displace or substitute for essential metal ions, cause disruption of cellular and organellar membranes, and interact with systems which normally protect against harmful effects of free radicals generated during normal metabolism (Gadd 1992b, 1993a; Avery *et al.* 1996; Howlett & Avery 1997). Despite apparent toxicity, many fungi survive, grow and flourish in apparently metal-polluted locations and a variety of mechanisms, both active and incidental, contribute to tolerance. Fungi possess many properties that influence metal toxicity, including the production of metal-binding proteins, organic and inorganic precipitation, active transport and intracellular compartmentalization, while major constituents of fungal cell walls (e.g. chitin, melanin) have significant metal binding abilities (Gadd & Griffiths 1978; Gadd 1993a). All these mechanisms are highly dependent on the metabolic and nutritional status of the organism, as this will affect expression of energy-dependent resistance mechanisms, as well as synthesis of wall structural components, pigments and metabolites, which gratuitously affect metal availability and organism response (Gadd 1992b, 1993a; Ramsay *et al.* 1999).

Fungi are able to restrict entry of toxic metal species into cells by: (1) reduced metal uptake and/or increased metal efflux; (2) metal immobilization, e.g. cell wall adsorption, extracellular precipitation of secondary neoformed minerals (e.g. oxalates); and (3) extracellular metal sequestration by, e.g. exopolysaccharides and other extracellular metabolites (Gadd 1993a, 2001a, b, c; Macreadie *et al.* 1994; Blaudez *et al.* 2000a; Perotto & Martino 2001; Baldrian 2003). Metal tolerant fungi can survive due to their abilities of intracellular chelation by, for example metallothioneins and phytochelatins, and metal localization/sequestration within vacuoles. Fungal vacuoles have an important role in the regulation of cytosolic metal ion concentrations and the detoxification of potentially toxic metals (White & Gadd 1986; Gadd 1993a; Gharieb & Gadd 1998; Liu & Culotta 1999). Metals preferentially sequestered by the vacuole include Mn^{2+} (Okorokov *et al.* 1985; Gadd & Laurence 1996), Fe^{2+} (Bode *et al.* 1995), Zn^{2+} (White & Gadd 1987), Co^{2+} (White & 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 & Gadd 1993a, 1993b). 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 zinc, manganese, cobalt and nickel (Ramsay & Gadd 1997), metals mainly detoxified in the vacuole (Gadd 1993a; Joho *et al.* 1995).

For copper and cadmium, intracellular detoxification appears to depend predominantly on cytosolic sequestration by induced metal-binding molecules (Macreadie *et al.* 1994; Ow *et al.* 1994; Hayashi & Mutoh 1994; Rauser 1995). These include low molecular weight cysteine-rich proteins (metallothioneins) and peptides derived from glutathione (phytochelatins) (Macreadie *et al.* 1994; Ow *et al.* 1994; Mehra & Winge 1991; Rauser 1995; Wu *et al.* 1995; Inouhe *et al.* 1996; Gharieb & Gadd 2004). The latter peptides have a general structure of $(\gamma\text{Glu–Cys})_n$–Gly where the γGlu–Cys repeating unit may extend up to 11 (Ow *et al.* 1994). In *Schizosaccharomyces pombe* the value of n ranges from two to five, while in *Saccharomyces cerevisiae*, only an n_2 isopeptide has been observed (Macreadie *et al.* 1994). As well as being termed phytochelatins, such peptides are also known as cadystins and metal γ-glutamyl peptides, although the chemical structure, $(\gamma EC)_nG$, is an alternative description. Although $(\gamma EC)_nG$ induction has been reported with a wide variety of metal ions, including silver, gold, mercury, nickel, lead, tin and zinc, metal binding has only been shown for a few, primarily cadmium and copper (Ow *et al.* 1994). For cadmium, two types of complexes exist in *S. pombe* and *Candida glabrata*. A low molecular weight complex consists of $(\gamma EC)_nG$ and cadmium, whereas a higher molecular weight complex also contains acid-labile sulphide (Murasugi *et al.* 1983; Ow *et al.* 1994). The $(\gamma EC)_nG\text{-Cd-S}^{2-}$ complex has a greater stability and higher cadmium binding capacity than the low molecular weight complex, and has a structure consisting of a cadmium sulphide (CdS) crystallite core and an outer layer of $(\gamma EC)_nG$ peptides (Dameron *et al.* 1989). The higher binding capacity of the sulphide-containing complex confers a greater degree of tolerance to cadmium (Ow *et al.* 1994). In *S. pombe*, evidence has also been presented for subsequent vacuolar localization of $(\gamma EC)_nG\text{–Cd–S}^{2-}$ complexes (Ortiz *et al.* 1992, 1995; Ow 1993), confirming a link between cytosolic sequestration and vacuolar compartmentation.

Although the main function of *Saccharomyces cerevisiae* metallothionein (yeast MT) could be cellular copper homeostasis, induction and synthesis of MT, as well as amplification of MT genes leads to enhanced copper resistance in both *S. cerevisiae* and *C. glabrata* (Macreadie *et al.* 1994; Howe *et al.* 1997). Production of MT has been detected in both copper and cadmium-resistant strains of *S. cerevisiae* (Tohoyama *et al.* 1995; Inouhe *et al.* 1996). However, it should be noted that other determinants of tolerance also occur in these and other organisms, for example transport phenomena (Gadd & White 1989; Inouhe *et al.* 1996; Yu *et al.* 1996), while some other organisms, such as *Kluyveromyces lactis*, are not capable of MT or $(\gamma EC)_nG$ synthesis (Macreadie *et al.* 1994). In *S. cerevisiae*, changes in amino acid pools can occur in response to nickel exposure with the formation of vacuolar nickel–histidine complexes being proposed as a survival mechanism (Joho *et al.* 1995). Little work has been carried out on MT or $(\gamma EC)_nG$ peptides in filamentous fungi to date (Gadd 1993a; Galli *et al.* 1994; Howe *et al.* 1997; Kameo *et al.* 2000).

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 cadmium exposure. Both responded to increasing cadmium 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).

Survival mechanisms found in non-mycorrhizal fungi seem to be used in ectomycorrhizal fungi as well. These include reduction of metal uptake into the cytosol by extracellular chelation through extruded ligands and binding to cell-wall components. Intracellular chelation of metals by a range of ligands (glutathione, metallothioneins), or increased efflux from the cytosol or into sequestering compartments are also key mechanisms conferring tolerance. Free-radical scavenging capacities through the activity of superoxide dismutase or production of glutathione are another defence mechanism against toxic effects of metals (Bellion *et al.* 2006). Complexation of cadmium by phenolic compounds, or by complexing peptides such as metallothioneins, is probably a key determinant of the cellular response to cadmium in *Paxillus involutus*. In addition, the synthesis of hydrophobins may be reduced, thus redirecting Cys to the manufacture of Cys-enriched compounds such as metal-protective biomolecules (Jacob *et al.* 2004). Glutathione and γ-glutamylcysteine contents increased when ectomycorrhizal *P. involutus* was exposed to cadmium. An additional compound with a 3 kDa molecular mass, probably related to a metallothionein, increased dramatically in mycelia exposed to cadmium. The relative lack of phytochelatins and the presence of a putative metallothionein suggest that ectomycorrhizal fungi may use a different mechanism to tolerate metals such as cadmium, than their plant hosts (Courbot *et al.* 2004).

Metal transformations

The mechanisms by which fungi (and other microorganisms) effect changes in metal speciation and mobility are important components of biogeochemical cycles for metals, as well as all other elements including carbon, nitrogen, sulphur and phosphorus (Gadd 1999, 2001b, 2004, 2006, 2007a–c). As already discussed, rocks and minerals, including mineral components of soil, contain considerable quantities of metals that are biologically unavailable. Some of the mechanisms by which fungi and other microorganisms solubilize metals have already been discussed. These may increase metal bioavailability and potential toxicity. Other microbe-mediated mechanisms may immobilize bioavailable metals. However, there is not necessarily any direct relationship between bioavailability and toxicity. This is especially true for fungi where an acidic pH can increase the chemical availability of metals, but greatly reduce toxicity (Gadd & Griffiths 1980b; Gadd 1992b, 1993a). The relative balance between mobilization and immobilization varies depending on the organisms involved and the physico-chemical properties of their environment. As well as being integral components of biogeochemical cycles for metals and associated elements, these processes have potential for treatment of metal-contaminated solid and liquid wastes (see below).

Metal mobilization

Metal mobilization can be achieved by chelation by metabolites and siderophores, and methylation, which can result in volatilization. The biochemical actions of fungi on minerals have been discussed above, and these are an important means of metal mobilization from rock and mineral sources, building stone, etc. Such mechanisms can also result in metal mobilization from other sources, including soil components, sewage sludge, and other solid wastes. When in environments of reduced iron content, fungi produce iron(III)-binding ligands, commonly of a hydroxamate nature, termed siderophores. These may also act to mobilize other metals, albeit with lower specificity. A variety of fungi can methylate metalloids (e.g. selenium, tellurium, arsenic) to yield volatile derivatives (Gadd 1993b, 2001b; Brady *et al.* 1996; Gharieb *et al.* 1999). Several fungi can also mobilize metals, metalloids and organometallic compounds and attack mineral surfaces by redox processes (Timonin *et al.* 1972; Grote & Krumbein 1992; Gadd 1993a; de la Torre & Gomez-Alarcon 1994; Gharieb *et al.* 1999): iron(III) and manganese(IV) solubility is increased by reduction to iron(II) and manganese(II), respectively, while mercury(II) reduction results in formation of less toxic elemental mercury(0). Translocation can be considered as a mechanism for metal mobilization through different parts of the fungus. Root-organ culture has been used to demonstrate that the extraradical mycelium of the AM *Glomus lamellosum* can translocate radiocaesium from a caesium-137 (^{137}Cs)-labelled synthetic root-free compartment to a root compartment and within the roots (Declerck *et al.* 2003).

Metal immobilization

Toxic metal species, including radionuclides, can be bound, accumulated, and precipitated by fungi. Fungal biomass can act as a metal sink, either by: (1) metal biosorption to biomass (cell walls, pigments and extracellular polysaccharides); or (2) intracellular accumulation and sequestration; or (3) precipitation of metal compounds onto and/or around hyphae (Figs 6,8,9). In addition to immobilizing metals, this also reduces the external free metal concentration, and may therefore drive the equilibrium to release more metal ions into the soil solution (Gadd 1993a, 2000a; Sterflinger 2000). Fungi can be highly efficient accumulators of soluble and particulate forms of metals (e.g. nickel, zinc, silver, copper, cadmium, lead), especially from dilute external concentrations (Gadd 1993a, 2000b, 2000c, 2001b, 2001c; Baldrian 2003). Binding of metal ions onto cell walls and other external surfaces can be an important passive process in both living and dead fungal biomass (Gadd 1990, 1993a; Sterflinger 2000). The hyphal wall has a key role in such metal accumulation, for instance comprising 38–77 % of copper uptake by wood-rotting fungi (Baldrian 2003). Metal-binding capacity can be influenced by pH, with the metal-binding capacity decreasing at low pH for, for example, copper, zinc, and cadmium (de Rome & Gadd 1987). Melanin and chitin in fungal hyphal walls strongly influences their ability to act as biosorbents (Gadd & Mowll

1985; Manoli *et al.* 1997; Fomina & Gadd 2002b). Melanin-containing chlamydospores of *Aureobasidium pullulans* can absorb three times more copper than hyaline cells (Gadd & Mowll 1985). In *A. pullulans*, pullulan production also played an important role in metal accumulation. This polysaccharide inhibited accumulation of toxic metals into cells while added pectin protected the organisms due to a binding effect (Breierova *et al.* 2004). Fungi have also been shown to accumulate radionuclides, not only from aqueous solution (Gadd & White 1989, 1990, 1992) but also from radioactive substrata. In an investigation using mitosporic fungi, isolated from the Chernobyl site and its vicinity, many of the strains showed a tendency to grow towards and overgrow the hot radioactive particles, and dissolve them after prolonged contact. The accumulation of radionuclides from intact hot particles was generally more intensive for europium-152 (^{152}Eu) than for ^{137}Cs. The main factors influencing caesium and europium accumulation were the particular species and strains and the size and composition of the hot particles (Zhdanova *et al.* 2003). Metal localization was investigated in the lichenized *Trapelia involuta* growing on a range of uraniferous minerals, including metazeunerite [$Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$], metatorbernite [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$], autunite [$Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$], and uranium-enriched iron oxide and hydroxide minerals. The highest uranium, iron, and copper concentrations occurred in the outer parts of melanized apothecia, indicating that metal biosorption by melanin-like pigments were likely to be responsible for the metal fixation (Purvis *et al.* 2004).

For mycorrhizal fungi, metal binding properties have been suggested as important in ameliorating the effects of metal toxicity on the symbiosis (Galli *et al.* 1994; Vodnik *et al.* 1998). Most studies on mycorrhizas indicate that extramatrical mycelium provides the major metal binding sites, and that most metals are bound to hyphal wall components or, in interhyphal spaces, to extracellular polysaccharide (Jones & Hutchinson 1988; Denny & Wilkins 1987b; Colpaert & van Assche 1992, 1993; Turnau *et al.* 1996; van Tichelen *et al.* 2001; Adriaensen *et al.* 2003; Meharg 2003; Christie *et al.* 2004; Krupa & Kozdroj 2004). Radiotracer flux analyses of cadmium compartmentation in mycelium of the ectomycorrhizal *Paxillus involutus* demonstrated that the hyphal-wall-bound fraction contained 50 % of accumulated cadmium, the cytoplasmic fraction 30 %, and the vacuolar compartment 20 % of accumulated cadmium (Blaudez *et al.* 2000a). Accumulation of toxic metals by fungal cultures is inter- and intra-specific. It has been reported that lead uptake (^{210}Pb tracer) was higher in *Suillus bovinus* than other ectomycorrhizal species tested (*Laccaria laccata*, *Lactarius piperatus*, *Pisolithus tinctorius*, and *Amanita muscaria*) (Vodnik *et al.* 1998). *Suillus* isolates were also efficient lead bioaccumulators when grown on media containing pyromorphite (Fomina *et al.* 2004). *S. granulatus* was reported to accumulate all the cadmium solubilized from rock phosphate (Leyval & Joner 2001). Investigations into the solubilization of zinc phosphate and pyromorphite by ericoid mycorrhizal and ectomycorrhizal fungi showed that a strain of *Thelephora terrestris* isolated from a metal-polluted environment accumulated the highest concentrations of zinc and lead in both axenic culture and mycorrhizal association (Fomina *et al.* 2004). This ability of the same strain of *T. terrestris* to concentrate toxic metals could explain the successful protection of *Pinus sylvestris*) against copper toxicity, despite the lack of extramatrical mycelium compared with *S. bovinus* (van Tichelen *et al.* 2001). However, such protection seems to be dependent on the fungal strain and its metal tolerance. For example, in a study of zinc toxicity in associations of ectomycorrhizal fungi with *Pinus sylvestris*, it was reported that another *T. terrestris* strain that was less tolerant to zinc increased the zinc concentration in host-plant shoots compared with non-mycorrhizal plants and pines infected with other fungi (*Paxillus involutus*, *Laccaria laccata*, *Suillus bovinus*, and *Scleroderma citrinum*) (Colpaert & van Assche 1992). A zinc-tolerant *Suillus bovinus* was particularly efficient in protecting pines from zinc stress. A zinc-sensitive genotype was inhibited at high zinc concentrations, and this isolate could not sustain acquisition of nutrients by the pine. Such observations show that well-adapted microbial root symbionts are a major component of the survival strategy of trees that colonize contaminated soils (Adriaensen *et al.* 2004). In general, zinc-tolerant isolates of ectomycorrhizal fungi accumulated significantly less zinc (including the sum of water-soluble and sodium chloride-extractable zinc) than non-tolerant strains (Fomina *et al.* 2004). This could play a key role in metal tolerance and indicate some kind of 'avoidance' strategy, possibly by decreased uptake and/or enhanced efflux (Gadd 1993a; Gadd & Sayer 2000; Perotto & Martino 2001; Meharg 2003). Alleviation of metal phytotoxicity, particularly zinc toxicity, by AM fungi may be by both direct and indirect mechanisms. Binding of metals in mycorrhizal structures and immobilization of metals in the mycorrhizosphere may contribute to direct effects. Indirect effects may include the mycorrhizal contribution to balanced plant nutrition, especially phosphorus acquisition, leading to increased plant growth and enhanced metal tolerance (Christie *et al.* 2004). In metal-rich lateritic soils, there were strong positive correlations between black AM spore abundance and concentrations of available metals, indicating the role of the biotic component in the release of metals, and suggesting that these symbioses are important in adaptation of the endemic plants to these soils (Perrier *et al.* 2006).

Mechanisms for metal immobilization include intracellular uptake with complexation to ligands, such as sulphur-containing peptides (e.g. metallothionein) (Gadd 1993a; Sarret *et al.* 1998, 2002; Fomina *et al.* 2005). Some fungi can also precipitate metals in amorphous and crystalline forms, such as oxalates and other secondary mycogenic minerals as already discussed (Gadd 1999; Burford *et al.* 2003a, 2006).

X-ray absorption spectroscopy has revealed that oxygen ligands play a major role in metal coordination within *Beauveria caledonica* mycelium, being carboxylic groups in copper phosphate-containing medium, and phosphate groups in pyromorphite-containing medium (Fig 10) (Fomina *et al.* 2004, 2006b, 2006c). Other experiments with axenic cultures of the ectomycorrhizal *Rhizopogon rubescens* grown on media containing copper phosphate, have shown that metal speciation within the mycelium may depend on the nitrogen source, with carboxylate coordination of copper for ammonium, and copper oxalate coordination for nitrogen (Fomina *et al.* 2006b). Further, our studies on *Paxillus involutus*/*Pinus sylvestris* ectomycorrhizas grown in mesocosms with zinc phosphate

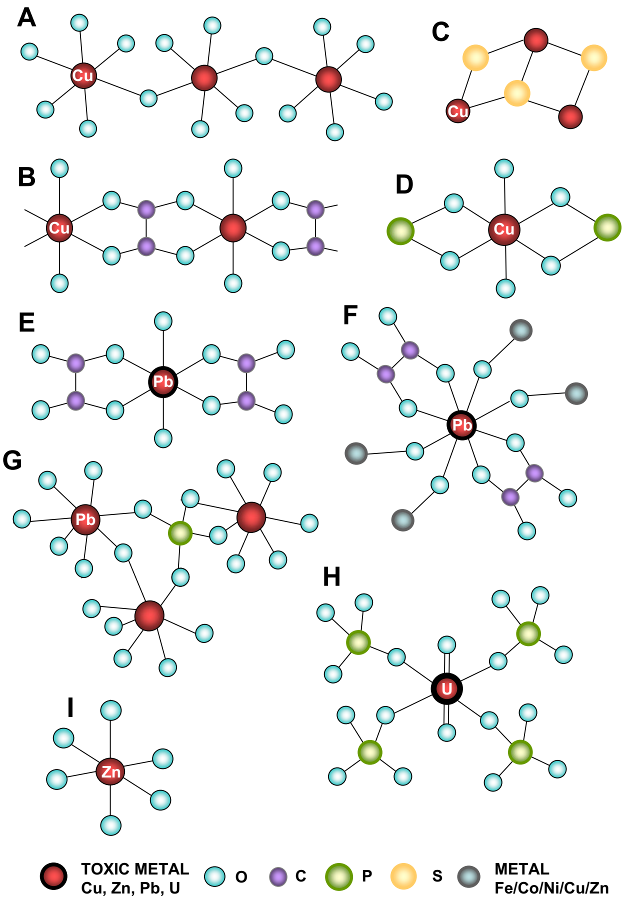

Fig 10 – Models of possible coordination geometry of toxic metals accumulated by fungi: (A–D) copper, (E–G) lead, (H) uranium, and (I) zinc accumulated by fungi and mycorrhizas grown in the presence of toxic metal minerals. (A–B) Effect of nitrogen source on copper coordination within biomass of *Rhizopogon rubescens* in axenic culture and ectomycorrhizal association with Scots pine grown in the presence of copper phosphate: (A) model of mixed copper carboxylate/phosphate coordination on medium containing ammonium; (B) model of copper carboxylate/oxalate coordination on medium containing nitrate. (C–D) The effect of age/physiological state of mycelium on copper coordination within *Aspergillus niger* biomass grown in the presence of azurite or malachite: (C) model of sulphide coordination of copper in the marginal zone of colony; (D) model of phosphate coordination of copper in central part of colony. (E–F) Models for carboxylate coordination of lead accumulated by fungi: (E) *Beauveria caledonica* grown on lead tetroxide (Pb_3O_4) and ammonium-containing medium, and (F) *A. niger* grown on lead oxide (PbO) and nitrate-containing medium. (G) Model of phosphate coordination of lead accumulated within biomass of a variety of mycorrhizal and saprotrophic fungi grown in the presence of pyromorphite. (H) Model of phosphate coordination of uranyl ion for fungal biomass grown in the presence of uranium oxides UO_3 and U_3O_8; (I) Model of zinc coordination by six oxygen atoms for fungi and mycorrhizas grown in the presence of zinc phosphate. From Fomina, Bowen, Charnock & Gadd (unpubl.); see also Fomina *et al.* (2006a, 2007).

showed that ectomycorrhizal infection decreased the ratio of the most bioavailable zinc (water-soluble and salt-extractable) in the root biomass compared with non-mycorrhizal seedlings. However, the speciation of zinc within root biomass was similar in both ectomycorrhizal and non-mycorrhizal seedlings, and showed octahedral coordination of zinc by oxygen-containing ligands fitting carboxylate coordination and, in part, phosphate coordination models (Fig 10) (Fomina *et al.* 2006b).

Many fungi can precipitate reduced forms of metals and metalloids [e.g. elemental silver, gold, selenium, tellurium, chromium(VI) → chromium(III)] within and around fungal cells (Gadd 1993b, 2004). The reductive ability of such fungi is manifest by a black colouration of the colonies precipitating elemental silver or tellurium, and a red colouration for precipitation of elemental selenium (Gharieb *et al.* 1999).

Accumulation of metals and radionuclides by macrofungi

Elevated concentrations of toxic metals and radionuclides can occur in the fruit bodies of macromycetes in polluted environments. This is of significance in relation to the use of macrofungi as bioindicators of metal pollution, and because of toxicity to humans from the consumption of wild fungi. In general, levels of lead, cadmium, zinc and mercury found in macrofungi from urban or industrial areas are higher than from corresponding rural areas, although there are wide differences in uptake abilities between different species and metals (Tyler 1980; Bressa *et al.* 1988; Lepsova & Mejstrik 1989). Cadmium is accumulated to quite high levels in macrofungi, averaging around 5 mg kg d.w.$^{-1}$ although levels of up to 40 mg kg d.w.$^{-1}$ have also been recorded (Byrne *et al.* 1976). *Laccaria amethystina* caps exhibited total As concentrations of 100–200 mg kg d.w.$^{-1}$ (Stijve & Porette 1990; Byrne *et al.* 1991). Accumulation of silver-110 (^{110}Ag) and mercury-203 (^{203}Hg) was studied in *Agaricus bisporus*, and concentration factors (metal concentration in mushroom: metal concentration in substrate) were found to be up to 40 and 3.7, respectively, with the highest silver and mercury contents recorded being 167 and 75 mg kg d.w.$^{-1}$, respectively (Byrne & Tusek-Znidaric 1990). Levels of antimony in macrofungi from unpolluted areas were mostly less than 100 μg kg d.w.$^{-1}$. The highest concentrations (units of mg kg^{-1}) were found in various species of the ectomycorrhizas *Chalciporus* and *Suillus*. Antimony contents of macrofungi growing in antimony-polluted areas were considerably higher, with the highest content found in a single collection of *C. piperatus* (1423 mg kg^{-1}) (Borovicka *et al.* 2006). Ectomycorrhizal and saprobic macrofungi were collected from non-auriferous and unpolluted areas and analysed for gold. Gold contents of the both groups were mostly less than 20 ng g d.w.$^{-1}$. The highest concentrations were found in the ectomycorrhizal *Amanita strobiliformis* (136 ng g^{-1}), *Russula claroflava* (148 ng g^{-1}), *Cantharellus lutescens* (156 and 210 ng g^{-1}), and *Boletus edulis* (235 ng g^{-1}). Among the saprobic fungi, the highest values were found in *Langermannia gigantea* (160 ng g^{-1}) and *Morchella esculenta* (189 ng g^{-1}). Species of *Agaricus* commonly had relatively high gold values, tens of nanograms per gram (Borovicka et al. 2005). *Sarcosphaera eximia* was found to contain arsenic concentrations reaching 1000 mg kg D.W.$^{-1}$. *Agaricus bitorquis*, *A. arvensis*, *A. essettei*, *A. albertii*, *R. pinophilus*, *Clitocybe geotropa*, and *Chlorophyllum rachodes* had mercury contents within the range 5–10 mg kg D.W.$^{-1}$ (Cocchi *et al.* 2006). In some mushrooms from the East Black Sea region, the highest lead level was 6.88 ± 2.85 mg kg^{-1} for *Hypholoma fasciculare* collected near a road. The lowest lead levels were 0.12 ± 0.04 mg kg^{-1} in *Pleurotus ostreatus*, and 0.38 ± 0.22 mg kg^{-1} in *A. bisporus*. The highest cadmium level found was 3.48 ± 0.58 mg kg^{-1} in *Hydnum repandum*. Amongst wild mushrooms, the lowest cadmium level was 0.56 ± 0.22 mg kg^{-1} for *Armillaria mellea*. The highest mercury level was 0.91 ± 0.30 mg kg^{-1} in *H. repandum*, whereas the lowest was 0.06 ± 0.02 mg kg^{-1} in *Russula foetens*. The highest copper content was 92.5 ± 14.1 mg kg^{-1} in *Amanita muscaria*, and the lowest 5.11 ± 0.67 mg kg^{-1} for *P. ostreatus* and 5.22 ± 0.72 mg kg^{-1} for *H. repandum*. The highest manganese and zinc levels were 138.0 ± 15.8 and 199.6 ± 26.7 mg kg^{-1}, respectively, for *Polyporus squamosus*. The lowest zinc levels were 17.2 ± 6.3 mg kg^{-1} and 17.8 ± 5.8 mg kg^{-1} in *Tricholoma terreum* and *H. repandum*, respectively (Demirbas 2003). As well as fruit bodies, rhizomorphs (e.g. of *Armillaria* spp.) can concentrate metals up to 100 times the level found in soil. Concentrations of aluminium, zinc, copper and lead in rhizomorphs were 3440, 1930, 15 and 680 mg kg D.W.$^{-1}$ respectively, with the metals primarily located in extracellular portions (Rizzo *et al.* 1992).

Accumulation of radiocaesium by macrofungi

Free-living and mycorrhizal basidiomycetes can accumulate radiocaesium (Haselwandter 1978; Elstner *et al.* 1987; Byrne 1988; Dighton & Horrill 1988; Haselwandter *et al.* 1988; Clint *et al.* 1991; Dighton *et al.* 1991); these organisms appear to have a slow turnover rate for caesium, and comprise a major pool of radiocaesium in soil (Clint *et al.* 1991). Mean activities of 25 Ukrainian, six Swedish and ten North American collections were 4660, 9750 and 205 Bq kg D.W.$^{-1}$, respectively (Smith *et al.* 1993). Deviations in the ^{137}Cs:^{134}Cs ratios attributable to the Chernobyl accident in 1986 have revealed considerable accumulation of pre-Chernobyl caesium in macrofungi, probably as the result of weapons testing (Byrne 1988; Dighton & Horrill 1988). About 20 % of the ^{137}Cs in Eastern Europe (Moscow area, Belarus, Ukraine) was of non-Chernobyl origin (Smith *et al.* 1993). The highest activity concentration of ^{137}Cs measured in Slovakia was 966 Bq kg D.W.$^{-1}$ for *Suillus luteus*. In comparison, the corresponding activity concentration in a sample taken within the 30 km zone around Chernobyl was 6000 Bq kg D.W.$^{-1}$ (Dvorak *et al.* 2006). Radiocaesium accumulation in basidiomycetes appears to be species-dependent, with influences exerted by soil properties. Significantly higher activities may be found in mycorrhizal species compared with saprotrophic and parasitic fungi (Smith *et al.* 1993). Smith *et al.* (1993) found that many prized edible mycorrhizal fungi may contain unacceptably high levels of ^{137}Cs, that is, at levels of greater than 1000 Bq kg D.W.$^{-1}$. Radionuclide activities in *Xerocomus badius* were in the ranges: 330–6670 (^{137}Cs), 180–1520 (potassium-40; ^{40}K) and 0.70–32.0 (lead-210; ^{210}Pb) Bq kg D.W.$^{-1}$. The highest measured concentration of ^{137}Cs was in caps of *X. badius* from the Borecka Forest, caps showing significantly higher activity compared with the stalks (Malinowska *et al.* 2006). It has also been demonstrated that the fungal component of soil can immobilize the total Chernobyl radiocaesium fallout received in upland grasslands (Dighton *et al.* 1991), although grazing of fruit bodies by animals may lead to radiocaesium transfer along the food chain (Bakken & Olsen 1990).

Fungi as bioindicators of metal and radionuclide contamination

Some research has demonstrated a correlation between the quantities of metals in a growth substrate and the amounts subsequently found in fruit bodies (Table 4; Wondratschek & Roder 1993). The concept of bioindicators has been usually discussed in terms of reaction indicators and accumulation indicators. Reaction indicators may comprise individual organisms and/or communities that may decline or disappear (sensitive species) or show increases (tolerant species). For accumulation indicators, the indicator organism is analysed for the pollutant. Some organisms, in theory, can therefore serve as both reaction and accumulation indicators. As mentioned above, alteration of macrofungal communities by metal pollution has frequently been recorded. Ruhling *et al.* (1984) noted a decline from about 40 species per 100 m^2 to about 15 species near the source of metal contamination (smelter emissions), with only *Laccaria laccata* increasing in frequency at more polluted locations. Other macromycetes that are apparently tolerant of high metal pollution include *Amanita muscaria* and several species of *Boletus*; conversely, some *Russula* species appear metal sensitive (Wondratschek & Roder 1993). *Hebeloma cylindrosporum* exhibited the highest uranium and thorium transfer factors, suggesting that this species was a good bioindicator of soil radioactive content (Baeza & Guillen 2006). *H. cylindrosporum* and *Lycoperdon perlatum* exhibited plutonium-239 (^{239}Pu) + plutonium-240 (^{240}Pu) and americium-241 (^{241}Am) transfer values that were greater than or similar to those for strontium-90 (^{90}Sr). These species were therefore

Table 4 – Some larger fungi proposed as bioindicators for metal pollution based on metal analyses of fruit bodies (see Mejstrik & Lepsova 1993; Wondratschek & Roder 1993)

Species	Metal(s)
Agaricus arvensis	Mercury, cadmium
A. campestris	Mercury, cadmium
A. edulis	Mercury, cadmium
A. haemorrhoidarius	Mercury
A. xanthodermus	Mercury
Agaricus sp.	Lead, zinc, copper
Amanita rubescens	Mercury
A. strobiliformis	Mercury
Coprinus comatus	Mercury
Lycoperdon perlatum	Mercury
Lycoperdon sp.	Lead, zinc, copper
Marasmius oreades	Mercury
Mycena pura	Mercury, cadmium

proposed as bioindicators for $^{239}Pu + ^{240}Pu$ and ^{241}Am (Baeza *et al.* 2006). In another study, metal concentrations were species-dependent, and the highest levels were found in *Calvatia utriformis* (235.5 mg copper kg^{-1}), *Macrolepiota procera* (217.8 mg copper kg^{-1}), and *Agaricus macrosporus* (217.7 mg copper kg^{-1}) and *C. utrifomis* (265.8 mg zinc kg^{-1}), *Lactarius delicious* (231.0 mg zinc kg^{-1}), and *A. macrosporus* (221.3 mg zinc kg^{-1}) for copper and zinc, respectively. Some species were metal excluders, such as *Hydnum repandum*, *Cantharellus cibarius*, and *Coprinus comatus*, which exhibited very small bioconcentration factors (BCF < 1) (Alonso *et al.* 2003).

Fungi possess some advantages over plants as metal accumulation indicators. The fruit bodies may accumulate greater amounts of metals than plants, while the large area of mycelium ensures contact with and translocation from a larger area of soil. Furthermore, fruit bodies may project above the ground for only a short period, thereby minimizing contamination from aerial or wet deposition of metal pollutants. Sporophores are also easily harvested, and amenable to rapid chemical analysis (Mejstrik & Lepsova 1993). However, it is debatable whether a sufficiently clear relationship exists between indicator species and the metal pollutant under consideration. For mercury, wide variations in metal content of fruit bodies occur in different species sampled at the same site, ranging over as much as three orders of magnitude, with some species showing extremely high values. Mercury concentrations in fungi generally occur in the range 0.03–21.6 mg $kg_{D.W.}^{-1}$, although concentrations greater than 100 mg $kg_{D.W.}^{-1}$ have been recorded from polluted sites. Despite this, several macrofungi have been suggested as being suitable bioindicators of mercury pollution (Mejstrik & Lepsova 1993; Wondratschek & Roder 1993).

A wide variation in cadmium content has also been recorded in macrofungi with ranges of reported values from <0.1–229 mg $kg_{D.W.}^{-1}$ (Tyler 1980). However, there is frequently a lack of correlation between the fungal cadmium content and the cadmium content of the soil (Wondratschek & Roder 1993). Compared with other common metal pollutants, lower concentrations of lead tend to be found in macrofungi, with much of the lead content being derived from aerial sources. Levels of lead around 0.4–36 mg $kg_{D.W.}^{-1}$ have been reported in fruit bodies, with higher levels occurring in urban areas (Tyler 1980). Zinc, an essential metal for fungal growth and metabolism, occurs at high concentrations within fungi, 50–300 mg $kg_{D.W.}^{-1}$ (Tyler 1980), with a few genera apparently showing high affinities for the metal. Copper may also be found at high levels (20–450 mg $kg_{D.W.}^{-1}$) in macrofungi (Tyler 1980). However, with both copper and zinc, there is a tendency for metal concentrations in fruit bodies to be independent of soil concentrations, which reduces their value as bioindicators (Gast *et al.* 1988). The concentrations of seven metals (lead, cadmium, manganese, copper, nickel, silver, and chromium) were determined in 32 species of wild mushrooms from Konya, an Inner Anatolian region of Turkey. The highest metal concentrations were given as 39 mg kg^{-1} lead and 3.72 mg kg^{-1} cadmium in *Trichaptum abietinum*, 467 mg kg^{-1} manganese in *Panaeolus sphinctrinus*, 326 mg kg^{-1} copper in *Trametes versicolor*, 69.4 mg kg^{-1} nickel in *Helvella spadicea*, 6.97 mg kg^{-1} silver in *Agaricus campestris*, and 84.5 mg kg^{-1} chromium in *Phellinus igniarius*. The maximum contents were 1.52, 2.22, and 60.2 mg kg^{-1} in *Pleurotus eryngii* (for lead), *Amanita vaginata* (for cadmium), and *Helvella leucomelana* (for copper), respectively (Dogan *et al.* 2006).

Many factors contribute to the wide variations in recorded metal contents of macrofungal fruitbodies, even in the same species sampled at the same site. Despite numerous studies, most investigations tend to be contradictory and provide little useful information (Wondratschek & Roder 1993). There were no obvious simple positive relationships between the fruit body contents of the examined metals, cadmium, mercury and lead, and the contents of total metals in the soil organic layer (Svoboda *et al.* 2006). Apart from organism-related factors, environmental factors are of paramount importance in relation to metal accumulation by macrofungi, and include physicochemical soil properties like moisture and temperature, all of which influence metal availability as well as the physiological activity of the fungus. It can be concluded, therefore, that a perfect macrofungal bioindicator does not exist, although macrofungi may be useful in determining the extent of a polluted or unpolluted area.

However, the situation is quite different in the case of lichens, which accumulate heavy metals from the air and not the soil. There is an enormous literature on this topic (e.g. Bargagli & Mikhailova 2000), which is beyond the scope of this review.

Mineral and metal transformations and environmental biotechnology

Bioremediation

Fungal involvement in element cycling at local and global scales has important implications for living organisms, plant production and human health. Some of the processes detailed previously have the potential for treatment of contaminated land and waters (Thomson-Eagle & Frankenberger 1992; Gadd 2000a, 2000b, 2001a, 2001b, 2001c, 2002, 2004, 2007b; Hochella 2002; Fomina *et al.* 2005b). Solubilization provides a route for removal of metals from industrial wastes and byproducts, low-grade ores, and metal-bearing minerals, which is relevant to bioremediation of soil matrices and solid wastes, and metal recovery and recycling (Burgstaller & Schinner 1993; Kadoshnikov *et al.* 1995; Gadd 2000b; Gadd & Sayer 2000; Brandl 2001; Kartal *et al.* 2006; Tang & Valix 2006). One study investigated the potential use of *Agaricus macrosporus* for bioextraction of metals from contaminated substrates, the metal content data indicating that this species effectively extracted cadmium, mercury and copper (though not lead) from the contaminated substrates. Although these results suggest that fungi such as *A. macrosporus* may be effective for bioremediation of metal-contaminated substrates, cultivation of mushrooms of this type may be difficult in many contaminated environments (Garcia *et al.* 2005). Immobilization processes enable metals to be contained and/or transformed into chemically more inert forms (Gadd 2000b). Fungi with chromium(VI)-reducing activity may have potential for treatment of chromium-polluted soils since insoluble chromium(III) results (Cervantes *et al.* 2001).

Living or dead fungal biomass and fungal metabolites have been used to remove metal or metalloid species, compounds and particulates, radionuclides and organometal(loid) compounds, from solution by biosorption (Gadd & White 1989, 1990, 1992, 1993; Gadd 1990; Kadoshnikov *et al.* 1995; Wang & Chen 2006). These processes are best suited for use in bioreactors (Gadd 2000b). Biosorption occurs *via* a variety of mechanisms of a chemical and physical nature, including ion exchange, complexation, hydrogen bonding, hydrophobic and van der Waals forces, and entrapment in fibrillar capillaries and spaces of the mycelial network (Gadd 1990, 1999). Certain pretreatments and immobilization of fungal biosorbents may make metal sorption more efficient. For example, growth of melanin-producing fungi in a medium containing bentonite significantly enhanced the copper sorption ability of the resultant fungal biomineral sorbent (Fomina & Gadd 2002b). Potential binding sites on fungal biomass can include acetoamino groups from chitin, amino groups from proteins, sulphydryl groups from proteins and peptides, hydroxyl groups, phosphate groups, and carboxyl groups from organic acids, polysaccharides, (poly)phenols/quinones, and melanin (Sarret *et al.* 1998; Gadd 1999; Tobin 2001; Fomina & Gadd 2002b). Phosphate and carboxyl groups are of principal importance in metal biosorption to fungal hyphal walls. Phosphate groups were responsible for 95 % of the lead bound to *Penicillium chrysogenum*, carboxyl groups for 55 % of the zinc sorbed to *P. chrysogenum* and 70 % of the zinc sorbed to *Trichoderma reesei* (Fourest *et al.* 1996; Sarret *et al.* 1999). Fungal-clay complex biomineral sorbents may combine 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 & Gadd 2002a).

Regarding metal mobilization, extracellular ligands excreted by fungi have been used, especially from *Aspergillus* and *Penicillium* spp., to leach metals such as zinc, copper, nickel and cobalt from a variety of solid materials, including low-grade mineral ores (Brandl 2001; Mulligan & Galvez-Cloutier 2003). A spent refinery processing catalyst was physically and chemically characterized and subjected to one-step and two-step bioleaching processes using *Aspergillus niger* (Santhiya & Ting 2005). Siderophores can complex other metals apart from iron, in particular actinides. Because of such metal-binding abilities, there are potential applications for siderophores in medicine, reprocessing of nuclear fuel, bioremediation of metal-contaminated sites, and the treatment of industrial wastes (Renshaw *et al.* 2002).

The ability of fungi, along with bacteria, to transform metalloids has been used 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 & Frankenberger 1992).

Mycorrhizal associations may also be used with plants for metal clean up in the general area of phytoremediation (van der Lelie *et al.* 2001; Gohre & Paszkowski 2006). Phytoextraction involves the use of plants to remove toxic metals from soil by accumulation in above-ground parts. Mycorrhiza may enhance phytoextraction directly or indirectly by increasing plant biomass, and some studies have shown increased plant accumulation of metals, especially when inoculated with mycorrhiza isolated from metalliferous environments. Inoculation with a mixture of AM enhanced the uptake of ^{137}Cs by leeks under greenhouse conditions. It was suggested that there might be a potential for selecting fungal strains that stimulate ^{137}Cs accumulation in crops as part of soil remediation strategies (Rosen *et al.* 2005). However, many complicatory factors affect successful exploitation (Meharg 2003). The potential impact of mycorrhizal fungi on bioremediation may be conditional and dependent on the metal tolerance of fungal strains, their mycorrhizal status, and the nutritional status of contaminated soils (Meharg 2003). In addition, several studies have shown mycorrhizas can reduce plant metal uptake (Tullio *et al.* 2003). AM depressed the translocation of zinc to shoots of host plants in soils moderately polluted with zinc by binding metals in mycorrhizal structures and immobilizing metals in the mycorrhizosphere (Christie *et al.* 2004). AM from metal-contaminated sites are often more metal tolerant to, for example, cadmium and zinc, than other isolates, suggesting a possible benefit to the plant *via* increased metal tolerance, though in some instances, AM plants do not necessarily require fungal colonization for survival (Griffioen 1994). It is generally concluded that local conditions in metal-contaminated sites may determine the cost–benefit relationship between the plant and the AM fungus, as detrimental, neutral or beneficial interactions have all been documented (Meharg & Cairney 2000). A protective metal-binding effect of ectomycorrhizal fungi has been postulated (e.g. Leyval *et al.* 1997) though other workers point out the lack of clear evidence for this (Dixon & Buschena 1988; Colpaert & van Assche 1993). However, ectomycorrhizal plants possessed higher tissue phosphorus concentrations, indicating some benefit from the association (Meharg & Cairney 2000). A copper-adapted *Suillus luteus* isolate provided excellent protection against copper toxicity in pine seedlings exposed to elevated copper levels. Such a metal-adapted combination might be suitable for large-scale land reclamation at phytotoxic metalliferous and industrial sites (Adriaensen *et al.* 2005). Ectomycorrhizal fungi persistently fixed cadmium(II) and lead(II), and formed an efficient biological barrier that reduced movement of these metals in birch tissues (Krupa & 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 copper, cadmium, lead, and manganese. The insoluble glycoprotein, glomalin, produced in copious amounts on hyphae of AM fungi can sequester such metals, and could be considered a useful stabilization phenomenon in remediation of polluted soils (Gonzalez-Chavez *et al.* 2004).

Phytostabilization strategies may be suitable to reduce the dispersion of uranium and the environmental risks of uranium-contaminated soils (Rufyikiri *et al.* 2004). *Glomus intraradices* increased root uranium concentration and content, but decreased shoot uranium concentrations. AM fungi and root hairs improved not only phosphorus acquisition but also root uptake of uranium, and the mycorrhiza generally decreased uranium translocation from plant root to shoot. Hence, mycorrhizas are of potential use in the phytostabilization of uranium contaminated environments (Rufyikiri *et al.* 2004; Chen *et al.* 2005a, 2005b). Some results have suggested that selected bacterial inoculation can improve the mycorrhizal benefit in nutrient uptake and in decreasing nickel toxicity. Inoculation of adapted beneficial microorganisms (as autochthonous *Brevibacillus brevis* and *G. mosseae*) may therefore have potential as a means to enhance plant performance in soil contaminated with nickel (Vivas *et al.* 2006).

For ericaceous mycorrhizas, clear host protection has been observed in, for instance *Calluna*, *Erica*, and *Vaccinium* spp. growing on copper and zinc 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 & Read 1997). The development of stress-tolerant plant–mycorrhizal associations may therefore be a promising new strategy for phytoremediation and soil amelioration (Schutzendubel & Polle 2002). Because of the symbiosis with ericoid mycorrhizal fungi, ericaceous plants are able to grow in highly polluted environments, where metal ions can reach toxic levels in the soil substrate (Perotto *et al.* 2002; Martino *et al.* 2003). Ericoid mycorrhizal fungal endophytes, and sometimes their plant hosts, can evolve toxic metal resistance that enables ericoid mycorrhizal plants to colonize polluted soil. This seems to be a major factor in the success of ericoid mycorrhizal taxa in a range of harsh environments (Cairney & Meharg 2003).

Rocks and minerals represent a vast reservoir of elements, many of which are essential to life and must be released into bioavailable forms (Gadd 2004). Free-living and symbiotic microbial populations associated with plant roots significantly alter the physico-chemical characteristics of the rhizosphere, which may have significant consequences for the biogeochemical mobility of metals and associated elements (Wenzel *et al.* 1994; Olsson & Wallander 1998; Whitelaw *et al.* 1999). 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 sulphate) in pure culture and in mycorrhizal association has been widely studied (Callot *et al.* 1985a, 1985b; Lapeyrie *et al.* 1990, 1991; Gharieb & 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 the release of cadmium and phosphorus from rock phosphate (Leyval & Joner 2001), while the ericoid mycorrhizal fungus *Oidiodendron maius* can solubilize zinc oxide and phosphate (Martino *et al.* 2003). Our experimental studies on ericoid mycorrhizal and ectomycorrhizal fungi showed that many tested cultures were able to solubilize zinc, cadmium, copper phosphates and lead chlorophosphate (pyromorphite) releasing phosphate and metals (Fomina *et al.* 2004, 2005c). 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.* 2006b).

Pyromorphite or lead chlorophosphate [$Pb_5(PO_4)_3Cl$] is a geochemically stable lead mineral, which forms in urban and industrially contaminated soils (Cotter-Howells & Caporn 1996). Because of the very low solubility product of pyromorphite, the formation of such a form of lead phosphate in lead-contaminated soil (phosphate-induced metal stabilization, PIMS) has been proposed as a potentially cost-effective *in situ* remediation technology (Cotter-Howells & Caporn 1996; Conca 1997; Zhang *et al.* 1997; Brown *et al.* 2004). However, pyromorphite, as the reaction product of PIMS-remediation, can be solubilized and transformed by several saprotrophic and mycorrhizal fungi (Sayer *et al.* 1999; Fomina *et al.* 2004, 2005b, 2005c). A correlation between pH and lead mobilization from pyromorphite by mycorrhizal fungi in liquid medium confirmed that acidification was the main mechanism of pyromorphite dissolution for the majority of tested fungi (Fomina *et al.* 2004). However, the ability of certain other fungi to over-excrete such strong chelators as oxalic acid shifted the mechanism of pyromorphite dissolution from proton-promoted to ligand-promoted and lead to a dramatic increase in lead mobilization (Fomina *et al.* 2004). Lead accumulation by fungal biomass grown on pyromorphite-containing agar also provided evidence that pyromorphite solubilization by mycorrhizal fungi occurred even in the absence of any clearing zone-visualization of this processes (Fomina *et al.* 2005c). The ability of free-living and mycorrhizal fungi to transform pyromorphite (and other toxic metal-containing minerals) should clearly 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

It is clear that fungi have important biogeochemical roles in the biosphere, and are intimately involved in the cycling of elements and transformations of both organic and inorganic substrates. Fungi are ubiquitous members of subaerial and subsoil environments, and often become a dominant group in metal-rich or metal-polluted habitats. Their ability for oligotrophic growth, their explorative filamentous growth habit, flexible growth strategies, and resistance to extreme environmental factors, including metal toxicity, irradiation, and desiccation, make them successful colonizers of rock surfaces and other metal-rich habitats. Fungal weathering of rocks and minerals occurs through biomechanical and biochemical attack. The main mechanisms of biochemical weathering are proton-promoted, ligand-promoted, and metal accumulation within fungal biomass, and fungal impact on dissolution depends on species, mineral types and conditions. Despite proton-promoted mechanisms being the most common mechanism for the majority of fungi, ligand-promoted dissolution of minerals by strong chelators such as oxalic and citric acids may provide a more efficient attack. One of the paramount reasons for fungal success in biogeochemical processes in terrestrial ecosystems is their ability to form mutualistic symbiotic associations with photosynthetic plants, algae and cyanobacteria (mycorrhizas and lichens), which make them responsible for major transformations and redistribution of inorganic nutrients, e.g. metals and phosphate, as well as carbon flow. Fungi are also major agents of the biodeterioration of stone, wood, plaster, cement, concrete, and other building materials, and are important components of rock-inhabiting microbial communities with significant roles in mineral dissolution and secondary mineral formation. It is timely to draw attention to 'geomycology' and to the interdisciplinary approach that is necessary to further understand the important roles that fungi play in the biogeochemical cycling of elements, the chemical and biological mechanisms that are involved, and their environmental and biotechnological significance.

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Supplementary data

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