Mineralogical Magazine, December 2003, Vol. 67(6), pp. 1127–1155

Fungal involvement in bioweathering and biotransformation of rocks and minerals

E. P. BURFORD, M. FOMINA AND G. M. GADD*

Division of Environmental and Applied Biology, Biological Sciences Institute, School of Life Sciences, University of Dundee, Dundee DD1 4HN, UK

ABSTRACT

In the Earth's lithosphere, fungi are of fundamental importance as decomposer organisms, animal and plant pathogens and symbionts (e.g. lichens and mycorrhizas), being ubiquitous in sub-aerial and sub-soil environments. The ability of fungi to interact with minerals, metals, metalloids and organic compounds through biomechanical and biochemical processes, makes them ideally suited as biological weathering agents of rock and building stone. They also play a fundamental role in biogeochemical cycling of nutrients, (e.g. C, N, P and S) and metals (e.g. Na, Mg, Ca, Mn, Fe, Cu, Zn, Co and Ni) essential for the growth of living organisms in the biosphere. In addition they play an integral role in the mobilization and immobilization of non-essential metals (e.g. Cs, Al, Cd, Hg and Pb). Most studies on mineral-microbe interactions and microbial involvement in geological processes have concentrated on bacteria and archaea (Prokaryota): fungi (Eukaryota) have, to a certain extent, been neglected. This article addresses the role of fungi in geomicrobiological processes, emphasizing their deteriorative potential on rock, building stone and mineral surfaces and involvement in the formation of secondary mycogenic minerals. Such roles of fungi are also of importance for the global carbon reservoir and have potential biotechnological applications, e.g. in the bioremediation of xenobiotic-, metal- and/or radionuclide-contaminated soils and wastes, and metal/radionuclide recovery.

KEYWORDS: lithosphere, biosphere, rocks, minerals, metals, bioweathering, fungi, microorganisms, oxalates, silicates, carbonates, sandstone, limestone, clay, soil, heavy metals, radionuclides, bioremediation.

Introduction

WEATHERING processes play an integral role in shaping the composition of the Earth's lithosphere, biosphere, hydrosphere and atmosphere (Schwartzman and Volk, 1989; Berner, 1990; Ferris *et al.*, 1994; Banfield *et al.*, 1999; Grace, 2001; Vaughan *et al.*, 2002). Rock substrates (aggregates of minerals), and their mineral constituents can be weathered through physical (mechanical), chemical and biological processes, although near-surface weathering of rocks and minerals, which occurs in sub-aerial (i.e. situated, formed, or occurring on or immediately adjacent to the surface of the earth) and sub-soil (i.e. not exposed to the open air) environments, often involves an interaction between the three types (White *et al.*, 1992). The weathering of rocks in the sub-aerial environment results in chemical and mineralogical changes in the host-rock leading to the evolution of sediments in aquatic environments and soils in terrestrial environments (White *et al.*, 1992). Lithospheric weathering of rocks and minerals can result in the mobilization of essential nutrients (e.g. P, S) and metals (e.g. Na, K, Mg, Ca, Mn, Fe, Cu, Zn, Co and Ni) required for plant and microbial growth. In addition, non-essential metals (e.g. Cs, Al, Cd, Hg, and Pb) may also be mobilized (Gadd, 1993, 2001*a,b*; Morley *et al.*, 1996).

The controlling mechanisms and rate at which rocks and minerals are weathered often depends on environmental factors (e.g. mineral-water interactions) and mineral properties of the host-

* E-mail: g.m.gadd@dundee.ac.uk
DOI: 10.1180/0026461036760154

rock (e.g. chemical structure and reactivity of mineral surfaces) (Hochella, 2002; Vaughan *et al.*, 2002). Weathering can also be influenced by the activities of microbial populations, by processes sometimes termed 'bioweathering' and 'microbial mediation'. Bioweathering can be defined as the erosion, decay and decomposition of rocks and minerals induced by living organisms, which received early recognition by Sollas (1880). Microorganisms, animals and higher plants can weather rock aggregates through biomechanical and biochemical attack on mineral constituents (Goudie, 1996).

Filamentous microorganisms, higher plants and burrowing animals can enhance the weathering of rock substrates through physical attack and fractionation of mineral constituents (e.g. rocks can be split and fractionated by the disruptive (hydraulic) pressure of growing roots and hyphae) (Sterflinger, 2000; Money, 2001). However, the biochemical action of organisms on rocks is believed to be a more important process than mechanical degradation (Sterflinger, 2000; Etienne, 2002). Microbes, e.g. bacteria, algae and fungi, and plants can induce chemical weathering of rocks and minerals through the excretion of, e.g. H^+, organic acids and other metabolites, and even CO_2 produced during respiration can lead to carbonic acid attack on mineral surfaces (Johnstone and Vestal, 1993; Ehrlich, 1998; Sterflinger, 2000; Gadd and Sayer, 2000). Biochemical weathering of rocks can result in changes in the micro-topography of minerals through pitting and etching of mineral surfaces, mineral displacement reactions and even complete dissolution of mineral grains (Ehrlich, 1998; Kumar and Kumar, 1999).

Minerals and microbes have been interacting on Earth since the early Precambrian (Ehrlich, 1998; Hochella, 2002) and the important role that early life forms played in the formation of the Earth's lithosphere, hydrosphere and atmosphere is now generally acknowledged (Bengston, 1994). Recent discoveries of well-preserved microfossils from as early as 3500 million years before present (MYBP) indicate that microbial life probably existed on Earth by the time that the oldest preserved sediments and meta-sediments were being deposited (Buick, 1990; Schopf, 1993). It is probable, therefore, that all sedimentary rocks have been influenced by microbial activity (Summer, 2000).

Mineral-microbe interactions can either directly or indirectly influence virtually every biological, geological and biogeochemical process occurring at or near the Earth's surface. Microorganisms, including the prokaryotes (bacteria and archaea) and eukaryotes (fungi, algae and protozoa), inhabit almost every environment on Earth, existing under the most extreme conditions (e.g. in hot and cold deserts, geothermal soils, hot springs and geysers, hypersaline and evaporite habitats, Arctic lakes, the deep sub-surface) (Howoritz *et al.*, 1972; Friedmann and Ocampo, 1976; Staley *et al.*, 1982; Javor, 1989; Fredrickson and Onstott, 1996; Redman *et al.*, 1999; Renaut and Jones, 2000; Gerdes *et al.*, 2000; Machel and Foght, 2000; Hochella, 2002). In these environments, microbes can interact with approximately 4000 mineral species, each exhibiting a wide variability in surface chemistry, and can influence a number of mineralogical processes (Hochella, 2002).

Lithobiotic microbial communities often colonize mineral surfaces forming a 'biofilm' at the mineral-microbe interface, i.e. immobilized microbial cells growing on the substrate frequently within a matrix of extracellular polymers or 'exopolymers' (Decho, 2002; Vaughan *et al.*, 2002). It is now accepted that the majority of microorganisms living under a wide range of conditions occur within biofilms (Decho, 2000). Microbial biofilms occur in aquatic, sub-soil and sub-aerial environments (Decho, 2000; Gorbushina and Krumbein, 2000). In aquatic sediments, microbial biofilms are a ubiquitous and biogeochemically important feature. They commonly occur on the surfaces of sediment and detrital particles and rapidly form on any new surface placed in sediments (Decho, 2000). The exopolymer matrix of the biofilm plays a major role in attachment of cells to sediment particles as well as acting as a cohesive 'glue' to bind sediment particles together (Decho, 2000). While biofilms under permanent water cover contain between 95 and 98% biologically stabilized water at ambient temperature, those in atmospheric conditions, i.e. sub-aerial environments, can be regarded as containing the most biomass, maintaining metabolic potential in the presence of limited water availability (Gorbushina and Krumbein, 2000).

The weathering of rock substrata can lead to the proliferation of microbial communities in sub-aerial and sub-soil environments. No single factor works in isolation. Physical weathering of a mineral substrate acts to enhance or accelerate rates of chemical, biomechanical and biochemical weathering and *vice versa*. The development of cracks, fissures and weathering rinds in rocks accelerates biological weathering by providing a niche that can easily be exploited by opportunistic microorganisms. In addition, growth, death, degradation and re-colonization of mineral substrates by microbial communities occurs. Microbial communities increase in abundance and diversity as rock is weathered and transformed into soil (Banfield *et al*., 1999).

Microorganisms can influence mineralogical processes as a result of mineral dissolution, mineral formation (sometimes termed 'biomineralization'), and mineral surface chemistry and reactivity alteration, where one mineral or mineral assemblage is often replaced by a more stable assemblage (Hochella, 2002; Putnis, 2002). Mineral dissolution can be inhibited by metabolic activities of microorganisms, e.g. the formation of extracellular polysaccharides that passivate reactive centres on minerals (Welch and Vandevivere, 1994; Welch *et al*., 1999). In contrast, mineral dissolution may be accelerated by microbially-mediated pH variations and many other changes in solution chemistry (e.g. indirect effects on sulphide dissolution by iron-oxidizing bacteria, excretion of organic ligands and siderophores by bacteria and fungi) (Grote and Krumbein, 1992; Maurice *et al*., 1995; Hersman *et al*., 1995; Nordstrom and Southam, 1997; Stone, 1997; Gadd, 1999; Kraemer *et al*., 1999; Liermann *et al*., 2000).

Microbial processes can also be influenced by minerals (e.g. energy and nutrient acquisition, cell adhesion, biofilm formation and natural organic matter formation) (Hochella, 2002). Many bacteria use minerals for respiration, a process that involves using the mineral as a terminal electron acceptor, resulting in mineral components being chemically reduced (Lovley, 1991; Nealson and Saffarini, 1994; Lower *et al*., 2001*a*). Furthermore microorganisms can acquire essential nutrients for microbial growth from mineral surfaces, which effectively concentrates these nutrients far above surrounding environmental levels (e.g. C, N, P, Fe and various organic compounds) (Atlas and Bartha, 1998). Many environmental contaminants, which are often concentrated on mineral surfaces due to various sorption reactions, can also be displaced by similar microbial interactions (Kraemar *et al*., 1999). Mineral surface properties (e.g. microtopography, surface composition, surface charge and hydrophobicity) play an integral role in microbial attachment and detachment processes, and biofilm formation (Wolfaardt *et al*., 1994; Fredrickson *et al*., 1995; Bennett *et al*., 1996; Rogers *et al*., 1998). In addition, the formation of organic matter, e.g. humic acids, can result from a combination of processes that rely on both mineral surfaces and microbial metabolism (Stevenson, 1994; Ehrlich, 1996; Brady and Weil, 1999).

The Mycota: fungal involvement in geological processes

Fungi are a major component of the biota in soils and mineral substrates and under certain environmental conditions (e.g. low pH) often become the dominant group when compared to other microorganisms such as bacteria. Bacteria are prolific under both aerobic and anaerobic conditions and also play a significant role in weathering processes. For example, sulphur and sulphide-oxidizing bacteria can produce sulphuric acid which can attack rocks and mineral substrates resulting in leaching of constituent metals (Rawlings, 2003). Under anaerobic conditions, where most fungi do not grow, feldspars can be rapidly weathered by bacteria (Bennett *et al*., 2000). Over the last decade 'Geomicrobiology', the study of microbial-mineral interactions, has largely concentrated on the prokaryotes. The role of fungi (Mycota) in geological and weathering processes has, to a large extent, been neglected, with the exception of lichens (a symbiotic relationship between a fungus, cyanobacterium or alga) (Jones *et al*., 1981; Kerr and Zavada, 1989; Johnstone and Vestal, 1993; Prieto Lamas *et al.,* 1995, Easton, 1997; Banfield *et al.,* 1999; Matthes *et al*., 2000). Fungi are chemoheterotrophic organisms and are ubiquitous in terrestrial environments, occurring as unicellular yeasts, polymorphic and filamentous fungi, both free-living and symbiotic (Gadd, 1993, 1999). They are important as decomposer organisms, animal and plant symbionts and pathogens, spoilage organisms of natural and synthetic materials and play an important role in biogeochemical cycles (e.g. C, N, P, S, metals) (Gadd, 1993, 1999, 2001*a*; Morley *et al*., 1996). The purpose of this article is to review and emphasize the important roles of fungi in Earth-surface weathering processes. Due to their filamentous growth habit and ability to produce and exude organic acids, protons and other metabolites, fungi are perfectly suited as biological weathering agents of natural rock, minerals and building materials (Kutuzova, 1969; Gu *et al.*, 1998; Gadd, 1993, 1999).

Fungal communities in sub-aerial and sub-soil environments

The fossil record of fungi in terrestrial environments

Fossilized fungal structures have been reported from a variety of mineral substrates including Devonian Rhynie Chert, as fossil lichen mycobionts in stromatolites, in Djebel-Onk phosporites, Triassic silicified rock, Bitterfield amber and Tertiary Dominican Amber (Klappa 1979*a,b*; Dahanayake *et al.,* 1985; Dahanayake and Krumbein, 1985; Taylor and White, 1989; McMenamin and McMenamin 1994; Taylor *et al.*, 1999; Rikkinen and Poinar, 2000, 2001). Although there is geochemical evidence for prokaryotic life in terrestrial ecosystems as early as 2600 million years before present (MYBP) and microfossil evidence 1200 to 800 MYBP, the earliest undisputed fossil record of eukaryotes including fungi and primitive plants in terrestrial ecosystems occurs during the Ordivician period (480 to 460 MYGP) (Heckman *et al.*, 2001) (Fig. 1). However, it has been speculated that they may have occurred earlier, during the Precambrian, as lichens, which may have led to other symbioses between fungi and phototrophs (Heckman *et al.*, 2001). Many fungi and lichens and free-living cyanobacteria, often with bryophytic plants, form a biological crust in harsh terrestrial environments today and potentially could have done so in the Neoproterozoic period (900 to 544 MYBP) or even earlier, perhaps along with extremophilic animals such as tardigrades (Heckman *et al.*, 2001).

If fungi did occur earlier, their potential effect on the environment and other biota should be considered. Currently two phenomena explained by other mechanisms could equally well be the result of an early colonization of land by fungi and plants. One is a period of global glaciations known as 'Snowball Earth' events (750 to 580 MYBP). The second is a Neoproterozoic rise in O_2 levels, possibly leading to the Cambrian explosion of animal life (Kirschvink *et al.,* 2000; Heckman *et al.*, 2001). Fungi can enhance weathering, which in turn can lead to lower CO_2 levels and global temperatures. In addition the burial of terrestrial carbon, rich in decay-resistant compounds of land plants and less dependent on abundant phosphorus, would further affect global climate (Heckman *et al.*, 2001). Either or both these mechanisms could contribute to lower global temperatures and a rise in oxygen in the Neoproterozoic. However, examination of sediments from this time period has so far failed to reveal fossil evidence for early colonization of land by fungi and plants. It is equally true, however, that most fungi and primitive plants do not preserve well in the fossil record, leaving open the possibility of an earlier, unrecorded history (Heckman *et al.*, 2001).

Fungi in present-day terrestrial environments

In present-day terrestrial ecosystems, fungi are ubiquitous components of microbial communities. Sub-aerial rock surfaces can be considered one of the most inhospitable habitats for fungal growth due to their high degree of insolation, moisture deficit and limited availability of essential nutrients, being characterized as oligotrophic and oligocarbotrophic environments (Gorbushina and Krumbein, 2000). Rocks or other sub-aerial surfaces are inhabited by poikilotrophic (i.e. able to deal with varying extremes in micro-climatic conditions, e.g. light, salinity, pH, water potential) microorganisms that thrive under these extreme conditions over considerable periods of time. Microbial biofilms on and in rocks are believed to be major factors in rock decay, and the formation of patinas, films, varnishes, crusts and stromatolites in rock substrates (Gorbushina and Krumbein, 2000).

In many coastal regions and hypersaline environments, high salinity (osmotic stress) further inhibits microbial life on exposed rock surfaces (Javor, 1989; Sterflinger, 2000). Inorganic rock substrates do not necessarily favour fungal growth, although the presence of organic and inorganic residues on mineral surfaces or within cracks and fissures within the mineral substrate is thought to encourage proliferation of fungi and other microbes. In addition the waste products of algae and bacteria (or dead cells of these organisms), decaying plant material, dust particles, aerosols and animal faeces can all act as nutrient sources for fungi (Sterflinger, 2000)

Extremophilic fungi have evolved to survive in and exploit microhabitats on the surface and within mineral substrata, commonly occurring as lichens or as free-living forms, e.g. microcolonial fungi (Gorbushina *et al.*, 1993; Bogomolova *et al.*, 1998; Sterflinger, 2000) (Fig. 2*a–d*). Fungi have been reported from a wide range of rock types including limestone, soapstone, marble, granite, sandstone, andesite, basalt, gneiss,

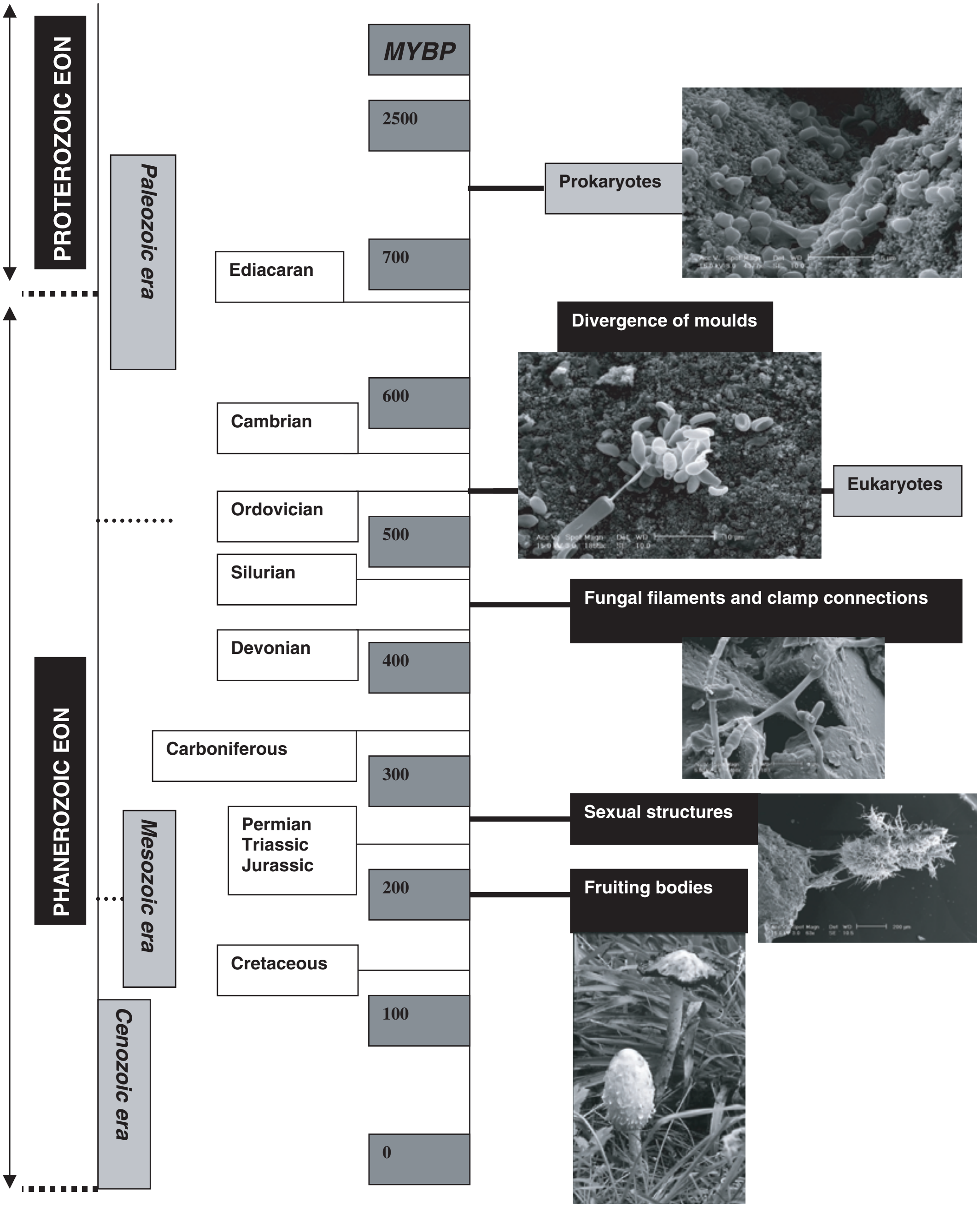


FIG. 1. Fossil record of fungi in terrestrial environments.

dolerite, amphibolite and quartz, even from the most harsh environments, e.g. hot and cold deserts (Staley *et al*., 1982; Gorbushina *et al*., 1993; Sterflinger, 2000; Verrecchia, 2000). However, it is likely that they are ubiquitous components of the microflora of all rocks and building stone, occurring over a wide range of geographical and climatic zones (Table 1).

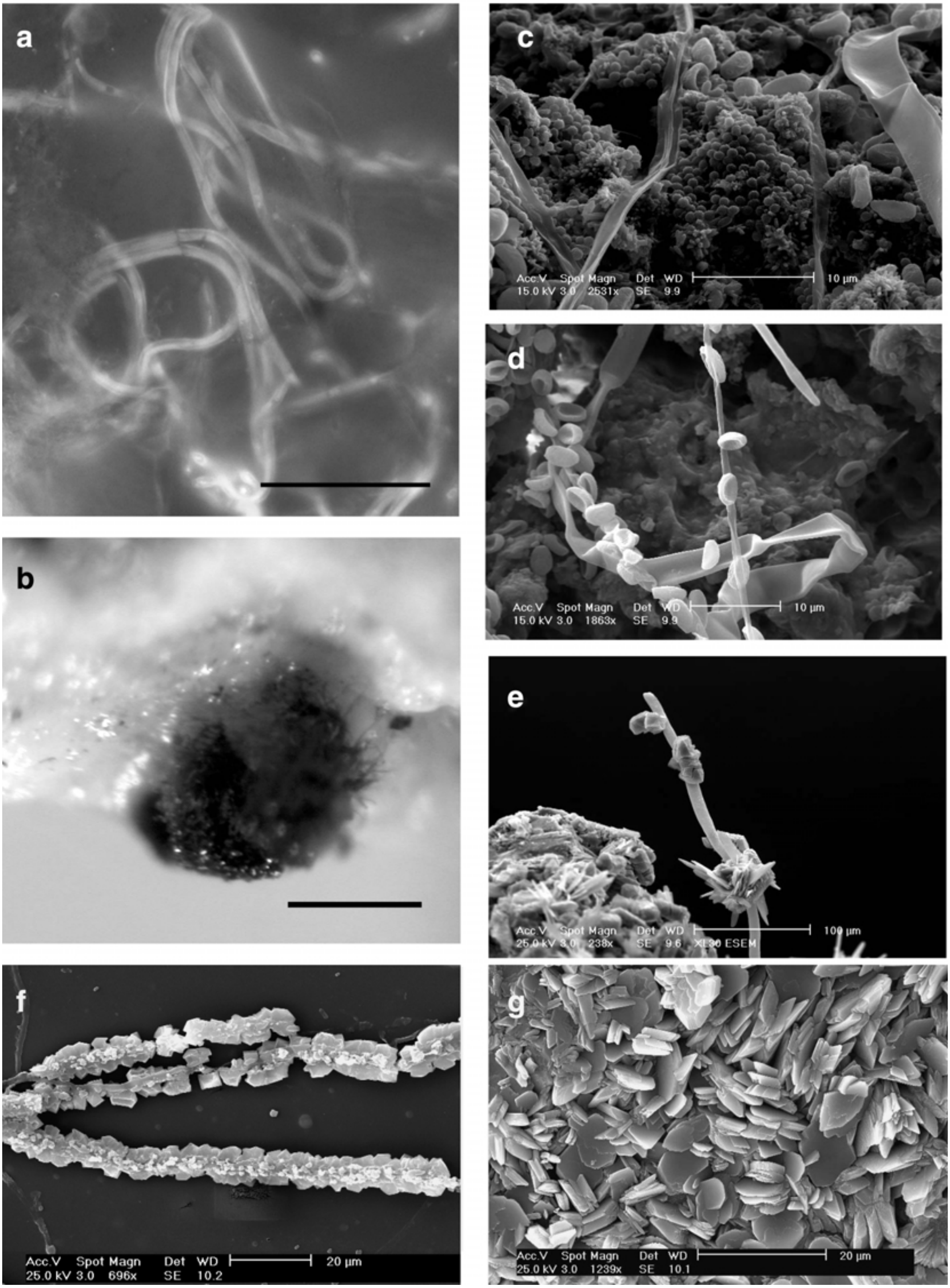


FIG. 2. SEM images of (*a*) *in situ* visualization of filamentous microbes in a weathered limestone thin-section using Calcoflour White M2R stain (scale bar = 50 μm); (*b*) clump-like colony of black fungi growing on the surface of

Microcolonial fungi include those black-coloured fungi that occur on the surface of the mineral substrate as spherical clusters of tightly packed thick-pigmented-walled cells or as moniliform thick-walled hyphae (Gorbushina *et al.*, 1993; Bogomolova, 1998) (Fig. 2*b*). In contrast, other filamentous fungi, including zygomycetes, ascomycetes and basidiomycetes often occur on rock surfaces (epiliths) and in the cracks, fissures and pores of the rock sub-surface (endoliths). Many fungi also actively burrow into rock substrates (cryptoendoliths). In addition, mitosporic fungi (Deutermycotina or Fungi Imperfecti), which only exhibit asexual reproduction, are also commonly found in mineral subtrates (Kumar and Kumar, 1999; Sterflinger, 2000; Verrecchia, 2000).

In the soil, fungi comprise the largest pool of biomass (including other microbes and invertebrates). This combined with their filamentous explorative growth habit and high-surface-area-to-mass-ratio, ensures that fungus-mineral interactions are an integral component of environmental cycling processes (Gadd, 1993, 1999, 2000*a*). In the soil environment, fungi occur as free-living filamentous forms, plant symbionts, unicellular yeasts and animal and plant pathogens, and play an important role in carbon cycling and other biogeochemical cycles (Gadd and Sayer, 2000). Mycorrhizal fungi in particular are one of the most important ecological groups of soil fungi in terms of mineral weathering and dissolution of insoluble metal compounds (Paris *et al.*, 1995; Jongmans *et al.*, 1997; Lundstrom *et al.*, 2000; Hoffland *et al.*, 2002; Martino *et al.*, 2003).

The micro-environment (e.g. the presence of inorganic and organic surfaces, solid adsorbents and exopolysaccharides) plays a fundamental role in weathering and mineral dissolution by fungi (Burgstaller and Schinner, 1993). Biologically-mediated weathering involves a complex dissolution/selective transport/recrystallization mechanism occurring within the acidic extracellular gels and coating on mineral surfaces (Banfield and Nealson, 1998). Once established in a specific micro-environment, fungi can degrade mineral substrates by biomechanical and biochemical action (Haigler, 1969; Silverman and Munoz, 1970; Bassi *et al.*, 1984; Eckhardt, 1985; Griffen *et al.*, 1991).

Mechanisms of rock weathering by fungi

Biomechanical deterioration of rock by fungi

Fungi are an important component of lithobiotic communities (an association of microorganisms forming a biofilm at the mineral-microbe interface), where they interact with the lithic substrate, mainly laminar minerals, both geophysically and geochemically (de los Rios *et al.*, 2002; Burford *et al.*, 2004). Biomechanical deterioration of rocks is believed to occur through extensive penetration by fungal hyphae (e.g. into decayed limestone), and by burrowing into otherwise intact mineral material. Hyphal penetration for example, can occur along crystal planes in calcitic and dolomitic rocks (Kumar and Kumar, 1999; Sterflinger, 2000).

Fungal hyphae can exploit grain boundaries, cleavages and cracks to gain access to mineral surfaces, resulting in accumulations of cleavage-bound mineral fragments as small as 5 µm within the lower lichen thallus (Banfield *et al.*, 1999). Biotite directly in contact with the lichen thallus is intimately interpenetrated by fungal hyphae growing along cleavages (Banfield *et al.*, 1999). An important feature of growth of fungal hypha is that it enables spatial exploration of the environment in order to locate and exploit new substrates (Jacobs *et al.*, 2002*a*). This is facilitated by a range of sensory responses, known as tropisms, that determine direction of hyphal growth. Thigmotropism or contact guidance is a well-known property of fungi that grow on mineral surfaces and within solid substrates (Watts *et al.*, 1998). The direction of fungal growth is often influenced by grooves, ridges and pores in the solid substrate and is more prevalent in weakened mineral surfaces.

The process of invasive hyphal growth due to hydrostatic pressure inside hyphae (turgor) allows fungi to acquire nutrients from diverse solid materials (Money, 2001). Highly pressurized hyphae can penetrate tougher substrates than

limestone (scale bar = 1 mm); (*c*) fungal hyphae *in situ* in limestone (scale bar = 10 µm); (*d*) dimorphic growth of fungi *in situ* in limestone (scale bar = 10 µm); (*e*) crystalline precipitates bound to fungal hyphae *in situ* in limestone (scale bar = 100 µm); (*f*) calcite and whewellite precipitated on the hyphae of *Serpula himantiodes* in microcosms amended with limestone (scale bar = 20 µm); (*g*) biogenic calcite and whewellite precipitated under colonies of *Serpula himantiodes* in microcosms amended with limestone (scale bar = 20 µm).

TABLE 1. Fungi commonly associated with different rock substrata in different geographical and climatic zones (adapted from Staley *et al.*, 1982; de la Torre and Gomez-Alarcon, 1994; Hirsch *et al.*, 1995; Kumar and Kumar, 1999; Sterflinger, 2000; Verrecchia, 2000; Burford and Gadd, 2003 (*) (unpublished data on the microflora of limestone)).

Common fungal species inhabiting rock and building stone in humid/tropical climates (▼)	Sandstone	Marble	Granite	Lime-stone	Soapstone	Quartzite	Andesite	Basalt
Alternaria alternata	▼	▼	▼					
Aspergillus elegans							▼	
Aspergillus flavus	▼	▼		▼			▼	
Aspergillus fumigatus	▼	▼	▼					
Aspergillus nidulans	▼	▼						
Aspergillus niger	▼	▼		▼				
Aspergillus versicolor		▼		▼				
Aureobasidium pullulans	▼	▼	▼					
Botrytis cinerea	▼	▼	▼					
Candida albicans								▼
Cephalosporium sp.				▼				
Cladosporium cladosporioides	▼	▼	▼				▼	
Cladosporium oxysporum	▼	▼	▼					
Cladosporium sphaerospermum	▼	▼	▼		▼	▼	▼	
Cladosporium tenuissimum	▼	▼	▼					
Coniothyrium cerealis	▼	▼	▼					
Cunninghamella echinulata							▼	
Curvularia lunata	▼	▼					▼	
Curvularia verrugulosa	▼	▼						
Engydodontium album	▼	▼	▼					
Epicoccum purpurascens	▼	▼	▼					
Exophiala jeanselmei	▼	▼	▼					
Fusarium roseum		▼		▼			▼	
Fusarium solani	▼	▼	▼					
Gliocladium virens							▼	
Hormonema sp.	▼	▼	▼					
Humicola grisea	▼	▼						
Lecythophora sp.	▼	▼	▼					
Lipomyces neoformans	▼							
Macrophoma sp.	▼	▼		▼				
Monilia sp.				▼				
Paecilomyces farinosus	▼	▼	▼					
Paecilomyces lilacinus	▼	▼	▼					
Paecilomyces variotii	▼	▼	▼					
Penicillium aurantiogriseum	▼	▼	▼					
Penicillium brevicompactum	▼	▼	▼					
Penicillium chrysogenum	▼	▼	▼					
Penicillium citrinum	▼	▼	▼					
Penicillium crustosum					▼	▼		
Penicillium expansum	▼	▼	▼					
Penicillium frequentans		▼		▼				
Penicillium glabrum	▼	▼	▼		▼	▼		
Penicillium lilacinum							▼	
Penicillium multicolor							▼	
Penicillium nigricans	▼	▼	▼					
Penicillium notatum	▼	▼						
Penicillium purpurogenum	▼	▼	▼					
Penicillium spinulosum	▼	▼	▼					

Phaeococcomyces catenatus	▼	▼	▼					
Phoma lavellei	▼	▼	▼					
Phoma putaminum	▼	▼	▼					
Phoma terricola	▼	▼	▼					
Rhizopus arrhizus	▼	▼	▼					
Rhodotorula minuta	▼	▼	▼					
Trichoderma harzianum	▼	▼	▼					
Trichoderma koningii	▼	▼	▼					
Verticillium lecanii	▼	▼	▼					
Verticillium psalliotae	▼	▼	▼					

Common fungal species inhabiting rock in arid and semi-arid climates (●)	Sandstone	Marble	Granite	Limestone	Soapstone	Quartzite	Andesite	Basalt
Alternaria alternata	●	●	●					
Bahusakala sp.						●	●	
Caloplaca callopisma				●				
Cladosporium sphaerospermum	●	●	●					
Coniosporium apollinis	●	●	●					
Coniosporium perforans	●	●	●					
Coniosporium uncinatum	●	●	●					
Fungi Imperfecti				●				
Hormonema demantioides	●	●	●					
Hortaea werneckii	●	●	●					
Humicola sp.						●	●	
Lichenothelia sp.	●	●	●					
Phaeotheca sp.	●	●	●					
Phoma glomerata	●	●	●					
Sarcinomyces crustaceus	●	●	●					
Sarcinomyces petricola	●	●	●					
Taeniolella subsessilis						●	●	
Trimmatostroma sp.	●	●	●					
Ulocladium chartarum	●	●	●					
Verrucaria sp.				●				

Common fungal species inhabiting karstic caves, cave deposits and waters (▽)	Sandstone	Marble	Granite	Limestone	Soapstone	Quartzite	Andesite	Basalt
Mucor sp.				▽				
Parmelia sp.				▽				
Penicillium sp.				▽				
Rhizocarpon sp.				▽				
Rhizopus sp.				▽				

Common fungal species inhabiting building stone in mediterranean climates (☆)	Sandstone	Marble	Granite	Limestone	Soapstone	Quartzite	Andesite	Basalt
Alternaria alternata	☆		☆	☆				
Cladosporium cladosporoides	☆		☆	☆				
Penicillium frequentans	☆		☆	☆				
Penicillium steckii	☆		☆	☆				
Phoma glomerata	☆		☆	☆				

TABLE 1 (*contd.*)

Common fungal species inhabiting building stone in temperate climates (□)	Sandstone	Marble	Granite	Lime-stone	Soapstone	Quartzite	Andesite	Basalt
Alternaria sp.	□							
Aspergillus sp.	□							
Aureobasidium sp.			□					
Chaetomium sp.*	□			□				
Cladosporium sp.	□							
*Cryptococcus magnus**				□				
*Filobasidium floriforme**				□				
Fusarium sp.	□							
Paecilomyces sp.	□							
Penicillium sp.	□		□					
*Penicillium corylophilum**				□				
*Petriella setifera**				□				
Phoma sp.			□					
Phialophora sp.*				□				
*Pseudallescheria boydii**				□				
Rhizopus sp.	□							
Trichoderma sp.	□							

Common fungal species inhabiting rocks in cold deserts, e.g. Antarctica (■)	Sandstone	Marble	Granite	Dolerite	Amphi-bolite	Quartzite	Andesite	Basalt
Aspergillus sp.						■		
Candida sp.	■							
Fusarium sp.						■		
Mucor sp.						■		
Paecilomyces sp.				■	■			
Penicillium sp.	■		■			■		
Rhizopus sp.						■		
Rhodotorula sp.	■							
Sporobolomyces sp.	■							

those with lower pressures, and fungi that naturally invade hard materials generate extraordinarily high pressure. For example, various human and plant pathogenic fungi (e.g. *Wangiella dermatitis*, *Gaeumannomyces graminis*, *Magnaporthe grisea*) were able to exert pressure of 8–20 μN (Money, 1999; Money and Howard, 1996). Melanin has also been implicated as playing a major role in the ability of plant pathogenic fungi to penetrate solid materials as this black pigment facilitates the development of infection structures (Wheeler and Bell, 1987; Money and Howard, 1996). Rock-dwelling fungi are ubiquitous and very often melanized and can be potentially pathogenic for humans (e.g. *Aureobasidium pullulans*, *Cryptococcus sp.*, *Exophiala sp.*, *Phialophora sp.*, *Cladosporium cladosporioides*) (Horre and de Hoog, 1999; Kantarcioglu *et al.*, 2002). However, as in other fungi, surface biophysical weathering is combined with surface and subsurface biochemical weathering. Although, biochemical weathering can be limited by depth, progressive leaching of elements increases the porosity of the weathering rind, thereby facilitating water penetration and the maintainance of chemical processes to greater depth (Etienne, 2002).

Biochemical deterioration of rock by fungi

The biochemical action of fungi on rocks is believed to be a more important process than mechanical degradation (Kumar and Kumar, 1999). Fungi can solubilize minerals and metal compounds through four main mechanisms: (1) acidolysis (2) complexolysis (3) redoxolysis and (4) mycelial metal accumulation (Burgstaller and Schinner, 1993). Heterotrophic leaching by fungi primarily involves the first two mechanisms and occurs as a result of several processes including proton efflux via the plasma membrane H^+-ATPase, maintenance of charge balance, production of siderophores (e.g. in the case of Fe and Mn) or as a result of respiratory carbon dioxide accumulation. In many fungal strains however, heterotrophic leaching occurs mainly through the production of organic acids (e.g. oxalic and citric acid) (Adams *et al*., 1992; Gadd, 1999, 2001*a*; Jarosz-Wilkołazka and Gadd, 2003).

Fungi generally acidify their micro-environment and this acidification results from (1) the excretion of protons via the proton translocating ATPase (2) the absorption of nutrients in exchange for protons (3) excretion of organic acids (4) carbonic acid formed as result of respiratory CO_2 production (Burgstaller and Schinner, 1993). In addition, fungi, like most heterotrophs, excrete primary and secondary metabolites with chelating properties (e.g. carboxylic acids, amino acids and phenolic compounds) (Manley and Evans, 1986; Muller *et al*., 1995). Fungal-derived carboxylic acids can play an integral role in chemical attack on mineral surfaces (Muller *et al*., 1995; Gadd, 1999, 2001*a*). The production of organic acids provides a source of protons for solubilization and metal-chelating anion to complex the metal cation. Metal complexation is often dependent on the concentration of anions and metals in solution, pH and the stability constants of the various complexes (Devevre *et al*., 1996).

Fungal deterioration of rock and building stone by biomechanical and biochemical processes

Microbial attack on minerals is usually specific and may depend on the groups of microorganisms involved (e.g the hyphae of lichens have been shown to overgrow augite and mica but actively avoid quartz) (Aristovskaya, 1980). In podzols, quartz and kaolin are usually overgrown by fungi and algae, with abundant fungal hyphae also being found to envelope apatite particles. Bacteria, on the other hand, develop mainly on biotite (Aristovskaya, 1980). Laboratory experiments have demonstrated that alkaline (basic) rocks are generally more susceptible to fungal attack than acidic rocks (Eckhardt, 1985; Kumar and Kumar, 1999).

Fungi are believed to contribute to the weathering of silicate-bearing rocks, e.g. mica and orthoclase, and Fe- and Mn-bearing minerals, e.g. biotite, olivine and pyroxene, but the amount of degradation of these substrates that can be directly attributed solely to fungal activity is still undetermined (Kumar and Kumar, 1999). Callot *et al*. (1987) demonstrated the ability of siderophore-producing fungi (or siderofungi) to pit and etch microfractures in samples of olivine and glasses under laboratory conditions. The ability of fungi to deteriorate natural and man-made antique and medieval glass was also shown by Krumbein *et al*. (1991). Fungal degradation of aluminosilicates and silicates is believed to occur as a result of the production of organic acids, inorganic acids and complexing agents (Rossi and Ehrlich, 1990). However, it is also plausible that CO_2 released during fungal respiration can enhance silicate degradation by carbonic acid attack of mineral surfaces (Sterflinger, 2000). Among the most important fungi to attack silicates include oxalic-acid-producing species, e.g. *Aspergillus niger*, has been shown to degrade olivine, dunite, serpentine, muscovite, feldspar, spodumene, kaolin and nepheline. *Penicillium expansum* causes extensive degradation of basalt while *Penicillium simplicissimum* and *Scopulariopsis brevicaulis* have been shown to release Al from aluminosilicates (Mehta *et al*., 1979; Rossi, 1979; Sterflinger, 2000).

In podzol E horizons under European coniferous forests, the weathering of hornblendes, feldspars and granitic bedrock has been attributed to exudation of oxalic, citric, succinic, formic and malic acids by saprotrophic and mycorrhizal hyphae. Fungal hyphal tips were found to produce micro- to millimolar concentrations of these acids that could effectively dissolve Ca-rich plagioclase feldspars at rates of 0.3 to 30 $\mu m\ y^{-1}$ (Jongmans *et al*., 1997). The chemical weathering of primary Si- and Al-bearing minerals by non-fungal derived organic acids was demonstrated under laboratory conditions by Huang and Keller (1972) and Wilson (1975).

Fungal weathering of limestone, sandstone and marble, is also known to occur (Kumar and Kumar, 1999; Ehrlich, 1996). Carbonates, especially calcium carbonate ($CaCO_3$) and calcium magnesium carbonate ($CaMg(CO_3)_2$), occur extensively on the Earth's surface as limestone and dolomite (Ehrlich, 1996). Near-surface calcretes and dolocretes cover as much as 13% of the total land surface and are an important reservoir of carbon accounting for 78.5% of the total HCO_3^-, CO_3^{2-} and CO_2 in the Earth's lithosphere (Ehrlich, 1996; Goudie, 1996). Numerous microorganisms including bacteria and fungi have been isolated from natural limestone formations.

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 within rocks) fungi are known to bore into limestone. Cavities in limestone provide a major habitat for these organisms particularly in extreme environments like cold deserts (Ehrlich, 1996). The production of organic acids (e.g. oxalic and gluconic acids) is believed to play a major role in biochemical degradation of limestone material (Ehrlich, 1996).

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

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (1)$$
$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \qquad (2)$$
$$H_2CO_3 \rightleftharpoons H_2O + CO_2 \qquad (3)$$

Since $Ca(HCO_3)_2$ is very soluble compared with $CaCO_3$, the $CaCO_3$ dissolves even in weakly acidic solutions. In strong acid solutions the $CaCO_3$ dissolves more rapidly as carbonate is lost from solution as CO_2. Biochemically, any organism capable of forming acids through its metabolism is capable of dissolving insoluble carbonates. Even the metabolic generation of CO_2 during respiration can have the same effect:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (4)$$
$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (5)$$

Degradation of sandstone by fungi is also well documented (Gomez-Alarcon *et al.*, 1994; Hirsch *et al.*, 1995; Sterflinger, 2000). The weathering of sandstone monuments by fungi has been attributed to the production of, e.g. acetic, oxalic, citric, formic, fumaric, glyoxylic, gluconic, succinic and tartaric acids (Gomez-Alarcon *et al.*, 1994; Hirsch *et al.*, 1994). 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). In contrast to the acid-producing hyphomycetes, microcolonial fungi have never been shown to produce organic acids under laboratory conditions (Wollenzien *et al.*, 1995). However, analysis of desert rock samples has shown colonies or single cells in connection with pitting and etching patterns suggesting acid attack of the mineral surface, possibly a result of the production of organic acids or carbonic acid (Sterflinger, 2000). Microcolonial fungi have also been shown to be common inhabitants of biogenic oxalate crusts on granitic rocks. It is thought that the crusts in these cases are initially formed by bacteria and later colonized, penetrated and partially destroyed by fungi (Blazquez *et al.*, 1997).

Fungi can also attack rock surfaces through redox attack of mineral constituents such as Mn and Fe (Timonin *et al.*, 1972; Grote and Krumbein, 1992; de la Torre and Gomez-Alarcon, 1994). Desert varnish, an oxidized metal layer (patina) a few mm thick found on rocks and in soils of arid and semi-arid regions, is believed to be of fungal and bacterial origin. For example, fungi of the *Lichenothelia* genus can oxidize Mn and Fe in metal-bearing minerals such as siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$), or from metals absorbed from rainfall or wind-blown dust and precipitate them as oxides (Grote and Krumbein, 1992). Similarly the oxidation of Fe(II) and Mn(II) by fungi leads to the formation of dark patinas on glass surfaces. Fungi produce chelating agents that mask the ions dissolved from glass surface by chemical processes (e.g. Ca^{2+}). The chemical equilibrium is changed and the process of ion dissolution is increased (Erkhardt, 1985).

The mycelial sink: metal/mineral binding, accumulation and precipitation

Fungal biomass provides a metal sink, either by (1) metal biosorption to biomass (cell walls, pigments and extracellular polysaccharides); (2) intracellular accumulation and sequestration, or (3) precipitation of metal compounds onto hyphae. In addition to immobilizing metals, this also reduces the external free metal activity, and may shift the equilibrium to release more metal into the soil solution (Gadd, 1993, 2000*b*; Sterflinger, 2000).

Fungi are known to be highly effective biosorbents for a variety of metals including Ni, Zn, Ag, Cu, Cd and Pb (Gadd, 1990, 1993). Metal binding by fungi can occur through metabolism-dependent or metabolism-independent binding of ions onto cell walls and other external surfaces and can be an important passive process of both living and dead fungal biomass (Gadd, 1990, 1993; Sterflinger, 2000). Metal-binding capacity can be influenced by environmental pH, with the binding capacity of biomass decreasing at low pH for metals such as Cu, Zn and Cd (de Rome and Gadd, 1987). Cell density also effects binding capacity, with lower cell densities allowing a higher yield per unit of biomass (Gadd, 1993). The presence of melanin and chitin in fungal cell walls may also strongly influence the ability of fungi to act as biosorbents (Gadd and Mowll, 1995; Manoli *et al*., 1997). Gadd and Mowll (1995) reported that melanin-containing chlamydospores of *Aureobasidium pullulans* could absorb three times more Cu than hyaline cells. Manoli *et al*. (1997) demonstrated that chitin, a nitrogen-containing polysaccharide and major component of fungal cell walls, is a substrate on which calcite will readily nucleate and subsequently grow, favouring deposition from supersaturated solutions at pH 8.5 at 25ºC.

Formation of biogenic minerals (mycogenic precipitates) by fungi

Fungi have been shown to precipitate a number of inorganic and organic compounds, e.g. oxalates and oxides (Arnott, 1995; Verrecchia, 2000; Gadd, 2000*a*; Grote and Krumbein, 1992) (Fig. 2*e*). Precipitation, including crystallization, will immobilize metals in the soil environment and therefore limit bioavailability, as well as perhaps leading to release of nutrients like sulphate and phosphate (Gadd, 2000*a,b*).

Oxalate precipitation

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

Fungi can also produce other metal oxalates with a variety of different metals and metal-bearing minerals, e.g. Cd, Co, Cu, Mn, Sr and Zn (Gadd, 2000*a,b*; Jarosz-Wilkołazka and Gadd, 2003; Burford *et al*., 2003, 2004). The formation of metal oxalates may provide a mechanism whereby fungi can tolerate environments containing potentially high concentrations of toxic metals. A similar mechanism is thought to occur in lichens observed growing on copper-sulphide bearing rocks, where precipitation of copper oxalate occurs within the thallus (Arnott, 1995; Easton, 1997). Under laboratory conditions, media amended with powdered minerals have revealed fungal production of metal oxalates which adhere to fungal hyphae or are deposited nearby (Sayer *et al*., 1997; Burford *et al*., 2004). However, oxalates are not the only crystalline precipitates to be associated with fungal hyphae and lichen thalli. The precipitation of carbonates on fungal hyphae, particularly calcite ($CaCO_3$), has also been reported *in situ* in calcareous soils and near surface limestones (calcretes) (Kahle, 1977; Klappa, 1979*a,b*; Calvet, 1982; Callot *et al*., 1985*a,b*; Verrecchia *et al*., 1990; Monger and Adams, 1996; Bruand and Duval, 1999; Burford *et al*., 2003, 2004).

Calcified fungal filaments in limestone and calcareous soils

The precipitation of carbonate minerals by microorganisms is well documented suggesting that microbial carbonate precipitation coupled with silicate weathering could provide a potential sink for CO_2 in terrestrial environments (Krumbein and Giele, 1979; Callot *et al*., 1985*a,b*; Thompson and Ferris, 1990; Verrecchia *et al*., 1990; Bruand and Duval, 1999; Rivadeneyra *et al*., 1993; Folk and Chavetz, 2000; Fujita *et al*., 2000; Knorre and Krumbein, 2000; Merz-Preiß, 2000; Riding, 2000; Warren *et al*., 2001; Hammes and Verstraete, 2002). In limestone, dolomite and marble, fungi are considered to be important agents of carbonate mineral deterioration, weathering carbonate-bearing minerals through a combination of physical and chemical processes. However, fungi can also play a fundamental role in secondary carbonate precipitation. Fungal filaments mineralized with calcite ($CaCO_3$), together with whewellite (calcium oxalate monohydrate, $CaC_2O_4.H_2O$), have been reported in limestone and calcareous soils from a range of localities (Kahle, 1977; Klappa, 1979*a,b*; Calvet, 1982; Callot *et al*., 1985*a,b*; Verrecchia *et al*., 1990; Monger and Adams, 1996; Bruand and Duval, 1999). In addition, near-surface limestones (calcretes), calcic and petrocalcic horizons in soils are often secondarily cemented and indurated with calcite ($CaCO_3$) and whewellite (calcium oxalate monohydrate, $CaC_2O_4.H_2O$) implying that fungi play a prominent role in the transformation and subsequent stabilization of limestone rock substrates (Verrecchia, 2000).

Calcite formation by fungi may occur through indirect processes via the fungal excretion of oxalic acid and the precipitation of calcium oxalate (Verrecchia *et al*., 1990; 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, calcium carbonate 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 be released to act as sites of further secondary calcite precipitation (Verrecchia, 2000) (Fig. 2*f,g*).

Reduction of metals and metalloids

Many fungi precipitate reduced forms of metals and metalloids in and around fungal hyphae. For example, Ag(I) reduction to elemental silver Ag(0); selenate [Se(VI)] and selenite [Se(IV)] to elemental selenium; tellurite [Te(IV)] to elemental tellurium [Te(0)]. Reduction of Hg(II) to volatile Hg(0) can also be mediated by fungi (Gadd, 1993, 2000*a,b*).

Clays and fungi

Clay mineral formation and impact on soil properties

Silicon dioxide, when combined with oxides of Mg, Al, Ca and Fe, forms the silicate minerals in rocks and soil (Bergna, 1994). These high-temperature minerals are unstable at the temperatures of the biosphere, and they break down readily to form clays. Microorganisms modify the rates and mechanisms of chemical and physical weathering and clay growth, thus playing fundamental roles in the dissolution of silicate structure in the rock weathering process, in the genesis of clay minerals, and soil and sediment formation (Styriakova and Styriak, 2000; Banfield *et al*., 1999). The presence of clay minerals can be a typical symptom of biogeochemically-weathered rocks (Barker and Banfield, 1996, 1998; Rodriguez Navarro *et al*., 1997). For example, in the weathering of silicate minerals by lichens, Ca, K, Fe clay minerals and nanocrystalline aluminous Fe oxyhydroxides are mixed with fungal organic polymers (Barker and Banfield, 1998). It was also reported that biotite in contact with the lichen thallus was interpenetrated by fungal hyphae growing along cleavages and was partially converted to vermiculite (Barker and Banfield, 1996). Some evidence of fungal weathering of minerals in soil and their transformation into clay have been reported in study on ectomycorrhizal influence on chemical and mineralogical properties of soils (Arocena *et al*., 1999). The results suggested that the transformation rate of mica and chlorite to 2:1 expandable clays was predominant in the ectomycorrhizosphere compared to 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. In ectomycorrhizoplane samples, it was suggested that K^+ and possibly amorphous Al_2O_3 and Fe_2O_3 could reconstitute the degraded mica and chlorite through the formation of hydroxy-interlayered 2:1 clays.

Soil, being 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 is generally present in soil in larger amounts than organic matter and its total contribution to the chemical and physical properties generally equals or exceeds that of humus. Because of their ion-exchange capacity, their electronegative charge, and their adsorption powers, the silicates of clay perform a buffering function in mineral soils (Ehrlich, 1996; Dube *et al*., 2001). Their ion-exchange capacity and adsorption powers, moreover, make them important reservoirs of cations and organic molecules (Wild, 1993; Li and Li, 2000; Dinelli and Tateo, 2001; Dong *et al*., 2001; Krumhansl *et al*., 2001). Montmorillonites exhibit the greatest ion-exchange capacity, illites exhibit less, and kaolinites least (Kukovsky, 1966; Ehrlich, 1996).

Biological effects of clay minerals

The role of clay minerals in co-evolution of the biological and mineral worlds has attracted increasing attention (Bergna, 1994; Trevors, 1996; Hartman, 1998; Ferris, 2002; Pearson, 2002). Clays may have played a significant role

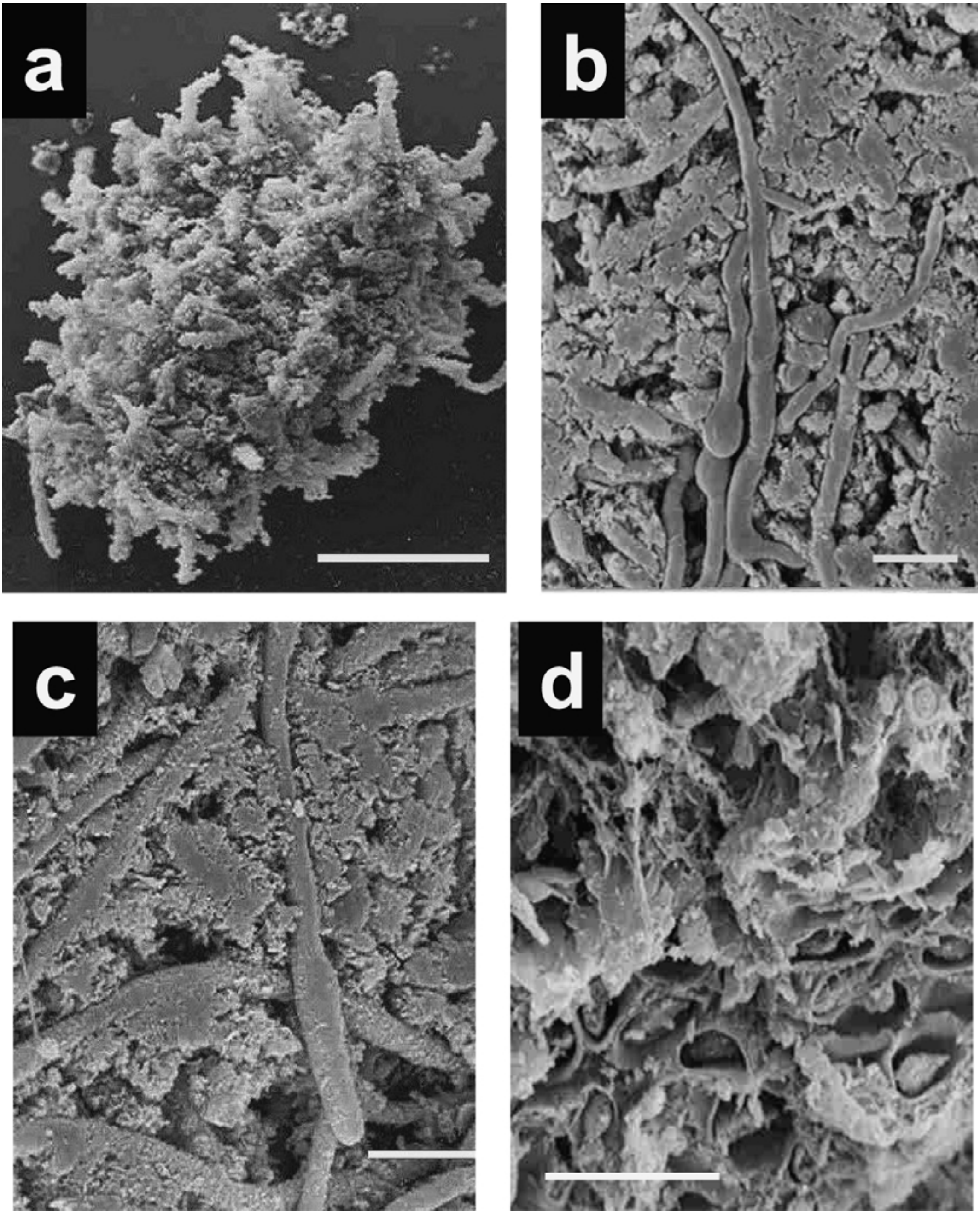
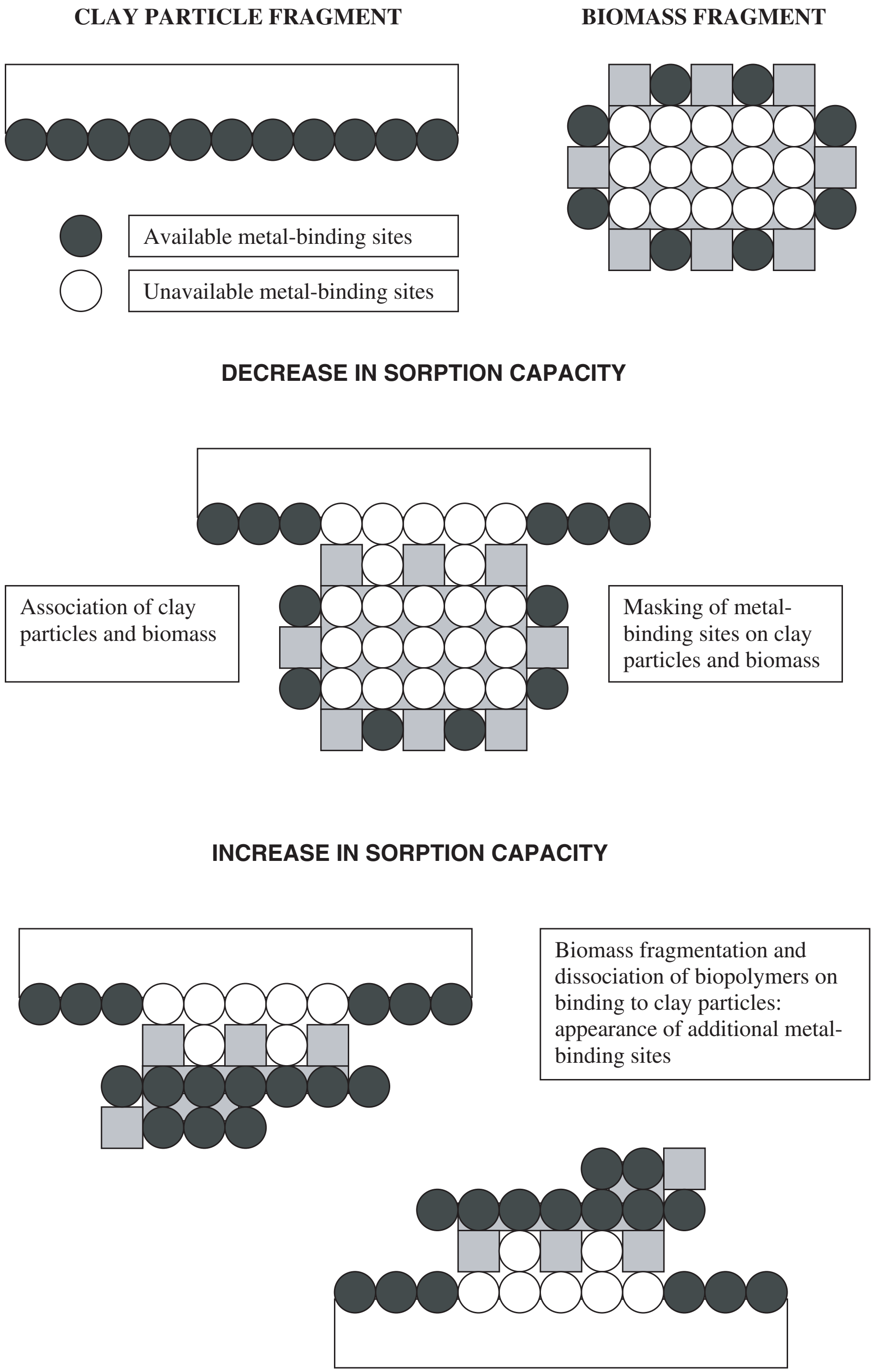


Fig. 3. SEM images of fungal pellets in the presence of 0.5% (w/v) bentonite: (*a*) whole pellet of *Cladosporium cladosporioides* grown for 17 h (scale bar = 100 μm); (*b*) structure of the central zone of a fractured pellet of *Humicola grisea* grown for 140 h (scale bar = 10 μm); (*c*) structure of the central zone of fractured pellet of *C. cladosporioides* grown for 38 h (scale bar = 10 μm); (*d*) structure of the central zone of a fractured pellet of *C. cladosporioides* grown for 140 h formed by a polysaccharide/clay matrix surrounding individual hyphae, (scale bar = 10 μm) (adapted from: Fomina and Gadd, 2002*b*).

in the evolution of life and synthesis of biologically viable molecules on prebiotic earth due to their ability to adsorb, concentrate, and subsequently catalyse the polymerization of important biological monomers (Winter and Zubay, 1995; Bosetto *et al*., 1997; Hartman, 1998; Porter *et al*., 2000).

Fungi are in close contact with clay minerals in soils and sediments. It is well known that microbial growth, metabolic activity and genetic processes can be strongly influenced by clays and numerous studies have shown that the interaction of microorganisms with solid adsorbents can lead to an increase of biomass yield and growth rate and production of enzymes and metabolites (Stotzky, 1966, 2000; Haider *et al*., 1970; Martin *et al*., 1976; Fletcher, 1987; Zvyagintcev, 1987; Marshall, 1988; Clause and Filip, 1990; Kurdish and Kigel, 1992; Lee and Stotzky, 1999; Lotareva and Prozorov, 2000; Lunsdorf *et al*., 2000; Demaneche *et al*., 2001; Fomina and Gadd, 2002*a*). Depending on conditions, some clays may stimulate or inhibit fungal metabolism (Fomina and Gadd, 2002). Stimulatory effects were explained by the various abilities of different clays to serve as (1) pH buffers, (2) a source of inorganic nutrients through their cation-exchange capacity, (3) specific adsorbents of one or more metabolic inhibitors (as well as nutrients and growth stimulators), and (4) modificators of the microbial microenvironment because of their surface area and adsorptive capacity that creates microzones with altered microbial growth conditions (Stotzky, 1966; Marshall, 1988; Martin *et al*., 1976; Fletcher, 1987; Zvyagintcev, 1987). Interactions between microorganisms and solid mineral particles also help the microorganisms to maintain themselves in higher layers of soil and offer protection from environmental stresses (Babich and Stotzky, 1977; McEldowney and Fletcher, 1986; Kurdish and Titova, 2000; Pereira *et al*., 2000; Vettori *et al*., 2000). A growth promotional role of montmorillonite was shown for *C. cladosporioides* grown in liquid medium at both deficiency of carbon or mineral nutrients and at high carbon source concentrations (Fomina *et al*., 2000). The protective role of clay against inhibitory concentrations of substrate can be explained by adsorption and thereby neutralization of toxic products of metabolism allowing a more effective use of the carbon substrate (Stotzky, 1966). It was also found that the inclusion of clay minerals (bentonite, palygorskite and kaolinite) in liquid medium influenced the size, shape and structure of the mycelial pellets (Fomina and Gadd, 2002*b*). At all stages of fungal growth, the clay particles were involved in the formation of fungal pellet structure serving as the mineral matrix or building material for the microcolony (Fomina and Gadd, 2002*b*) (Figs 3, 4). The presence of clay minerals, in general, increased the porosity of the pellets (the ratio of surface hyphae length to pellet radius) of *Cladosporium* species (Fomina and Gadd, 2002*b*). Such changes in fungal morphology as affected by the different clay minerals may reflect some differences in physiological activity. The presence of clay within fungal pellets may positively influence the diffusion of nutrients and oxygen or remove toxic metabolites. For example, a reduction of polysaccharide-like exopolymer production in *C. cladosporioides, H. grisea* and *C. herbarum* with increasing clay concentration may be a result of protection of the pellets from a decline in the stationary phase of growth by clay minerals (Fomina and Gadd, 2002*b*). Clays also have an affinity for enzymes secreted by cells or liberated by them on autolysis after death (Skujins, 1967).

FIG. 4. (*facing page*) Simple model of mechanisms for reduced or enhanced metal sorption abilities of fungal/clay sorbents. Available metal-binding sites on clay particles or on biomass are represented by closed circles (●); masked or blocked metal-binding sites are represented by open circles (○). Note that the metal-binding sites depicted may be heterogeneous both between the biomass and the clay, but also within the biomass. A decrease in sorption capacity of the clay-biomass complex due to masking of metal-binding sites on the biomass and clay particles may result in binding of clay minerals with biomass fragments by, e.g. Van der Waals forces; Al^{3+}, Fe^{2+}, Ca^{2+} and Mg^{2+} bridges; hydrogen bonding; direct interactions between active sites of clay minerals with corresponding groups on the biomass; complexing of exchange cations of clay minerals by carboxyl, phenolic and carbonyl groups of the organic phase. An increase in sorption capacity of the clay-biomass complex may result after biomass fragmentation and/or dissociation of biopolymers after interactions with clay mineral particles, leading to exposure of additional metal-binding sites. The nature of such interactions will clearly depend on physico-chemical conditions and also properties of individual clay minerals and biomass types (adapted from Fomina and Gadd, 2002*a*).


CLAY PARTICLE FRAGMENT
BIOMASS FRAGMENT
Available metal-binding sites
Unavailable metal-binding sites
DECREASE IN SORPTION CAPACITY
Association of clay particles and biomass
Masking of metal-binding sites on clay particles and biomass
INCREASE IN SORPTION CAPACITY
Biomass fragmentation and dissociation of biopolymers on binding to clay particles: appearance of additional metal-binding sites

Role of clay/fungal interactions in soil aggregation and sorption properties

Intimate contact of fungi with clay minerals and other solid adsorbents in their natural environment results in an aggregated condition being the norm. Interaction between cells and solid particles is subject to a complex of forces of both a physicochemical (electrostatic, ionic, hydrophobic etc.) and biological (chemotaxis, production of specific enzymes, polysaccharides, lectins and other adhesins, etc.) nature (Fletcher, 1987; Zvyagintcev, 1987; Lunsdorf *et al.*, 2000). Under physiological (or neutral) pH values, microorganisms have a net negative charge and mostly amino- and carboxyl groups on their surface (Zvyagintcev, 1987; Marshall, 1988). It was shown that positively charged edges of slices of montmorillonite were electrostatically attracted by negative carboxyl groups of bacterial surfaces, whereas positive sites on cell surfaces can attach to the negatively-charged lateral flatness of montmorillonite particles (Marshall, 1988). Fungal and clay mineral interactions have been shown to play an important role in the processes of soil evolution. The examination of the soil clay aggregation by saprophytic (*Rhizoctonia solani* and *Hyalodendron sp.*) and mycorrhizal (*Hymenoscyphus ericae* and *Hebeloma sp.*) fungi supported the hypothesis that fungal hyphae bring mineral particles and organic materials together to form stable micro-aggregates at least <2 μm, and enmesh micro-aggregates into stable aggregates >50 μm diameter (Tisdall *et al.*, 1997). Fungi not only entangle soil particles in their hyphae but take part in polysaccharide aggregation as well (Dorioz *et al.*, 1993; Martens and Frankenberger, 1992; Schlecht-Pietsch *et al.*, 1994; Puget *et al.*, 1999; Chantigny *et al.*, 1997). Our observations of polysaccharide-like exopolymer synthesis and the formation of a solid matrix from polysaccharide/clay mixtures in the central zone of fungal microcolonies, also contributes to considerations of the roles of soil fungi in soil aggregation and stabilization (Fomina and Gadd, 2002*b*) (Figs 3*d*, 4).

Interactions between clay minerals and fungi alter the filtration and sorption properties of soil and may have further implications for the fate of toxic metals. In an environmental context, pollution of the natural environment by toxic metals, metalloids and radionuclides has led to increased interest in fungi because of the ubiquitous presence of fungi in metal-polluted habitats, and their capacity for uptake and translocation of toxic metals and radionuclides (Gadd 1993; Gadd and Sayer, 2000). It was shown that metal inputs increased ergosterol and decreased bacterial-fungal PLFA ratios in most soils indicating the comparative increase of fungal biomass compared to bacteria in metal-contaminated soils (Khan and Scullion, 2000).

Fungi themselves are very potent biosorbing materials and another area of applied speculation is the use of fungal biomass for biosorptive detoxification of metal/radionuclide-containing industrial effluents (Gadd, 1986, 1990, 1992). Fungal biosorption depends on physicochemical conditions, strain properties, cell wall composition and, especially, the presence of pigments (Gadd and Griffiths, 1980; Gadd, 1984, 1990, 2001*a,b*; Gadd and de Rome, 1988; Zhdanova *et al.*, 1990; Fogarty and Tobin, 1996). Interactions of clay particles and fungal cells may alter adsorption properties of both constituents. Clay minerals, adsorbed on fungal mycelium, increase the low mechanical strength of fungal biomass improving its metal sorption characteristics. The presence of living microbial cells adsorbed on the soil particles should be regarded as a complex system of biotic-mineral complex being a natural biogeochemical barrier in the processes of toxic metal and radionuclides migration in soil. Both clays and fungal biomass have been investigated due to their ability to sorb toxic metals. However, most studies have concentrated on the uptake of metals by either clay minerals or microbial biomass as individual and separate entities (Inskeep and Baham, 1983; Farrah and Pickering, 1976*a,b*; Fujiyoshi *et al.*, 1992; van Bladel *et al.*, 1993; Volesky and Holan, 1995; Li and Li, 2000; Dinelli and Tateo, 2001; Dong *et al.*, 2001). Only a few studies have been carried out on the sorption properties of mixtures of clay minerals (montmorillonite, kaolinite) and microbial biomass (algae, fungi) (Garnham *et al.*, 1991; Kadoshnikov *et al.*, 1995; Morley and Gadd, 1995; Fomina and Gadd, 2002*a*).

The sorptive properties of clay-organic matter complexes has attracted considerable attention (Flemming *et al.*, 1990; Dumat *et al.*, 2000; Neubauer *et al.*, 2000; Leboda *et al.*, 2001; Voudrias, 2002). In general, a decrease in metal sorption has been found with increasing carbon deposited in the complex adsorbent (Leboda *et al.*, 2001) or increasing polymer adsorbed on the clay surface (Dumat *et al.*, 2000) due to partial or complete blocking of adsorption/catalytic centres. However, it has been shown that in montmorillonite suspensions, metal sorption was enhanced by the siderophore desferrioxamine B due to electrostatic interactions (Neubauer *et al*., 2000). The presence of kaolinite and palygorskite in the medium generally reduced both Cu and Cd sorption capacity and the metal-binding ability of the fungal-clay mixtures (Fomina and Gadd, 2002*a*). In contrast, bentonite addition into the medium did not considerably alter the Cd sorption ability but increased the sorption of Cu by *A. pullulans* and *C. cladosporioides* grown in this medium. A common feature for all fungal cultures growing in the presence of the bentonite was an increase in Cu sorption capacity ($Q_{\max}$) of the biomineral sorbents and a reduction of their affinity (Langmuir parameter *b*) compared to control biomass (Fomina and Gadd, 2002*a*). In a study of *R. arrhizus* and *T. viride*, mixtures of montmorillonite and fungal biomass showed a reduced uptake of metals, depressed below calculated values by up to 37% at pH 4, possibly because of masking of exchange sites (Morley and Gadd, 1995). The decrease in metal retention was explained as being the result of cation-enhanced aggregation between the cells and clays, the clays probably physically blocking regions of the microbial surface, thus reducing the cation binding capacity of the aggregate. However *C. cladosporioides* biomass grown in the form of small pellets in a medium containing 5% (w/v) kaolinite demonstrated an enhanced ability to sorb ^{90}Sr (2670 Bq/g) compared to pure clay (1951 Bq/g) and pure biomass (1551 Bq/g) (Fomina *et al*., 1999). As shown for *C. cladosporioides* and radionuclides (Fomina *et al*., 1999) and for Cu (Fomina and Gadd, 2002*a*), sorption ability generally increased with a decrease of fungal pellet size. Physical interactions therefore may not prove to be the sole explanation of changes in the metal-binding capacity of fungal/clay aggregates.

As clay minerals and biomass have some differences in mechanisms of sorption and are more efficient in different ranges of metal concentrations, fungal/clay complex biomineral sorbents could 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. Fungal biomass grown in a bentonite-containing medium generally showed increased metal sorption capacity compared to individual biomass, with the ability to sorb metals being especially efficient at higher concentrations of toxic metals (Fomina and Gadd, 2002*a*). The mechanisms underlying the changed sorption abilities of such complex biomineral sorbents can be blocking and masking of binding sites in the case of decreased sorption ability, and modification of binding sites and emergence of new ones in the case of increased sorption ability (Fomina and Gadd, 2002*a*) (Fig. 4).

Clay and silicate weathering by fungi

Clay minerals can be modified by microorganisms. Silicon in nature may follow a series of cyclical biogeochemical transformations (Ehrlich, 1996; Bergna, 1994). Silica liberated in these processes may be leached away by surface or groundwater, and then it may either be removed by chemical or biological precipitation at new sites, or may be transported into bodies of fresh water or the sea. The environmental distribution of silicon is significantly influenced by microbial activity, especially by those microorganisms which assimilate Si and incorporate it into cell-supporting structures, e.g. diatoms. Fungi and bacteria play an important role in the mobilization of silica and silicates in nature (Ehrlich, 1996). 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. A fungus (*Penicillium notatum*) was shown to be faster than a bacterium (*Pseudomonas sp.*) in silicate solubilization (Kutuzova, 1969). Fungi isolated from weathered rock surfaces (*Botrytis*, *Mucor*, *Penicillium* and *Trichoderma* spp.) were shown to be able to solubilize Ca, Mg and Zn silicates (Webley *et al*., 1963). Mobilization of silicate from clay minerals by *Aspergillus niger* was found to be a result of oxalic acid excretion (Henderson and Duff, 1963). *Aspergillus* sp., *Byssochlamys* sp. and *Penicillium* sp., that are known as bare rock invaders and prolific producers of various organic acids, were isolated from floodplain sandy-clay-loam sediments suggesting the role of such fungi in weathering of chemically and biologically immature sediments. The majority of fungal strains belonging to the genera *Aspergillus, Paecilomyces, Penicillium, Scopulariopsis* and *Trichoderma* could leach Fe in submerged culture from a China clay sample from West Bengal, India, (Mandal *et al*., 2002). *A. niger* NCIM 548 released 23% of total Fe from China clay in 15 days, whereas under identical conditions leaching with 0.1 M oxalic acid solution was only 14.8% and much less with culture filtrates of other strains. Large amounts of oxalic, citric and gluconic acids were produced by *Penicillium frequentans* in liquid cultures and caused extensive deterioration of clay silicates, as well as micas and feldspars from both sandstone and granite as a result of high cation release and organic salts formation such as Ca, Mg and ferric oxalates and calcium citrates (de la Torre *et al.*, 1993). The oxalate-excreting fungus *Hysterangium crassum* was found to weather clay minerals *in situ* (Cromack *et al.*, 1979).

Applied consequences of mineral mycotransformations and bioremediation

Concrete biodeterioration and radioactive waste disposal

Fungi, bacteria and algae are able to colonize all known structural materials, e.g. concrete, stone, brick, plaster, plastic, metal and wood, causing their biodeterioration and corrosion (Diercks *et al.*, 1991; Gaylarde and Morton, 1999; Kikuchi and Sreekumari, 2002; Roberts *et al.*, 2002). 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 (*Fusarium* sp.) degradation of concrete proceeded more rapidly than bacterium-mediated (*Thiobacillus* sp.) degradation with complexolysis suggested as the main mechanism of calcium mobilization (Gu *et al.*, 1998). This ability of fungi and other microorganisms to degrade concrete and other structural materials has significant implications for storage of nuclear waste. In high-level nuclear waste disposal, the bentonite buffer around the copper canisters is considered to be a hostile environment for most microbes due to the combination of radiation, heat and low water availability, but discrete microbial species can cope with each of these constraints (Pedersen, 1999). Endolithic, indigenous microorganisms are capable of surviving gamma irradiation doses simulating the near-field environment surrounding waste canisters (Pitonzo *et al.*, 1999). In 1997–1998, extensive fungal growth was observed on the walls and other building constructions in the inner part of the 'Shelter' built on the fourth Unit of the Chernobyl nuclear power plant damaged in 1986 (Zhdanova *et al.*, 2000). It was found that low-level gamma radiation did not affect spore germination of fungi isolated from the Chernobyl area but led to directed growth of fungal tips towards the radiation source (so called positive radiotropism) (Zhdanova *et al.*, 2001).

Bioremediation

Toxic metals in natural, industrial and agricultural soils are a risk to human health. Some of the processes outlined above have the potential for treatment of contaminated land (Gadd, 2000*a,b*; Hochella, 2002). Solubilization processes provide a route for removal of metals from soil matrices, whereas immobilization processes enable metals to be transformed into insoluble, chemically more inert forms. These processes could be used *in situ*, but are possibly best suited for use in bioreactors where, for example, immobilized metal can be separated from soil components (Gadd, 2000*b*). Living or dead fungal biomass and fungal metabolites have been used to remove metal or metalloid species, compounds and particulates and organometal(loid) compounds from solution by biosorption. There has also been the use of extracellular ligands excreted by fungi, especially from *Aspergillus* and *Penicillium* spp., to leach metals such as Zn, Cu, Ni and Co from a variety of solid materials, including low-grade mineral ores (Brandl, 2001).

The mycorrhizal association could also be used with plants for metal clean-up (phytoremediation). Phytoextraction involves the use of plants to remove toxic metals from soil by accumulation in above-ground parts. Mycorrhizas may enhance phytoextraction directly or indirectly by increasing plant biomass, and some studies have shown increased plant accumulation of metals, especially when inoculated with mycorrhizal fungi isolated from metalliferous environments.

Conclusions

It is clear that fungi have important biogeochemical roles in the biosphere but are frequently neglected within broader microbiological and geochemical research spheres, in contrast to bacteria. For example, symbiotic mycorrhizal fungi are associated with ~80% of plant species and are responsible for major transformations and redistribution of inorganic nutrients, e.g. essential metals, phosphate, as well as carbon flow, while free-living fungi have major roles in decomposition of plant and other organic materials, including xenobiotics, as well as, e.g. phosphate solubilization. Fungi are dominant members of the soil microflora, especially in acidic environments, and may operate over a wider pH range than most heterotrophic bacteria. Fungi are also major agents of biodeterioration of stone, wood, plaster, cement 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 the interdisciplinary approach that is necessary to further understanding of 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. To achieve a better understanding of fungal-mineral interactions, the development of experimental methods and techniques that reflect and interrogate environmental conditions more precisely is an urgent need.

Acknowledgements

The authors gratefully acknowledge financial support from the Biotechnology and Biological Sciences Research Council (94/MAF12243; 94/BRE13640), the Natural Environment Research Council, the Royal Societies of London and Edinburgh, and British Nuclear Fuels plc. We are grateful to Mr Martin Kierans (CHIPS Centre for High Resolution Imaging and Processing, University of Dundee, Dundee DD1 4HN, UK) for assistance with SEM imaging, Mrs Kirsty Harris (Soil-Plant Dynamics Group, Scottish Crop Research Institute, Invergowrie, Dundee DD2 5DA, UK) for assistance with thin sectioning of limestone, and Dr Jan Colpaert (Limburg Universitaire Centrum, Environmental Biology, B-3590, Diepenbeek, Belgium) for identification of fungal isolates.

References

Adams, J.B., Palmer, F. and Staley, J.T. (1992) Rock weathering in deserts – mobilization and concentration of ferric iron by microorganisms. *Geomicrobiology Journal*, **10**, 99–114.

Aristovskaya, T.V. (1980) *Microbiology of the Processes of Soil Formation*. Nauka, Leningrad, USSR (in Russian), 187 pp.

Arnott, H.J. (1995) Calcium oxalate in fungi. Pp. 73 – 111 in: *Calcium Oxalate in Biological Systems* (S.R. Khan, editor). CRC Press, Boca Raton, Florida, USA.

Arocena, J.M., Glowa, K.R., Massicotte, H.B. and Lavkulich, L. (1999) Chemical and mineral composition of ectomycorrhizosphere soils of subalpine fir (Abies lasiocarpa (Hook.) Nutt.) in the Ae horizon of a Luvisol. *Canadian Journal of Soil Science*, **79**, 25–35.

Atlas, R.M. and Bartha, R. (1998) *Microbial Ecology*. Benjamin Cummings. Redwood City, California, USA.

Babich, H. and Stotzky, G. (1977) Reduction in the toxicity of cadmium to microorganisms by clay minerals. *Applied and Environmental Microbiology*, **33**, 696–705.

Banfield, J.F. and Nealson, K.H., editors (1998) *Geomicrobiology: Interactions between Microbes and Minerals.* Reviews in Mineralogy, **35**. Mineralogical Society of America, Washington, D.C.

Banfield, J.P., Barker, W.W., Welch, S.A. and Taunton, A. (1999) Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. *Proceedings of the National Academy of Sciences USA*, **96**, 3404–3411.

Barker, W.W. and Banfield, J.F. (1996) Biologically versus inorganically mediated weathering reactions: relationships between minerals and extracellular microbial polymers in lithobiotic communities. *Chemical Geology,* **132**, 55–69.

Barker, W.W. and Banfield, J.F. (1998) Zones of chemical and physical interaction at interfaces between microbial communities and minerals: a model. *Geomicrobiology Journal*, **15**, 223–244.

Bassi, M., Barbieri, N. and Bonecchi, R. (1984) St. Christophers church in Milan: biological investigations. *Arte Lombarda*, **68/69**, 117–121.

Bengston, S., editor (1994) *Early Life on Earth*. Columbia University Press, New York.

Bennett, P.C., Hiebert, F.K. and Choi, W.J. (1996) Microbial colonization and weathering of silicates in petroleum-contaminated groundwater. *Chemical Geology*, **132**, 45–53.

Bennett, P.C., Hiebert, F.K and Rogers, J.R. (2000) Microbial control of mineral-groundwater equilibria: macroscale to microscale. *Hydrogeology Journal,* **8**, 47–62.

Bergna, H.E. (1994) Colloid chemistry of silica – an overview. *Colloid Chemistry of Silica*, **234**, 1–47.

Berner, R.A. (1990) Atmospheric carbon dioxide levels over phanerozoic time. *Science*, **249**, 1382–1386.

Blazquez, F., Garcia-Vallez, M., Krumbein, W.E., Sterflinger, K. and Vendrell-Saz, M. (1997) Microstromatolithic deposits on granitic monuments: development and decay. *European Journal of Mineralogy*, **9**, 889–901.

Bogomolova, E.V., Vlasov, D.Yu. and Panina, L.K. (1998) On the nature of the microcolonial morphology of epilithic black yeasts *Phaeococcomyces* de Hoog. *Doklady of Russian Academy of Sciences*, **363**, 707–709.

Bosetto, M., Arfaioli, P., Pantani, O.L. and Ristori, G.G. (1997) Study of the humic-like compounds formed from L-tyrosine on homoionic clays. *Clay Minerals*, **32**, 341–349.

Brady, N.C. and Weil, R.R. (1999) *The Nature and Properties of Soils.* Prentice Hall, New Jersey.

Brandl, H. (2001) Heterotrophic leaching. Pp. 383–423 in: *Fungi in Bioremediation* (G.M. Gadd, editor). Cambridge University Press, Cambridge, UK.

Bruand, A. and Duval, O. (1999) Calcified fungal filaments in the petrocalcic horizon of Eutrochrepts in Beauce, France. *Soil Science Society of America Journal*, **63**, 164–169.

Buick, R. (1990) Microfossil recognition in Archean rocks and appraisal of spheroids and filaments from a 3500 m.y. old chert barite unit at North Pole, Western Australia. *Palois*, **5**, 441–459.

Burford, E.P., Kierans, M. and Gadd, G.M. (2003) Geomycology: fungal growth in mineral substrata. *Mycologist* (in press).

Burford, E.P., Hillier, S. and Gadd, G.M. (2004) Mineralization of fungal hyphae with calcite ($CaCO_3$) and calcium oxalate monohydrate ($CaC_2O_4.H_2O$) in carboniferous limestone microcosms. *Geomicrobiology Journal* (in revision).

Burgstaller, W. and Schinner, F. (1993) Leaching of metals with fungi. *Journal of Biotechnology*, **27**, 91–116.

Callot, G., Guyon, A. and Mousain, D. (1985*a*) Interrelation entre aiguilles de calcite et hyphes mycéliens. *Agronomie*, **5**, 209–216.

Callot, G., Mousain, D. and Plassard, C. (1985*b*) Concentrations de carbonate de calcium sur les parois des hyphes mycéliens. *Agronomie*, **5**, 143–150.

Callot, G., Maurette, M., Pottier, L. and Dubois, A. (1987) Biogenic etching of microfractures in amorphous and crystalline silicates. *Nature*, **328**, 147–149.

Calvet, F. (1982). Constructive micrite envelope developed in vadose continental environment in pleistocene eoliantes of Mallorca (Spain). *Acta Geologica Hispanica*, **17**, 169–178.

Chantigny, M.H., Angers, D.A., Prevost, D., Vezina, L.P. and Chalifour, F.P. (1997) Soil aggregation and fungal and bacterial biomass under annual and perennial cropping systems. *Soil Science Society of America Journal*, **61**, 262–267.

Clause, H. and Filip, Z. (1990) Effects of clay and other solids on the activity of phenolozidases produced by some fungi and actinomyces. *Soil Biology and Biochemistry*, **22**, 483–488.

Cromack, K. Jr., Solkins, P., Grausten, W.C., Speidel, K., Todd, A.W., Spycher, G., Li, C.Y. and Todd, R.L. (1979) Calcium oxalate accumulation and soil weathering in mats of the hypogeous fungus *Hysterangium crassum. Soil Biology and Biochemistry*, **11**, 463–468.

Dahanayake, K. and Krumbein, W.E. (1985) Ultrastructure of a microbial mat-generated phosphorite. *Mineralium Deposita*, **20**, 260–265.

Dahanayake, K., Gerdes, K. and Krumbein, W.E. (1985) Stromatolites, oncolites, and oolites biogenically formed *in situ*. *Naturwissenschaften*, **72**, 513–518.

Decho, A.W. (2000) Exopolymer microdomains as a structuring agent for heterogeneity within microbial biofilms. Pp. 9–15 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

de la Torre, M.A. and Gomez-Alarcon, G. (1994) Manganese and iron oxidation by fungi isolated from building stone. *Microbial Ecology*, **27**, 177–188.

de la Torre M.A., Gomez-Alarcon, G., Vizcaino, C. and Garcia, M.T. (1993) Biochemical mechanisms of stone alteration carried out by filamentous fungi living on monuments. *Biogeochemistry*, **19**, 129–147.

De Los Rios, A., Wierzchos, J. and Ascaso, C. (2002) Microhabitats and chemical microenvironments under saxicolous lichens growing on granite. *Microbial Ecology*, **43**, 181–188.

Demaneche, S., Jocteur-Monrozier, L., Quiquampoix, H. and Simonet, P. (2001) Evaluation of biological and physical protection against nuclease degradation of clay-bound plasmid DNA. *Applied and Environmental Microbiology*, **67**, 293–299.

de Rome, L. and Gadd, G.M. (1987) Copper adsorption by *Rhizopus arrhizus*, *Cladosporium resinae*, and *Penicillium italicum*. *Applied Microbiology and Biotechnology*, **26**, 84–90.

Devevre, O., Garbaye, J. and Botton, B. (1996) Release of complexing organic acids by rhizosphere fungi as a factor in Norway Spruce yellowing in acidic soils. *Mycological Research*, **100**, 1367–1374.

Diercks, M., Sand, W. and Bock, E. (1991) Microbial corrosion of concrete. *Experientia*, **47,** 514–516.

Dinelli, E. and Tateo, F. (2001) Sheet silicates as effective carriers of heavy metals in the ophiolitic mine area of Vigonzano (northern Italy). *Mineralogical Magazine*, **65**, 121–132.

Dong, W.M., Wang, X.K., Bian, X.Y., Wang, A.X., Du, J.Z. and Tao, Z.Y. (2001) Comparative study on the sorption/desorption of radioeuropium on alumina, bentonite and red earth: effect of pH, ionic strength, fulvic acid, and iron oxide in red earth. *Applied Radiation and Isotopes*, **54**, 603–610.

Dorioz, J.M., Robert, M. and Chenu, C. (1993) The role of roots, fungi and bacteria on clay particles organization. An experimental approach. *Geoderma*, **56**, 179−194.

Dube, A., Zbytniewski, R., Kowalkowski, T., Cukrowska, E. and Buszewski, B. (2001) Adsorption and migration of heavy metals in soil. *Polish Journal of Environmental Studies*, **10**, 1−10.

Dumat, C., Quiquampoix, H. and Staunton, S. (2000) Adsorption of cesium by synthetic clay-organic matter complexes: effect of the nature of organic polymers. *Environmental Science and Technology*, **34**, 2985−2989.

Easton, R.M. (1997) Lichen-rock-mineral interactions: an overview. Pp. 209−239 in: *Biological-Mineralogical Interactions* (J.M. McIntosh and L.A. Groat, editors). Short Course Series, **21**. Mineralogical Association of Canada, Ottawa, Ontario, Canada.

Eckhardt, F.E.W. (1985) Solubilisation, transport, and deposition of mineral cations by microorganisms-efficient rock-weathering agents. Pp. 161−173 in: *The Chemistry of Weathering* (J. Drever, editor). NATO ASI Series C, **149**, 161−173.

Ehrlich, H.L. (1996) *Geomicrobiology*. Marcel Dekker, New York.

Ehrlich, H.L. (1998) Geomicrobiology: its significance for geology. *Earth-Science Reviews*, **45**, 45−60.

Etienne, S. (2002) The role of biological weathering in periglacial areas, a study of weathering in south Iceland. *Geomorphology*, **47**, 75−86.

Farrah, H. and Pickering, W.F. (1976*a*) The sorption of copper species by clays. 2. Illite and montmorillonite. *Australian Journal of Chemistry*, **29**, 1177−1184.

Farrah, H. and Pickering, W.F. (1976*b*) The sorption of zinc species by clay minerals. *Australian Journal of Chemistry*, **29**, 1649−1656.

Ferris, F.G., Wiese, R.G. and Fyfe, W.S. (1994) Precipitation of carbonate minerals by microorganisms: implications for silicate weathering and the global carbon dioxide budget. *Geomicrobiology Journal*, **12**, 1−13.

Ferris, J.P. (2002) Montmorillonite catalysis of 30-50 mer oligonucleotides: laboratory demonstration of potential steps in the origin of the RNA world. *Origins of Life and Evolution of the Biosphere*, **32**, 311−332.

Flemming, C.A., Ferris, F.G., Beveridge, T.J. and Bailey, G.W. (1990) Remobilization of toxic heavy metals adsorbed to bacterial wall-clay composites. *Applied and Environmental Microbiology*, **3**, 191−203.

Fletcher, M. (1987) How do bacteria attach to solid surfaces? *Microbiological Sciences*, **4**, 133−136.

Fogarty, R.V. and Tobin, J.M. (1996) Fungal melanins and their interactions with metals. *Enzyme and Microbial Technolology*, **19**, 311−317.

Folk, R.L. and Chafetz, H.S. (2000) Bacterially induced microscale and nanoscale carbonate precipitates. Pp. 41−49 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin, Heidelberg.

Fomina, M. and Gadd, G.M. (2002*a*) Metal sorption by biomass of melanin-producing fungi grown in clay-containing medium. *Journal of Chemical Technology and Biotechnology*, **78**, 23−34.

Fomina, M. and Gadd, G.M. (2002*b*) Influence of clay minerals on the morphology of fungal pellets. *Mycological Research*, **106**, 107−117.

Fomina, M.A., Kadoshnikov, V.M. and Zlobenko, B.P. (1999) Fungal biomass grown on media containing clay as a sorbent of radionuclides. Pp. 245−254 in: *Proceedings of the International Biohydrometallurgy Symposium IBS'99 'Biohydrometallurgy and the Environment toward the Mining of the 21st century'*, Elsevier, Madrid, Spain.

Fomina, M.A., Kadoshnikov, V.M., Gromosova E.N. and Podgorsky V.S. (2000) The role of clay minerals during fungal growth under extreme conditions. Pp. 146−148 in: *Proceedings of the International III International Seminar* '*Mineralogy and Life: Biomineral Homologies*'. Geoprint, Syktyvkar, Russia.

Fujiyoshi, R., Eugene, A.S. and Katayama, M. (1992) Behaviour of radionuclides in the environment. 1. Sorption of Zn(II) on clay minerals. *Applied Radiation and Isotopes*, **43**, 223−1226.

Fredrickson, J.K. and Onstott, T.C. (1996) Microbes deep inside the earth. *Scientific American*, **8**, 42−47.

Fredrickson, J.K., McKinley, J.P., Nierzwicki-Bauer, S.A., White, D.C., Ringelberg, D.B., Rawson, S.A., Shu-Mei, L., Brockman, F.J. and Bjornstad, B.N. (1995) Microbial community structure and biogeochemistry of Miocene subsurface sediments: implications for long-term microbial survival. *Molecular Ecology*, **4**, 619−626.

Friedman, E.I. and Ocampo, R. (1976) Endolithic blue-green algae in the dry valleys: primary producers in the Antarctic desert ecosystem. *Science*, **193**, 1247−1249.

Fujita, Y., Ferris, F.G., Lawson, D.R., Colswell, F.S. and Smith, R.W. (2000) Calcium carbonate precipitation by ureolytic subsurface bacteria. *Geomicrobiology Journal*, **17**, 305−318.

Gadd, G.M. (1984) Effect of copper on *Aureobasidium pullulans* in solid medium: adaptation not necessary for tolerant behaviour. *Transactions of the British Mycological Society*, **82**, 546−549.

Gadd, G.M. (1986) The uptake of heavy metals by fungi and yeasts: the chemistry and physiology of the process and applications for biotechnology.

Pp. 135–147 in: *Immobilization of Ions by Biosorption* (H. Eccles and S. Hunt, editors). Ellis Horwood Ltd, Chichester, UK.

Gadd, G.M. (1990) Fungi and yeasts for metal accumulation. Pp. 249–275 in: *Microbial Mineral Recovery* (H.L. Ehrlich and C. Brierley, editors). McGraw-Hill, New York.

Gadd, G.M. (1992) Microbial control of heavy metal pollution. Pp. 59–88 in: *Microbial Control of Environmental Pollution* (J.C. Fry, G.M. Gadd, R.A. Herbert, C.W. Jones and I. Watson-Craik, editors). Cambridge University Press, Cambridge, UK.

Gadd, G.M. (1993) Interactions of fungi with toxic metals. *New Phytologist*, **124**, 25–60.

Gadd, G.M. (1999) Fungal production of citric and oxalic acid: importance in metal speciation, physiology and biogeochemical processes. *Advances in Microbial Physiology*, **41**, 47–92.

Gadd, G.M. (2000*a*) Heavy metal pollutants: environmental and biotechnological aspects. Pp. 607–617 in: *Encyclopedia of Microbiology* (J. Lederberg, editor). Academic Press, New York.

Gadd, G.M. (2000*b*) Bioremedial potential of microbial mechanisms of metal mobilization and immobilization. *Current Opinion in Biotechnology*, **11**, 271–279.

Gadd, G.M. (2001*a*) Metal transformations. Pp. 359–382, in: *Fungi in Bioremediation*. (G.M. Gadd, editor). Cambridge University Press, Cambridge, UK.

Gadd, G.M. (2001*b*) Accumulation and transformation of metals by microorganisms. Pp. 225–264, in: *Biotechnology, a Multi-volume Comprehensive Treatise, Volume 10: Special Processes*. (H.-J. Rehm, G. Reed, A. Puhler and P. Stadler, editors). Wiley-VCH Verlag GmbH, Weinheim, Germany.

Gadd, G.M. (2002) Interactions between microorganisms and metals/radionuclides: the basis of bioremediation. Pp. 179–203 in: *Interactions of Microorganisms with Radionuclides* (M.J. Keith-Roach and F.R. Livens, editors). Elsevier, Amsterdam.

Gadd, G.M. and de Rome, L. (1988) Biosorption of copper by fungal melanin. *Applied Microbiology and Biotechnology* **29**, 610–617.

Gadd, G.M. and Griffiths, A.J. (1980) Effect of copper on morphology of *Aureobasidium pullulans*. *Transactions of the British Mycological Society*, **74**, 387–392.

Gadd, G.M. and Mowll, J.L. (1995) Copper uptake by yeast-like cells, hyphae and chlamydospores of *Aureobasidium pullulans*. *Experimental Mycology*, **9**, 230–240.

Gadd, G.M. and Sayer, J.A. (2000) Fungal transformations of metals and metalloids. Pp. 237–256 in: *Environmental Microbe-Metal Interactions* (D.R. Lovley, editor). American Society for Microbiology, Washington, D.C.

Garnham, G.W., Codd, G.A and Gadd, G.M. (1991) Uptake of cobalt and cesium by microalgal- and cyanobacterial-clay mixtures. *Microbial Ecology*, **25**, 71–82.

Gaylarde, C.C. and Morton, L.H.G. (1999) Deteriogenic biofilms on buildings and their control: a review. *Biofouling*, **14**, 59–74.

Gerdes, G., Krumbein, W.E. and Noffke, N. (2000) Evaporite microbial sediments. Pp. 197–207 in: *Microbial Sediments* (R.E. Riding, and S.M. Awramik, editors). Springer-Verlag, Berlin.

Gomez-Alarcon, G., Munoz, M.L. and Flores, M. (1994) Excretion of organic acids by fungal strains isolated from decayed limestone. *International Biodeterioration and Biodegradation*, **34**, 169–180.

Gorbushina, A.A. and Krumbein, W.E. (2000) Subaerial microbial mats and their effects on soil and rock. Pp. 161–169 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Gorbushina, A.A., Krumbein, W.E., Hamann, R., Panina, L., Soucharjevsky, S. and Wollenzien, U. (1993) On the role of black fungi in colour change and biodeterioration of antique marbles. *Geomicrobiology Journal*, **11**, 205–221.

Goudie, A.S. (1996) Organic agency in calcrete development. *Journal of Arid Environments*, **32**, 103–110.

Grace, J. (2001) Carbon cycle. Pp. 609–629 in: *Encyclopedia of Biodiversity.* Academic Press, New York.

Griffen, P.S., Indictor, N. and Koestler, R.J. (1991) The biodeterioration of stone, a review of deterioration mechanisms: conservation case histories and treatment. *International Biodeterioration and Biodegradation*, **28**, 187–207.

Grote, G. and Krumbein, W.E. (1992) Microbial precipitation of manganese by bacteria and fungi from desert rock and rock varnish. *Geomicrobiology Journal*, **10**, 49–57.

Gu, J.D., Ford, T.E., Berke, N.S. and Mitchell, R., (1998) Biodeterioration of concrete by the fungus *Fusarium*. *International Bioterioration and Biodegradation*, **41**, 101–109.

Haider, K., Filip, Z. and Martin, J. P. (1970) Einfluss von montmorillonit auf die buildung von biomass und stoffwechselzwischenproducten durch einige mikroorganismen. *Archives of Microbiology*, **73**, 201–215.

Haigler, S.A. (1969) Boring mechanism of *Polydora westeri* inhabiting *Crassostrea virginica*. *American Zoologist*, **9**, 821–828.

Hammes, F. and Verstraete, W. (2002) Key roles of pH, and calcium metabolism in microbial carbonate precipitation. *Reviews in Environmental Science and Biotechnology*, **1**, 3–7.

Hartman, H. (1998) Photosynthesis and the origin of life. *Origins of Life and Evolution of the Biosphere*, **28**, 515–521.

Heckman, D.S., Geiser, D.M., Eidell, B.R., Stauffer, R.L., Kardos, N.L. and Hedges, S.B. (2001) Molecular evidence for the early colonisation of land by fungi and plants. *Science*, **293**, 1129–1133.

Henderson, M.E.K. and Duff, R.B. (1963) The release of metallic and silicate ions from minerals, rocks and soils by fungal activity. *Journal of Soil Science*, **14**, 236–246.

Hersman, L., Lloyd, T. and Sposito, G. (1995) Siderophore-promoted dissolution of hematite. *Geochimica et Cosmochimica Acta*, **59**, 3327–3330.

Hirsch, P., Eckhardt, F.E.W. and Palmer, R.J. (1995) Fungi active in weathering rock and stone monuments. *Canadian Journal of Botany*, **73**, 1384–1390.

Hochella, M.F. (2002) Sustaining Earth: thoughts on the present and future roles in mineralogy in environmental science. *Mineralogical Magazine*, **66**, 627–652.

Hoffland, E., Giesler, R., Jongmans, T. and van Breemen, N. (2002) Increasing feldspar tunneling by fungi across a north Sweden podzol chronosequence. *Ecosystems*, **5**, 11–22.

Horre, R. and de Hoog, G.S. (1999) Primary cerebral infections by melanized fungi: a review. *Studies in Mycology*, **43**, 176–193.

Howoritz, N.H., Cameron, R.E. and Hubbard, J.S. (1972) Microbiology of the dry valleys of Antarctica: studies in the world's coldest and driest desert have implications for the Mars biological program. *Science*, **176**, 242–245.

Huang, W.H. and Keller, W.D. (1972) Organic acids as agents of chemical weathering of silicate minerals. *Science*, **239**, 149–151.

Inskeep, W.P. and Baham, J. (1983) Adsorption of Cd(II) and Cu(II) by Na-montmorillonite at low surface coverage. *Soil Science Society of America Journal*, **47**, 660–665.

Jacobs, H., Boswell, G.P., Ritz, K., Davidson, F.A. and Gadd, G.M. (2002*a*) Solubilization of calcium phosphate as a consequence of carbon translocation by *Rhizoctonia solani*. *FEMS Microbiology Ecology*, **40**, 65–71.

Jacobs, H., Boswell, G.P., Ritz, K., Davidson, F.A. and Gadd, G.M. (2002*b*) Solubilization of metal phosphates by *Rhizoctonia solani*. *Mycological Research*, **106**, 1468–1479.

Jarosz-Wilkołazka, A. and Gadd, G.M. (2003) Oxalate production by wood-rotting fungi growing in toxic metal-amended medium. *Chemosphere*, **52**, 541–547.

Javor, B., editor (1989) Yeasts and Fungi. Pp. 163–175 in: *Hypersaline Environments: Microbiology and Biogeochemistry*. Springer-Verlag, Berlin.

Johnstone, C.G. and Vestal, J.R. (1993) Biogeochemistry of oxalate in the antarctic cryptoendolithic lichen-dominated community. *Microbial Ecology*, **25**, 305–319.

Jones, D., Wilson, M.J. and McHardy, W.J. (1981) Lichen weathering of rock forming minerals: application of scanning electron microscopy and microprobe analysis. *Journal of Microscopy*, **124**, 95–104.

Jongmans, A.G., Van Breemen, N., Lungstrom, U., Van Hees, P.A.W., Finlay, R.D., Srinivasan, M., Unestam, T., Giesler, R., Melkerud, P.A. and Olsson, M. (1997) Rock-eating fungi. *Nature*, **389**, 682–683.

Kadoshnikov, V.M., Zlobenko, B.P., Zhdanova, N.N. and Redchitz, T.I. (1995) Studies of application of micromycetes and clay composition for decontamination of building materials. Pp. 61–63 in: *Mixed Wastes and Environmental Restoration – Working Towards A Cleaner Environment*, WM'95, Tucson, Arizona, USA.

Kahle, C.F. (1977) Origin of subaerial Holocene calcareous crusts: role of algae, fungi and sparmicristisation. *Sedimentology*, **24**, 413–435.

Kantarcioglu, A.S., Yucel, A. and de Hoog, G.S. (2002) Case report. Isolation of *Cladosporium cladosporioides* from cerebrospinal fluid. *Mycoses*, **45**, 500–503.

Kerr, S. and Zavada, M.S. (1989) The effect of the lichen *Acarospora sinopica* on the elemental composition of three sedimentary rock substrates in South Africa. *The Bryologist*, **92**, 407–410.

Khan, M. and Scullion, J. (2000) Effect of soil on microbial responses to metal contamination. Effect of soil on microbial responses to metal contamination. *Environmental Pollution*, **110**, 115–125.

Kikuchi, Y. and Sreekumari, K.R., (2002) Microbially influenced corrosion and biodeterioration of structural metals. *Journal of the Iron and Steel Institute of Japan*, **88**, 620–628.

Kirschvink, J.L., Gaidos, E.J., Bertani, L.E., Beukes, N.J., Gutzmer, J., Maepa, L.N. and Steinberger, R.E. (2000) Paleoproterozoic snowball Earth: extreme climatic and geochemical global change and its biological consequences. *Proceedings of the National Academy of Sciences of the USA*, **97**, 1400–1405.

Klappa, C.F. (1979*a*) Lichen stromatolites: criterion for subaeial exposure and mechanism for the formation of laminae calcretes (caliches). *Journal of Sedimentary Petrology*, **49**, 387–400.

Klappa, C.F. (1979*b*) Calcified filaments in Quaternary calcretes: organo-mineral interactions in the subaerial vadose environment. *Journal of Sedimentary*

Petrology, **49**, 955–968.

Knorre, Hv. and Krumbein, W.E. (2000) Bacterial calcification. Pp. 25–39 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Kraemer, S.M., Cheah, S.F., Zapf, R., Xu, J.D., Raymond, K.N. and Sposito, G. (1999) Effect of hydroxamate siderophores on Fe release and Pb(II) adsorption by goethite. *Geochimica et Cosmochimica Acta*, **63**, 3003–3008.

Krumbein, W.E. and Giele, C. (1979) Calcification in a coccoid cyanobacterium associated with the formation of desert stromatolites. *Sedimentology*, **26**, 593–604.

Krumbein, W.E., Urzi, C. and Gehrmann, C. (1991) On the biocorrosion and biodeterioration of antique and medieval glass. *Geomicrobiology Journal*, **9**, 139–160.

Krumhansl, J.L., Brady, P.V. and Anderson, H.L. (2001) Reactive barriers for Cs-137 retention. *Journal of Contaminant Hydrology*, **47**, 233–240.

Kukovsky, Ye.G. (1966) *Peculiarities of Structure and Physico-Chemical Properties of Clay Minerals*. Naukova Dumka, Kiev (in Russian).

Kumar, R. and Kumar, A.V. (1999) *Biodeterioration of Stone in Tropical Environments: an Overview.* The J. Paul Getty Trust, USA.

Kurdish, I.K. and Kigel, N.F. (1992) Effect of palygorskyte, a clay mineral, on physiologycal activity and adhesion of methanotrophic bacteria. *Mikrobiologichesky Zhurnal*, **54**, 73–78 (in Russian).

Kurdish, I.K. and Titova, L.V. (2000) Granular preparations of *Azotobacter* containing clay minerals. *Applied Biochemical Microbiology*, **36**, 418–420.

Kutuzova, R.S. (1969) The release of silica from minerals as a result of microbial activity. *Microbiologiya*, **38**, 714–721 (in Russian).

Leboda, R., Chodorowsky, S., Skubiszewska-Zieba, J. and Tarasevich, Y. I. (2001) Effect of the carbonaceous matter deposition on the textural and surface properties of complex carbon-mineral adsorbents prepared on the basis of palygorskite. *Colloids and Surfaces. A – Physicochemical and Engineering Aspects*, **178**, 113–128.

Lee, G.H. and Stotzky, G. (1999) Transformation and survival of donor, recipient, and transformants of *Bacillus subtilis in vitro* and in soil. *Soil Biology and Biochemistry*, **31**, 1499–1508.

Liermann, L.J., Kalinowski, B.E., Brantley, S.L. and Ferry, J.G. (2000) Role of bacterial siderophores in dissolution of hornblende. *Geochimica et Cosmochimica Acta*, **64**, 587–602.

Li, L.Y. and Li, R. S. (2000) The role of clay minerals and the effect of H^+ ions on removal of heavy metal (Pb^{2+}) from contaminated soils. *Canadian Geotechnology Journal*, **37**, 296–307.

Lotareva, O.V. and Prozorov, A.A. (2000) Effect of the clay minerals montmorillonite and kaolinite on the generic transformation of competent *Bacillus subtilis* cells. *Microbiology*, **69**, 571–574.

Lovley, D.R. (1991) Dissimilatory Fe(III) and Mn (IV) reduction. *Microbiological Reviews*, **55**, 259–287.

Lower, S., Hochella, M.F., Jr. and Beveridge, T.J. (2001*a*) Bacterial recognition of mineral surfaces: nanoscale interactions between *Shewanella* and α-FeOOH. *Science*, **292**, 1360–1363.

Lundstrom, U.S., Van Breemen, N. and Bain, D. (2000) The podzolization process. A review. *Geoderma*, **94**, 91–107.

Lunsdorf, H., Erb, R.W., Abraham, W.R., Timmis, K.N. (2000) 'Clay hutches': a novel interaction between bacteria and clay minerals. *Environmental Microbiology*, **2**, 161–168.

Machel, H.G. and Foght, J. (2000) Products and depth limits of microbial activity in petroliferous subsurface settings. Pp. 104–119 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Mandal, S.K., Roy, A. and Banerjee, P.C. (2002) Iron leaching from china clay by fungal strains. *Transactions of the Indian Institute of Metals*, **55**, 1–7.

Manley, E. and Evans, L. (1986) Dissolution of feldspars by low-molecular-weight aliphatic and aromatic acids. *Soil Science*, **141**, 106–112.

Manoli, F., Koutsopoulos, E. and Dalas, E. (1997) Crystallization of calcite on chitin. *Journal of Crystal Growth*, **182**, 116–124.

Marshall, K.C. (1988) Adhesion and growth of bacteria at surfaces in oligotrophic habitats. *Canadian Journal of Microbiology*, **34**, 593–606.

Martens, D.A. and Frankenberger, J.W.T. (1992) Decomposition of bacterial polymers in soil and their influence on soil structure. *Biology and Fertility of Soils*, **13**, 65–73.

Martin, J.P., Filip, Z. and Haider, K. (1976) Effect of montmorillonite and humate on growth and metabolic activity of some actinomycetes. *Soil Biology and Biochemistry*, **8**, 409–413.

Martino, E., Perotto, S., Parsons, R. and Gadd, G.M. (2003) Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biology and Biochemistry*, **35**, 133–141.

Matthes, U., Ryan, B.D. and Larson, D.W. (2000) Community structure of epilithic lichens on the cliffs of the Niagara Escarpment, Ontario, Canada. *Plant Ecology*, **148**, 233–244.

Maurice, P.A., Hochella, M.F., Parks, G.A., Sposito, G. and Schwertmann, U. (1995) Evolution of hematite surface microtopography upon dissolution by simple organic acids. *Clays and Clay Minerals*, **43**, 29–38.

McEldowney, S. and Fletcher, M. (1986) Effect of growth conditions and surface characteristics of aquatic bacteria on their attachment to solid surfaces. *Journal of General Microbiology*, **132**, 513–523.

McMenamin, M. and McMenamin, D. (1994) *Hypersea-life on Land*. Columbia University Press, New York, 343 pp.

Mehta, A.P., Torma, A.E. and Murr, L.E. (1979) Effect of environmental parameters on the efficiency of biodegradation of basalt rock by fungi. *Biotechnology and Bioengineering*, **21**, 875–885.

Money, N.P. (1999) Biophysics: fungus punches its way in. *Nature*, **401**, 332–333.

Money, N.P. (2001) Biomechanics of invasive hyphal growth. Pp. 3–17 in: *The Mycota VIII* (K. Esser, editor). Springer-Verlag, Berlin.

Money, N.P. and Howard, R.J. (1996) Confirmation of a link between fungal pigmentation, turgor pressure, and pathogenicity using a new method of turgor measurement. *Fungal Genetics and Biology*, **20**, 217–227.

Monger, C.H. and Adams, H.P. (1996) Micromorphology of calcite-silica deposits, Yucca Mountain, Nevada. *Soil Science Society of America Journal*, **60**, 519–530.

Morley, G.F. and Gadd, G.M. (1995) Sorption of toxic metals by fungi and clay minerals. *Mycological Research*, **99**, 1429–1438.

Morley, G., Sayer, J., Wilkinson, S., Gharieb, M. and Gadd, G.M. (1996) Fungal sequestration, solubilization and transformation of toxic metals. Pp. 235–256 in: *Fungi and Environmental Change* (J.C. Frankland, N. Magan and G.M. Gadd, editors). Cambridge University Press, Cambridge, UK.

Muller, B., Burgstaller, W., Strasser, H., Zanella, A. and Schinner, F. (1995) Leaching of zinc from an industrial filter dust with *Penicillium*, *Pseudomonas* and *Corynebacterium*: citric acid is the leaching agent rather than amino acids. *Journal of Industrial Microbiology*, **14**, 208–212.

Nealson, K.H. and Saffarini, D. (1994) Iron and manganese in anaerobic respiration: environmental significance, physiology, and regulation. *Annual Reviews in Microbiology*, **48**, 311–343.

Neubauer, U., Nowack, B., Furrer, G. and Schulin, R. (2000) Heavy metal sorption on clay minerals affected by siderophore desferrioxamine B. *Environmental Science and Technology*, **34**, 2749–2755.

Nica, D., Davis, J.L., Kirby, L., Zuo, G. and Roberts, D.J. (2000) Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers. *International Biodeterioration and Biodegradation*, **46**, 61–68.

Nordstrom, D.K. and Southam, G. (1997) Geomicrobiology of sulfide mineral oxidation. Pp. 361–390 in: *Geomicrobiology: Interactions between Microbes and Minerals* (J.F. Banfield and K.H. Nealson, editors). Reviews in Mineralogy, **35**. Mineralogical Society of America, Washington, D.C.

Paris, F., Bonnaud, P., Ranger, J. and Lapeyrie, F. (1995) *In vitro* weathering of phlogopite by ectomycorrhizal fungi. *Plant and Soil*, **177**, 191–201.

Pearson, V.K., Sephton, M.A., Kearsley, A.T., Bland, P.A., Franchi, I.A. and Gilmour, I. (2002) Clay mineral-organic matter relationships in the early solar system. *Meteoritics and Planetary Science*, **37**, 1829–1833.

Pedersen, K. (1999) Subterranean microorganisms and radioactive waste disposal in Sweden. *Engineering Geology*, **52**, 163–176

Pereira, M.O., Vieira, M.J. and Melo, L.F. (2000) The effect of clay particles on the efficacy of a biocide. *Water Science and Technology*, **41**, 61–64.

Perfettini, J.V., Revertegat, E. and Langomazino, N. (1991) Evaluation of cement degradation by the metabolic activities of two fungal strains. *Experientia*, **47**, 527–533.

Pitonzo, B.J., Amy, P.S. and Rudin, M. (1999) Effect of gamma radiation on native endolithic microorganisms from a radioactive waste deposit site. *Radiation Research*, **152**, 64–70

Prieto Lamas, B., Rivas Brea, M.T. and Silva Hermo, B.M. (1995) Colonization by lichens of granite churches in Galicia (northwest Spain). *Science of the Total Environment*, **167**, 343–351.

Porter, T.L., Eastman, M.P., Whitehorse, R., Bain, E. and Manygoats, K. (2000) The interaction of biological molecules with clay minerals: a scanning force microscopy study. *Scanning*, **22**, 1–5.

Puget, P., Angers, D.A. and Chenu, C. (1999) Nature of carbohydrates associated with water-stable aggregates of two cultivated soils. *Soil Biology and Biochemistry*, **31**, 55–63.

Putnis, A. (2002) Mineral replacement reactions: from macroscopic observations to microscopic mechanisms. *Mineralogical Magazine*, **66**, 689–708.

Rawlings, D.E., Dew, D. and du Plessis, C. (2003) Biomineralization of metal-containing ores and concentrates. *Trends in Biotechnology*, **21**, 38–44.

Redman, R.S., Litvintseva, A., Sheehan, K.B., Henson, J.M. and Rodriguez, R. (1999) Fungi from geothermal soils in Yellowstone National Park. *Applied and Environmental Microbiology*, **65**, 5193–5197.

Renaut, R.W. and Jones, B. (2000) Microbial precipitates around continental hot springs. Pp. 187–195 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Riding, R. (2000) Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. *Sedimentology*, **47**, 179–214.

Rikkinen, J. and Poinar, G.O. (2000) A new species of resinicolous *Chaenothecopis (Mycoaliciaceae, Ascomycota)* from 20 million year old Bitterfield amber, with remarks on the biology of resinicolous fungi. *Mycological Research*, **104**, 7–15.

Rikkinen, J. and Poinar, G.O. (2001) Fossilised fungal mycelium from Tertiary Dominican amber. *Mycological Research*, **105**, 890–896.

Rivadeneyra, M.A., Delgado, R., Delgado, G., Del Moral, A., Ferrer, M.R. and Ramos-Cormenzana, A. (1993) Precipitation of carbonates by *Bacillus* sp. isolated from saline soils. *Geomicrobiology Journal*, **11**, 175–184.

Roberts, D.J., Nica, D., Zuo, G. and Davis, J.L. (2002) Quantifying microbially induced deterioration of concrete: initial studies. *International Biodeterioration and Biodegradation*, **49**, 227–234.

Rodriguez Navarro, C., Sebastian, E. and Rodriguez Gallego, M. (1997) An urban model for dolomite precipitation: authigenic dolomite on weathered building stones. *Sedimentary Geology*, **109**, 1–11.

Rogers, J.R., Bennet, P.C. and Choi, W.J. (1998) Feldspars as a source of nutrients for microorganisms. *American Mineralogist*, **83**, 1532–1540.

Rossi, G. (1979) Potassium recovery through leucite bioleaching: possibilities and limitations. Pp. 279–319 in: *Metallurgical Applications of Bacterial Leaching and Related Phenomena* (L.E. Murr, A.E. Torma and J.E. Brierley, editors). Academic Press, New York.

Rossi, G. and Ehrlich, H.L. (1990) Other bioleaching processes. Pp. 149–170 in: *Microbial Mineral Recovery* (H.L. Ehrlich and C.L. Brierley, editors). McGraw-Hill, New York.

Sayer, J.A., Kierans, M. and Gadd, G.M. (1997) Solubilization of some naturally occurring metal-bearing minerals, limescale and lead phosphate by *Aspergillus niger*. *FEMS Microbiology Letters*, **154**, 29–35.

Schlecht-Pietsch, S., Wagner, U. and Anderson, T.H. (1994) Changes in composition of soil polysaccharides and aggregate stability after carbon amendments to different textured soils. *Applied Soil Ecology*, **1**, 145–154.

Schopf, J.W. (1993) Microfossils of the early Archean Apex Chert; new evidence of the antiquity of life. *Science*, **260**, 640–644.

Schwartzman, D.J. and Volk, T. (1989) Biotic enhancement of weathering and the habitability of Earth. *Nature*, **340**, 457–460.

Silverman, M.P. and Munoz, E.F. (1970) Fungal attack on rock: solubilisation and altered infra-red spectra. *Science*, **169**, 985–987.

Skujins, J.J. (1967) Enzymes in soil. Pp. 371–414 in: *Soil Biochemistry* (A.D. McLaren and G.H. Peterson, editors). Marcel Dekker, New York.

Sollas, W.J. (1880) On the action of a lichen on a limestone. *Report, British Association for the Advancement of Science*, 586 pp.

Staley, J.T., Palmer, F. and Adams, J.B. (1982) Microcolonial fungi: common inhabitants on desert rocks. *Science*, **215**, 1093–1095.

Sterflinger, K. (2000) Fungi as geologic agents. *Geomicrobiology Journal*, **17**, 97–124.

Stevenson, F.J. (1994) *Humus Chemistry: Genesis, Composition and Reactions*. John Wiley & Sons, New York.

Stone, A.T. (1997) Reactions of extracellular organic ligands with dissolved metal ions and mineral surface. Pp. 309–341 in: *Geomicrobiology: Interactions between Microbes and Minerals* (J.F. Banfield and K.H. Nealson, editors). Mineralogical Society of America, Washington, D.C.

Stotzky, G. (1966) Influence of clay minerals on microorganisms – II. Effect of various clay species, homoionic clays, and other particles on bacteria. *Canadian Journal of Microbiology*, **12**, 831–848.

Stotzky, G. (2000) Persistence and biological activity in soil of insecticidal proteins from *Bacillus thuringiensis* and of bacterial DNA bound on clays and humic acids. *Journal of Environmental Quality*, **29**, 691–705.

Styriakova, I. and Styriak, I. (2000) Iron removal from kaolins by bacterial leaching. *Ceramics–Silikaty*, **44**, 135–141.

Summer, D.Y. (2000) Microbial vs environmental influences on the morphology of late Archean Fenestrate microbialites. Pp. 307–313 in: *Microbial Sediments* (A.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Taylor, T.N. and White, J.F., Jr. (1989) Fossil fungi (Endogonaceae) from the triassic of Antarctica. *American Journal of Botany*, **76**, 389–396.

Taylor, T.N., Hass, H. and Kerp, H. (1999) The oldest fossil ascomycetes. *Nature*, **399**, 684.

Thompson, J.B. and Ferris, F.G. (1990) Cyanobacterial precipitation of gypsum, calcite and magnesite from natural alkaline lake water. *Geology*, **18**, 995–998.

Timonin, M.I., Illman, W.I. and Hartgerink, T. (1972) Oxidation of manganous salts of manganese by soil fungi. *Canadian Journal of Botany*, **18**, 793–799.

Tisdall, J.M., Smith, S.E. and Rengasamy, P. (1997) Aggregation of soil by fungal hyphae. *Australian Journal of Soil Research*, **35**, 55–60.

Trevors, J.T. (1996) DNA in soil: Adsorption, genetic transformation, molecular evolution and genetic microchip. *Antonie van Leeuwenhoek*, **70** 1–10.

van Bladel, R., Halen, H. and Cloose, P. (1993) Calcium-zinc and calcium-cadmium exchange in suspensions of various types of clays. *Clay Minerals*, **28**, 33–38.

Vaughan, D.J., Pattrick, R.A.D. and Wogelius, R.A. (2002) Minerals, metals and molecules: ore and environmental mineralogy in the new millennium. *Mineralogical Magazine*, **66**, 653–676.

Verrecchia, E.P., Dumont, J.L. and Rolko, K.E. (1990) Do fungi building limestones exist in semi-arid regions? *Naturwissenschaften*, **77**, 584–586.

Verrecchia, E.P. (2000) Fungi and sediments. Pp. 69–75 in: *Microbial Sediments* (R.E. Riding and S.M. Awramik, editors). Springer-Verlag, Berlin.

Vettori, C., Gallori, E. and Stotzky, G. (2000) Clay minerals protect bacteriophage PBS1 of *Bacillus subtilis* against inactivation and loss of trunsducing ability by UV radiation. *Canadian Journal of Microbiology*, **46**, 770–773.

Volesky, B. and Holan, Z. R. (1995) Biosorption of heavy metals. *Biotechnology Progress*, **11**, 235–250.

Voudrias, E.A. (2002) The concept of a sorption chemical barrier for improving effectiveness of landfill liners. *Waste Management and Research*, **20**, 251–258.

Warren, L.A., Maurice, P.A., Parmer, N. and Ferris, F.G. (2001) Microbially mediated calcium carbonate precipitation: implications for interpreting calcite precipitation and for solid-phase capture of inorganic contaminants. *Geomicrobiology Journal*, **18**, 93–115.

Watts, H.J., Very, A.A., Perera, T.H.S., Davies, J.M. and Gow, N.A.R. (1998) Thigmotropism and stretch-activated channels in the pathogenic fungus. *Candida albicans. Microbiology*, **144**, 689–695.

Webley, D.M., Henderson, M.E.F. and Taylor, I.F. (1963) The microbiology of rocks and weathered stones. *Journal of Soil Science*, **14**, 102–112.

Welch, S.A. and Vandevivere, P. (1994) Effect of microbial and other naturally occurring polymers on mineral dissolution. *Geomicrobiology Journal*, **12**, 227–238.

Welch, S.A., Barker, W.W. and Banfield, J.F. (1999) Microbial extracellular polysaccharides and plagioclase dissolution. *Geochimica et Cosmochimica Acta*, **63**, 1405–1419.

Wheeler, M.H. and Bell, A.A. (1987) Melanins and their importance in pathogenic fungi. Pp. 338–385 in: *Current Topics in Medical Mycology* **2** (M.R. McGuiness, editor). Springer-Verlag, New York.

White, I.D., Mottershead, D.N. and Harrison, S.J. (1992) *Environmental Systems: An Introductory Text.* Chapman & Hall, London, UK.

Wild, A. (1993) *Soils and the Environment: an Introduction*. Cambridge University Press, Cambridge, UK.

Wilson, M.J. (1975) Chemical weathering of some primary rock-forming minerals. *Soil Science*, **119**, 349–355.

Winter, D. and Zubay, G. (1995) Binding of adenine-related compounds to the clay montmorillonite and the mineral hydroxyapatite. *Origin of Life and Evolution of the Biosphere*, **25**, 61–81.

Wolfaardt, G.M., Lawrence, J.R., Robarts, R.D., Caldwell, S.J. and Caldwell, D.E. (1994) Multicellular organization in a degradative biofilm community. *Applied and Environmental Microbiology*, **60**, 434–446.

Wollenzien, U., de Hoog, G.S., Krumbein, W.E. and Urzi, C. (1995) On the isolation of microcolonial fungi occurring on and in marble and other calcareous rocks. *Science of the Total Environment*, **167**, 287–294.

Zhdanova, N.N., Vasilevskaya, A.I., Gavrilyuk, V.I., Sholokh, E.L. and Koval, L.A. (1990) Radioactive strontium accumulation by some soil micromycetes in model experiments. *Mycologiya I Fytopatologiya*, **24**, 106–111 (in Russian).

Zhdanova, N.N., Zakharchenko, V.A., Vember, V.V. and Nakonechnaya, L.T. (2000) Fungi from Chernobyl: mycobiota of the inner regions of the containment structures of the damaged nuclear reactor. *Mycological Research*, **104**, 1421–1426.

Zhdanova, N., Fomina, M., Redchitz, T. and Olsson, S. (2001) Chernobyl effects: growth characteristics of soil fungi *Cladosprorium cladosporioides* (Fresen) de Vries with and without positive radiotropism. *Polish Journal of Ecology*, **49**, 309–318.

Zvyagintcev, D.G. (1987) *Soil and Microorganisms*. Moscow University, Moscow, Russia (in Russian).

[*Manuscript received 31 January 2003: revised 16 May 2003*]