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### Geomicrobiology of Eukaryotic Microorganisms

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# Geomicrobiology of Eukaryotic Microorganisms

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Eukaryotic microbes participate in many biogeochemical cycles, although quantifying their role is not easy, and the discussion below comes generally to only qualitative conclusions. Eukaryotes lack a number of the biogeochemically important functions that are carried out only by archaea (e.g., methanogenesis), bacteria (the anammox chemolithotrophic denitrification reaction), or archaea and bacteria (e.g., chemolithotrophy, diazotrophy, and dissimilatory reduction of sulfate). Microbial eukaryotes have one ancestral attribute, phagotrophy, which adds a novel link to food webs and thus modifies biogeochemical cycles, and have endosymbioses as well as ectosymbioses which can recruit metabolism from archaeans (methanogenesis) and bacteria (chemolithotrophic sulfide oxidation, diazotrophy). The ability of eukaryotes to carry out oxidative phosphorylation and the related respiratory carbon metabolism, and photosynthesis, as genetically integrated processes is an outcome of bacterial symbioses. The biogeochemical importance of fungi is significant in several key areas. These include organic and inorganic transformations, nutrient and element cycling, rock and mineral transformations, bioweathering, mycogenic mineral formation, fungal-clay interactions, and metal-fungal interactions. Although such transformations can occur in both aquatic and terrestrial habitats, it is in the terrestrial environment where fungi probably have the greatest influence especially when considering soil, rock and mineral surfaces, and the plant root-soil interface. Of special significance are the mutualistic symbioses, lichens and mycorrhizas. Geochemical transformations that take place can influence plant productivity and the mobility and speciation of toxic elements, and are therefore of considerable socioeconomic relevance. Some fungal transformations have beneficial applications in environmental biotechnology, e.g., in metal and radionuclide leaching, recovery and detoxification, and xenobiotic

and organic pollutant degradation. They may also result in adverse effects when these processes are associated with the degradation of foodstuffs, natural products and building materials, including wood, stone and concrete.

**Keywords** algae, biogeochemical cycles, calcium carbonate, carbon, fungi, geomycology, lichens, metalloids, metals, minerals, mycorrhizas, phagotrophs, phosphorus, protozoa, saprotrophs, silica

## INTRODUCTION

Eukaryotes have a more restricted range of metabolic processes encoded in their genomes that have major biogeochemical consequences than do the Archaea and Bacteria (Falkowski et al. 2008; Madigan et al. 2008). Some of these “deficiencies” are compensated for by symbioses with Archaea and, more usually, Bacteria. The extreme of this compensation is seen in genetic integration into the eukaryote of the respiratory reactions using O<sub>2</sub> as the electron acceptor provided by the proteobacterial mitochondrial ancestor, and of the oxygenic photosynthesis provided by the cyanobacterial plastid ancestor (Mereschowsky 1905; Kowallik and Martin 1999). Such endosymbiosis was facilitated by a unique eukaryotic trait, that of the endomembrane and cytoskeletal system permitting phagotrophy and, more generally, endocytosis and exocytosis and the especially geomicrobiological important possibility of intracellular biomineralization (Cavalier-Smith 1982; Maynard Smith and Szathmáry 1995).

The discussion that follows expands on all these points, encompassing as many eukaryotic microbes and modes of metabolism as possible, and attempting quantitation of the biogeochemical roles of eukaryotic microbes relative to those of Archaea and Bacteria (Falkowski et al. 2008), as well as Metazoa and embryophytic (“higher”) plants. The paper also touches on the intracellular biomineralization and the possibility of using eukaryotic microbes in global bioremediation of anthropogenic environmental change, or biogeoeengineering. There is particular attention paid toward the end of the paper on the role of fungi in

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weathering and decomposition, but also other significant roles of fungi in geomicrobiology.

An important consideration is that the biogeochemical processes brought about by eukaryotic microbes do not necessarily directly contribute to the inclusive fitness of the responsible organisms, but rather are emergent outcomes of natural selection. Examples are some aspects of weathering, and some examples of the extracellular precipitation of particulate minerals that have no obvious skeletal role or modify the external environment in a way that increases fitness. An additional point is that the "obvious" evolutionary function of a given biogeochemical process for the causative organisms has rarely, if ever, been directly shown to increase inclusive fitness, however obvious it may seem that the function is subject to positive selection.

The paper emphasizes the roles of eukaryotic microorganisms relative to the roles of Archaea and Bacteria in the ocean and other water bodies as well as in and on rocks, soils, and man-made structures, making quantitative comparisons wherever possible. However, it is important to acknowledge that there is a poorly characterized habitat, the deep subsurface biosphere, which apparently has a larger volume than that of all the other habitats combined and in which there is no apparent role for eukaryotes. An early synthesis by Gold (1992) suggesting that life occurs down to 6 km in the Earth's crust has been followed by attempts to quantify the biomass, productivity and phylogenetic diversity of the chemolithotrophically-based deep subsurface biosphere (Jørgensen and D'Hondt 2006). Standard microbial culture techniques (Finster et al. 2009) and assembly of a genome from environmental genomic information (Chivian et al. 2007) have been used to characterize two bacteria from this habitat. The energy source for the Archaea and bacteria in the deep biosphere is thought to largely involve H<sub>2</sub> produced by radiolysis of water driven by decay of radionuclides of K, Th and U (Lin et al. 2004). Jørgensen and D'Hondt (2006) point out that metabolic rates of the deep biosphere organisms are very low, on both a cell and a volume of habitat basis.

## PRIMARY PRODUCTIVITY IN RELATION TO THE CARBON CYCLE

### Photosynthesis in Aquatic Habitats

Free-living photosynthetic microbial eukaryotes are major planktonic primary producers in the ocean and many freshwaters, with minor contributions from photosynthetic symbionts in various planktonic rhizaria (Acantharia, Foraminifera, Radiolaria): (Raven 2009a, Raven and Giordano 2009: Table 1). There are also significant free-living photosynthetic eukaryotic microorganisms in benthic habitats (epilithic, epipelagic, epipsammic), as well as in symbiosis with some benthic foraminifera and ciliates in the ocean and ciliates in freshwater, and metazoans in the sea (Porifera, Cnidaria, Trematoda, bivalve Mollusca) and freshwater (Porifera, Cnidaria, bivalve Mollusca) (Usher et al. 2007; Raven and Giordano 2009; Raven et al. 2009). The aquatic

benthic habitat also has photosynthetic macroalgae, sometimes considered with microbes since they are disowned by some plant biologists.

Where do photosynthetic eukaryotic microbes fit qualitatively and quantitatively into the range of organisms with photochemical energy transduction mechanisms, i.e., photosynthetic in the broad sense? There are a number of photosynthetic organisms among the Archaea and Bacteria. The rhodopsin-catalysed photochemical proton and chloride pumps in many Archaea and Bacteria, including one cyanobacterium (and one green alga) is not energetically coupled to photosynthesis in the sense of net autotrophic fixation of carbon dioxide (Raven 2009a,b) (Table 1). The same applies to the bacteriochlorophyll-based photochemistry in aerobic anoxygenic photosynthetic bacteria that are relatively common in the surface ocean, and to some obligately anaerobic photosynthetic bacteria (Raven 2009a).

In these cases the photosynthetic energy conversion functions in an essentially chemoorganotrophic organism to spare the use of respiratory substrates in energizing membrane transport and phosphorylating ADP. Bacteriochlorophyll-based photochemistry brings about autotrophic carbon fixation with sulfide as the major electron donor in many photosynthetic bacteria on a global scale. This anoxygenic, autotrophic carbon dioxide fixation only contributes 0.13% (Raven 2009a)-0.17% (Johnston et al. 2009) to global marine photosynthesis.

The Bacteria that carry out oxygenic photosynthesis are the cyanobacteria, which are also responsible for photosynthesis in eukaryotes via endosymbiotic cyanobacteria that ultimately became genetically integrated into the eukaryotic hosts (Mereschevsky 1905, Martin & Kowalik 1999; see Raven et al. 2009 for a recent review). At least one cyanobacterium, and a green alga, have a rhodopsin-based energy transduction system, of unknown function(s), in addition to chlorophyll-based photosynthetic systems, and an as yet un-named diazotrophic marine cyanobacterium, lacking photoreaction II and autotrophic carbon dioxide fixation, seems to function bioenergetically as do the aerobic anoxygenic photosynthetic bacteria (Raven 2009b). Some cyanobacteria with a functional photoreaction II can replace water as photosynthetic electron donor with sulfide, although if they operate in this mode in today's ocean they are constrained by sulfide availability to be part of the total biological sulfide oxidation of not more than 0.17% of global marine primary productivity (Johnston et al. 2009; Raven 2009a). The eukaryotic oxygen-evolvers do not seem to be able to replace water by sulfide as electron donor.

Granted that at least 99.93% of marine primary productivity of at least 50 Pg carbon per year (Field et al. 1998; del Giorgio and Williams 2005; Raven 2009a) is carried out by oxygenic photosynthesis, what is the quantitative importance of cyanobacteria and of eukaryotic microbial organisms? Estimates of marine benthic photosynthetic primary productivity, with most contributed by free-living and symbiotic algae, some by cyanobacteria (stromatolites, sponge symbioses) and some by seagrasses, range from < 1% to about 5% and most probably

TABLE 1  
Processes of biogeochemical significance carried out by microbial eukaryotes compared to Archaea and Bacteria

Process, Function	Genetically integrated process in eukaryotes	Means of acquisition by eukaryotes	Example of occurrence in microbial eukaryotes	References
Phagotrophy, Exocytosis	E	Evolved in earliest eukaryote	Endomembranes universal; phagotrophy at cell level common	Raven et al. (2009)
O <sub>2</sub> -linked respiration in mitochondria	A, B, E	Endosymbiosis of proteobacterium followed by genetic integration	Very widespread; mitochondria (sometimes as hydrogenosomes) universal	Raven et al. (2009)
Denitrification involving nitrate and nitrite reduction in mitochondria	A, B, E	With mitochondria	Relatively widespread among chemooorganotrophs	Finlay et al. (1983), Finlay (1985), Teitens et al. (2002)
Ammonium fermentation	B, E	?	Some fungi	Zhou et al. (2002)
converting nitrate and nitrite to ammonium (= Ammonification)				
Anammox	B	None known	None known	Raven (2009a)
chemolithotrophic denitrification				
Nitrification	A, B, E	?	Some fungi; not coupled to chemolithotrophy	Laughlin et al. (2008)
Nitrogen fixation	A, B	Symbiosis with diazotrophic bacteria (always cyanobacteria in eukaryotic microbes); not genetically integrated	Some diatoms; cyanolichens, tripartite lichens, <i>Geosiphon</i>	Usher et al. (2007), Wouters et al. (2009)
Sulfide oxidation by quinone in mitochondria	A, B, E	With mitochondria	Relatively widespread; coupled to energy conservation but not permitting chemolithotrophic growth	Tielens et al. (2002), Theissen et al. (2003)
Sulfide oxidation allowing chemolithotrophy	A, B	(Ecto)symbiosis of sulfide-oxidizing chemolithotrophic bacteria	Some ciliates	Finlay et al. (1991), Ott et al. (2005), Roy et al. (2009)
Reduction of sulphur as terminal electron acceptor in respiration	B	?	Some fungi	Abe et al. (2007)
Dissimilatory reduction of sulfate	A, B	None known	None known	Raven (2009a)

(Continued on next page)

TABLE 1  
Processes of biogeochemical significance carried out by microbial eukaryotes compared to Archaea and Bacteria (*Continued*)

Process, Function	Genetically integrated process in eukaryotes	Means of acquisition by eukaryotes	Example of occurrence in microbial eukaryotes	References
Oxygenic photosynthesis	B, E	Endosymbiosis of a cyanobacterium followed by genetic integration, once with a euglyphid amoeba and an $\alpha$ -cyanobacterium to produce <i>Paulinella</i> , once of a $\beta$ -cyanobacterium with another host to yield all other oxygenic eukaryotes	<i>Paulinella</i> . Glaucocystophyte, rhodophyte and chlorophyte (hence Embryophyta) algae from primary endosymbiosis; secondary and tertiary end-symbioses of photosynthetic eukaryotes gave spread genetically integrated photosynthesis to chlorarachniophytes, euglenoids, alveolates, chromistans. Also kleptoplastids and symbioses with cyanobacteria and eukaryotic phototrophs that are not genetically integrated	Raven (2009a,b), Raven et al. (2009)
Ion-pumping rhodopsin	A, B, E.	From plastid ancestor (known from a cyanobacterium)?	<i>Acetabularia</i> (marine green alga) only; sensory rhodopsins widespread	Raven (2009a)
Methanogenesis	A	Symbiosis with methanogenic archaean; never genetically integrated	Some ciliates from anoxic habitats	Irbitis and Ushida (2002)
Synthesis of phenyl-propanoids such as lignin	B, E	Vertical transmission to many eukaryotes, probably excluding Plantae (Archaeoplastida) where horizontal gene transfer occurred	Fungi (not able to make lignin). Plantae by horizontal transfer of the phenylalanine ammonia-lyase gene from a fungus (or a proteobacterium)	Emiliani et al. (2009); Mantore et al. (2009)
Ligninolysis	E	?	Dikaryotic fungi, free-living or in symbiosis with metazoa	Boddy et al. (2008)
Calcification	B, E	Extracellular deposition by cyanobacteria, some eukaryotes; intracellular in endomembrane system of some eukaryotes, usually with exocytosis of the calcified product	Extracellular in some rhodophyte, chlorophyte and phaeophyceean algae, some foraminifera and amoebozoans; intracellular with exocytosis in coccolithophores, some foraminifera	Raven and Giordano (2009)
Silicification	E	Intracellular in endomembrane system, usually with exocytosis of the silicified product	Chlorophyte algae, radiolarians, diatoms and several other ochristan classes	Raven and Waite (2004), Raven and Giordano (2009)

In column 2, A = Archaea, B = Bacteria, E = Eukarya.

1–2%, of the total marine primary productivity of > 50 Pg carbon per year (Charpy-Roubard & Sournia 1990; Field et al. 1998; del Giorgio and Williams 2005; Raven 2009a) (Table 2). For the phytoplankton which account for the rest of marine primary productivity, cyanobacteria in the ocean may dominate the large oligotrophic regions, but smaller but more productive areas are dominated by eukaryotes, and eukaryotes account for about half of the total marine planktonic net primary productivity (Field et al. 1998; Falkowski and Raven 2007; Raven 2009a) (Table 2).

Regardless of the phylogenetic attribution of phytoplankton, their primary productivity can be significantly limited by the availability of photosynthetically active radiation. A vertically well-mixed upper mixed layer can carry phytoplankton cells through a vertical cycle over many metres or tens of metres several times a day (Falkowski and Raven 2007). The extent of vertical attenuation of photosynthetically active radiation (PAR) means the cells could travel through an order of magnitude or more of PAR in each cycle, and the time scale of each cycle can be an order of magnitude greater than the rate at which acclimation (changes to the proteome and metabolome following changes in the transcriptome) to a given PAR can be completed. This temporal mismatch means that the acclimation state of the photosynthetic apparatus cannot track the changes in PAR but represents a compromise acclimation state which is not fully understood. In less well-mixed upper mixed layers there is the possibility that at least picophytoplankton cells (very slow sinking even if denser than surrounding water), larger but neutrally buoyant phytoplankton cells, and cells motile by flagellar activity, can occur at a relatively fixed depth and hence a more constant PAR and the possibility of greater acclimation. A special case is that of the Deep Chlorophyll Maximum in stratified waters or at the base of the upper mixed layer in the thermocline in waters with a more vigorously mixed upper layer where eddy diffusion of nutrients supplies N, P and Fe, albeit to cells growing at low photon flux densities (see Cockell et al. 2009).

### Primary Productivity on Land

On land, microbial eukaryotes, both free-living and (predominantly) symbiotic, are globally minor players in CO<sub>2</sub> fixation though, as is pointed out elsewhere in this paper, lichens dominate some 6% of the vegetated land surface. It is unlikely that the primary productivity per unit area of the lichen-dominated area is as high as that of the embryophyte-dominated land area; a figure of one-third the area-based annual primary productivity is probably a high estimate (Welgolaski 1975; Raven 1996) (Table 2). Free-living cyanobacteria are also significant in arid regions, and their global biomass is about 40% of that of marine cyanobacteria and over 20 times that of the cyanobacteria in inland waters (Garcia-Pichel et al. 2003).

The lower productivity of lichens, free-living cyanobacteria and bryophytes per unit habitat area than that of vascular plants does not imply that the “lower plants” are less well adapted to life on land; if vascular plants could fill the niches which the

“lower plants” occupy then presumably they would be there. For habitats that are subject to, for example, great temperature extremes and restricted and/or episodic water supply such as being restricted to dew for an hour after dawn, the dominant phototrophs are generally those at the desiccation tolerant end of the range of tolerance of water loss from vegetative cells, and the poikilohydric end of the capacity to control water loss to the atmosphere (Proctor and Tuba 2002).

### Chemoorganotrophs

Non-photosynthetic microbial eukaryotes in the ocean and freshwaters are generally phagotrophs or saprotrophs; some are parasites. For the saprotrophs, there exist metagenomic data for a substantial diversity of fungi in the ocean (Gao et al. 2009), but eukaryotes are not the dominant microbial saprotrophs in the ocean. Microbial phagotrophs are important in the microbial loop (Azam et al. 1983), in which they are the phagotrophs which graze on picoplanktonic and the smaller nanoplanktonic organisms. The organisms that microbial phagotrophs consume are some primary producers (picoplanktonic cyanobacteria, picoplanktonic and smaller nanoplanktonic eukaryotic algae), as well as saprotrophs (largely unicellular Bacteria with Archaea and a few eukaryotes) and the smaller flagellate and ciliate phagotrophs (Azam et al. 1983, Fuhrman 1999).

The dissolved organic matter consumed by the saprotrophs, which are consumed by the microbial phagotrophs, comes from dissolved organic compounds excreted or secreted by all the other marine organisms (Azam et al. 1983; Fuhrman 1999). Fuhrman (1999) emphasizes the importance of viral lysis in providing dissolved organic matter, thus promoting the microbial loop at the expense of the direct grazing of the larger phytoplankton by metazoan zooplankton. In quantitative terms, Fuhrman (1983) suggests that about half of primary productivity passes through microbial phagotrophs in today’s virus-rich ocean, while in the absence of viruses this would fall to just under 40% (Table 2). A similar pattern probably occurs in many inland waters.

It is important to remember that phagotrophy is a purely eukaryotic attribute, with no true equivalent among Archaea or Bacteria, and, among the microbial eukaryotes, involves endocytosis, with the exception of protist- and nematode-trapping fungi that use extracellular digestion. There has been significant recent attention paid to the category of mixotrophic microbial eukaryotes that combine phototrophy and phagotrophy (reviewed by Raven et al. 2009).

On land, soil-dwelling free-living fungi are very significant saprotrophic decomposers in soil, and some basidiomycetous and a few ascomycetous fungi are the sole significant means (Luo et al. 2005; Boddy et al. 2008) other than fire (Glasspool et al. 2004, 2006) of decomposing lignin. Mutualistic symbiotic fungi occur as lichens and mycorrhizas with relatively limited ligninolytic capacities, as well as lignin-digesting fungi in termites and other wood-digesting fungi (Geib et al. 2008; Smith and Read 2008). The mycorrhizal symbioses account for

TABLE 2  
Contribution of microbial eukaryotes to global biogeochemical cycles

Process	Global Flux	Contribution of eukaryotic microbes	References
Photosynthetic primary productivity in the ocean	$\geq 4.2$ Pmol C per year	About half	Field et al. (1998); Del Giorgio and Williams (2005); Raven (2009a)
Recycling of organic C to CO <sub>2</sub> by phagotrophic microbes and the smallest metazoan phagotrophs in the microbial loop in the ocean	$\sim 1.6$ Pmol C per year ( $\sim 2.1$ Pmol C per year in a hypothetical virus-free ocean)	Almost all by phagotrophic microbes	Fuhrman (1999)
Combined nitrogen assimilation by marine primary producers	$\geq 0.63$ Pmol N per year (from Redfield Ratio of 106C:16N:1P by atoms)	About half	Field et al. (1998); Del Giorgio and Williams (2005); Falkowski and Raven (2007); Raven (2009a)
Phosphate assimilation by marine primary producers	$\geq 0.039$ Pmol P per year (from Redfield Ratio of 106C:16N:1P by atoms)	About half	Field et al. (1998); Del Giorgio and Williams (2005); Falkowski and Raven (2007); Raven (2009a)
Photosynthetic primary production on land	$\sim 5$ Pmol C per year	About 1% of green algal lichens mean productivity for all lichens is 33% of that by embryophytes. Mycorrhizas important in uptake of N and P (and other elements) needed for growth	Welgolaski (1975); Raven (1995); Field et al. (1998)
Combined nitrogen assimilation by terrestrial primary producers	$\leq 0.44$ Pmol N per year, from elemental composition of flowering plant shoots, allowing for lower N content of roots and woody plants.	At least half of uptake is by mycorrhizas of embryophytes.	Raven et al. (1992); Broadley et al. (2004); Lambers et al. (2008); Smith and Read (2008)
Phosphate assimilation by terrestrial primary producers	$\leq 0.034$ Pmol P per year, from elemental composition of terrestrial flowering plant shoots, allowing for lower P content in roots and woody plants.	At least half of uptake is by mycorrhizas of embryophytes.	Raven et al. (1992); Broadley et al. (2004); Lambers et al. (2008); Smith and Read (2008)

<p>Calcium and carbonate alkalinity from weathering of carbonate and silicate rocks on land, and calcium and carbonate alkalinity removal from the ocean by sedimentation of biogenic calcium carbonate</p>	<p>~0.023 Pmol CaCO<sub>3</sub> equivalent from terrestrial weathering, and a similar amount sedimented in the ocean in the steady state. These net fluxes do not include recycling of biogenic CaCO<sub>3</sub> in soil, inland waters and the ocean. In the ocean gross biogenic CaCO<sub>3</sub> production is 0.092 Pmol per year, or 4 times the net accumulation in the sediment.</p>	<p>Substantial role of symbiotic fungi in the biological component of weathering. Almost all calcium carbonate deposition in the ocean is biogenic calcium carbonate produced by planktonic coccolithophores and foraminifera</p>	<p>Berner and Berner (1996), Feely et al. (2004), Langer (2008), ignoring minor inputs to, and outputs from, the ocean</p>
<p>Silicic acid from weathering of silicate rocks on land, and silicic acid removal from the ocean by sedimentation of biogenic silica</p>	<p>~0.005 Pmol Si from terrestrial weathering, and a similar amount sedimented in the ocean in the steady state. These net fluxes do not include recycling of biogenic silica in soil, inland waters and the ocean. In the ocean where gross biogenic silica production is 0.167 Pmol per year, or 30 times the net accumulation in sediments.</p>	<p>Substantial role for symbiotic fungi in the biological component of weathering. Almost all silica deposition in the ocean is biogenic silica produced by diatoms and radiolarians</p>	<p>Tréguer et al. (1995), Berner and Berner (1996), DeMaster (2002) ignoring minor non-biologically mediated inputs to, and outputs from, the ocean</p>

much of the combined N and the P uptake by embryophytic plants on land (Table 2), of a similar global magnitude as the uptake of combined N and of P by microbial eukaryotic phototrophs in the ocean (Table 2). Fossil evidence of the occurrence of the dikaryotic fungi, and thus decomposition of by them of organic matter, go back with certainty as ascomycetes to the Lower Devonian and as basidiomycetes, the major wood-decomposers today, to the Carboniferous (Taylor et al. 2009). However, there is evidence of wildfire consuming biomass back to the Upper Silurian (Glasspool et al. 2004, 2006). The timing of the origin of burning depends on the oxygen content of the atmosphere as well as the composition and biomass of vegetation. Fungi are thus important as mycorrhizas of early (Berbee and Taylor 2007; Strullu-Derrien & Strullu 2007; Smith and Read 2008) and later (Strullu-Derrien and Strullu 2007; Smith and Read 2008; Hibbett and Methaney 2009) stages of the colonization of land by embryophytes, and in the biological decomposition of lignin.

In addition to their important roles in terrestrial ecology, evidence exists that fungi are a source of phenylalanine ammonia-lyase (PAL) as a result of horizontal gene transfer. PAL catalyzes a key reaction in the beginning of the phenylpropanoid pathway to lignin and to many compounds that act in defence against biophages in embryophytic plants (Emiliani et al. 2009). There are, however, other possible sources of the PAL in embryophytes, such as horizontal gene transfer from proteobacteria, or retention of the PAL found in the ancestral eukaryote in embryophytes and lost in the rest of the Kingdom Plantae (Emiliani et al. 2009). If the hypothesis of horizontal gene transfer from fungi is correct, the donor could be essentially any fungus, possibly a glomeromycete of the kind that form mutualistic symbioses with most extant embryophyte species; fossils showing the symbiosis are known from the Lower Devonian onwards (Berbee and Taylor 2007; Strullu-Derrien and Strullu 2007; Smith and Read 2008; Strullu-Derrien et al. 2009). The evolutionary picture is further complicated by the finding of lignin (or a very lignin-like compound) in a red seaweed (Martone et al. 2009).

Parasitic (symbiotic in the broad sense) fungi are more diverse and significant in plant hosts than in animals. "Symbiosis in the broad sense" includes mutualistic (symbiosis in the narrow sense) and also antagonistic (parasitic) intimate, long-term associations between different species, i.e., Anton de Bary's "living together of differently named organisms". Kirk et al. (2001) cite suggestions that the majority of fungi are associated with plants and that there is at least one species of fungus associated with each species of vascular plant of which there are about 282,000 described species (Mabberley 2006), although Kirk et al. (2001) have only about 80,000 described species of fungi. Not all of these plant-associated fungi are parasites or pathogens: there are also commensals and mutualists. As a whole, these comprise the plant-symbiotic fungi in the broad sense. Kirk et al. (2001), like others, do not cite global numbers of described species of fungi symbiotic with vascular plants. By comparison, there are 750 described species of entomoge-

nous (insect-associated) fungi (Kirk et al. 2001), again including commensals and mutualists as well as parasites, associated with insects and other arthropods, with just over a million described species of arthropod (Orme et al. 2002) and estimates of about 3.6 million (Novotny et al. 2002). In all cases, these fungi depend on nutrients derived directly from plant photosynthate or from arthropods dependent on plants. Thus, the symbiotic fungi recycle the organic carbon they consume to CO<sub>2</sub> without the intervention of grazers or separate decomposers, including a large number of fungi, in the food chain.

Phagotrophic eukaryotic microbes are also significant in freshwaters, as mentioned above under marine phagotrophy, and in the soil. The microbial loop in soil was considered by Coleman (1994), who pointed out that, relative to their bacterial or fungal food sources, the protozoan microbial phagotrophs (and very small nematodes) have a very low biomass and a very rapid turnover, as with larger phagotrophs and decomposers, releasing CO<sub>2</sub> and other plant nutrients in producing their own biomass. Bonkowski (2004) considers the effects of soil protozoa on plant growth in the context of a microbial loop, with the grazing of rhizosphere bacteria as a link to root development and hence root architecture. However, there are data that are not in accord with this mechanism of interaction between protozoa and plant roots (Ekeleund et al. 2009). Regardless of the mechanism, there are very significant effects of soil protozoa on root architecture, and hence on the various biogeochemical influences of roots (reviewed by Raven and Edwards 2001). Phagotrophic protozoa also occur in metazoan guts, where some have methanogenic archaean endosymbionts (Irbis and Ushida 2002) (Table 1).

### Nitrogen Cycle

There are no diazotrophic eukaryotic microbes; diazotrophic symbioses with cyanobacteria occur in a few marine and freshwater diatoms, in cyano-lichens and in cyanobacteria-containing cephalodia in tripartite lichens (Usher et al. 2007; Wouters et al. 2009). Photosynthesis by the cyanobionts is only significant in the cyano-lichens, i.e. symbioses with cyanobacteria as the sole phototrophs. In the other diazotrophic symbioses the photosynthetic eukaryote supplies organic carbon to the chemoorganotrophic or photoorganotrophic cyanobiont (Table 1). Growth of the diazotrophic marine cyanobacterium *Trichodesmium* in natural conditions can be limited by iron, co-limited by iron and phosphate, or phosphate and light (Raven et al. 2005b); it is possible that these limitations could apply to the symbioses involving diazotrophic cyanobacteria. The need for additional iron, PAR and, possibly, phosphate in diazotrophy could be part of the explanation of why primary production is restricted by the availability of combined nitrogen in many parts of the ocean as well as in some inland waters (Maberly et al. 2002; Raven et al. 2005; Falkowski and Raven 2007). This may also apply on land where the age of soil, which affects the availability of combined nitrogen rather than phosphorus, is a significant determinant in plant growth limitation (Lambers et al. 2008).

Anthropogenic emissions of CO<sub>2</sub> may increase the C:N ratio in organisms, with implications for food quality for use at other trophic levels. Finkel et al. (2010) considered changed elemental stoichiometry with respect to phytoplankton.

Photosynthetic and saprotrophic eukaryotic microbes assimilate “combined nitrogen”, i.e. biologically available inorganic or organic low molecular mass organic nitrogen other than N<sub>2</sub>. In the ocean the total annual assimilation of combined nitrogen by eukaryotic microbial photolithotrophs is of a similar magnitude as the combined nitrogen assimilation involving mycorrhizas of embryophytes on land (Table 2).

The ability to use recalcitrant high molecular mass N compounds in the environment is a significant aspect of the metabolism of some fungi, including a number of some mycorrhizal symbionts (Smith & Read 2008). Phagotrophic eukaryotic microbes excrete ammonium and low molecular mass organic nitrogen, since the organisms they consume have C:N ratios lower than  $(C(\text{organism}) + C(\text{respiration})):N(\text{organism})$ , where  $C(\text{organism})$  is the C per cell in the phagotroph,  $C(\text{respiration})$  is the C lost in growth and maintenance in generating a cell of the phagotroph and  $N(\text{organism})$  is the N per cell in the phagotroph. Similar considerations apply to extracellular digestion of some substrates by saprotrophs. Phagotrophic mixotrophic eukaryotes have frequently been shown to use phagotrophy merely as a means to acquire N, P and Fe rather than organic C (Raven 1997, Raven et al. 2009). Some soil fungi carry out non-chemolithotrophic nitrification when there is an excess of reduced combined nitrogen (Laughlin et al. 2008) (Table 1).

A number of non-photosynthetic eukaryotic microbes can carry out denitrification via dissimilatory nitrate and/or nitrite reduction, i.e. using organic substrates under hypoxic or anoxic conditions in the reduction of nitrate and nitrite to N<sub>2</sub>O or N<sub>2</sub>. This reduction occurs in the mitochondria (Finlay et al. 1983; Finlay 1985; Tielens et al. 2002; Risgaard-Petersen et al. 2006; Ma et al. 2008; Sutka et al. 2008) (Table 1). Nitrite reduction involves the copper-containing nitrite reductase *NirK* which has been found in a number of eukaryotic microorganisms. This enzyme could have been a component of the “promitochondrion”, i.e. acquired by the host cell with the proteobacterial endosymbiont with subsequent loss from many clades of eukaryotes (Kim et al. 2009). Some fungi can perform ammonia fermentation or ammonification, converting nitrate or nitrite to ammonium, under anoxic conditions (Zhou et al. 2002). There are no known cases of eukaryotes carrying out the anammox reaction, i.e. exergonic conversion by some chemolithotrophic bacteria of one mole ammonium and one mole nitrite to one mole of N<sub>2</sub> and two moles of H<sub>2</sub>O under hypoxic or anoxic conditions (see Raven 2009a) (Table 1).

### Phosphorus Cycle

Eukaryotic microbial phototrophs and saprotrophic chemoorganotrophs assimilate inorganic and organic (via extracellular esterases) phosphate (Raven et al. 2005; Raven 2008). Cyanobacteria, but not eukaryotic algae, are known to also use phosphonates (Dyhrman et al. 2009) (Table 1).

Phosphate is a limiting nutrient in parts of the ocean and in some inland waters (Maberly et al. 2002; Raven et al. 2005b; Falkowski and Raven 2007). As for combined nitrogen, the extent of assimilation of phosphorus by marine primary producers exceeds that of primary producers on land, since the marine carbon-based primary productivity is at least as great as that on land and the mean carbon:phosphorus ratio in primary producers is lower in the ocean (Raven 2005a). Again as for nitrogen, the fact that there is a much greater contribution of cyanobacteria to marine than to terrestrial primary production on a carbon basis means that there is not necessarily more phosphorus assimilation by marine eukaryotic algal marine primary producers than by terrestrial macrophyte primary producers, the latter mainly involving mycorrhizas (Table 2). On land, leaching of phosphate over time means that in older soils the supply of phosphorus rather than of combined nitrogen restricts the growth rate of plants (Lambers et al. 2008).

Two stoichiometric considerations are relevant to the phosphorus content of microbial eukaryotes. One is that anthropogenic emissions of CO<sub>2</sub> to the atmosphere, and hence to the ocean, may increase the C:P ratio in at least some photosynthetic organisms, with implications for food quality for other trophic levels: this is considered for marine phytoplankton by Finkel et al. (2010). The other stoichiometric consideration is that there are observations showing that, for some organisms including non-photosynthetic eukaryotic microbes, slower growth means a lower content of rRNA and, since rRNA is a major P-containing component in many organisms, lower P content.

This applies to variation of growth rates of cultures of a single genotype, as well as to variations in growth rate among closely related organisms, as a function resource supply, including the supply of phosphorus. It has been formalized as the Growth Rate Hypothesis (Stern and Elser 2002), which is related to P as an element which, on the basis of geochemistry, limits global productivity. However, the hypothesis only applies to about half of the microalgae for which data are available (Flynn et al. 2010; cf. Nicklisch and Steinberg 2009).

Polyphosphates produced by diatoms are important in the sedimentary phosphorus cycle in the ocean. Polyphosphates are important phosphorus storage products in most eukaryotic microbes examined (Raven and Knoll 2010, this issue). Phagotrophs produce inorganic phosphate as by-products of growth and maintenance after consumption of organisms with C:P ratios lower than  $(C(\text{organism}) + C(\text{respiration})):P(\text{organism})$ , where  $C(\text{organism})$  is the C per cell of the phagotroph,  $C(\text{respiration})$  is the C lost in growth and maintenance respiration in generating a cell of the phagotroph and  $P(\text{organism})$  is the P per cell in the phagotroph. The same could be true in the extracellular digestion of some substrates by saprotrophs.

### Sulfur Cycle

Eukaryotic microbial phototrophs and saprotrophic chemoorganotrophs typically use sulfate as their S source, although many can also use organic S. There are no known

eukaryotic analogues of the absence of a capacity to use sulfate in the SAR11 clade (e.g., *Pelagibacter ubique*) of saprotrophic bacteria, the most abundant (as number of cells) organisms in the world. A major reduced S source is dimethylsulfoniopropionate (DMSP) produced, mainly, by eukaryotic microorganisms (Tripp et al. 2008). The reduced sulfur-oxidizing chemolithotrophic bacterium *Thiobacillus intermedius* can be grown chemoorganotrophically with glucose as the C-source provided the requirement for S in organic components of the cells is met by reduced S compounds (Smith and Rittenberg 1974).

Photosynthetic eukaryotic microbes assimilate sulfate into organic sulfur in proteins, glutathione, metallothioneins, phytochelatins, sulfolipids. Marine haptophytes and dinophytes (and, to a lesser extent, some other taxa extent) are the only producers of the compatible solute and cryoprotectant dimethylsulfoniopropionate (DMSP) which can attain concentrations inside cells of up to half of the osmotic equivalent of seawater. DMSP is broken down in the ocean to acrylic acid and the volatile dimethylsulfide (DMS), which can escape to the atmosphere and be oxidized to  $\text{SO}_2$  and then  $\text{SO}_3$  which hydrates to  $\text{H}_2\text{SO}_4$  (Giordano et al. 2008). Sulfuric acid forms cloud condensation nuclei which could lead to changes in the geographical distribution of clouds and of precipitation, and so have impacts on weathering on land, as proposed in the CLAW hypothesis (Charleson et al. 1987).

There is a minor effect of this cycling of S through the atmosphere on the spatial distribution of pH and of alkalinity in the surface ocean. Making the simplifying assumption that the surface ocean—lower atmosphere system equilibrates rapidly with respect to  $\text{CO}_2$ , the production of a mole of DMSP from five mole  $\text{CO}_2$  and one mole of  $\text{SO}_4^{2-}$  generates two moles  $\text{OH}^-$  in the medium, with a corresponding increase in pH. Conversion of one mole DMSP to one mole DMS, lost to the atmosphere, and one mole of non-volatile acrylic acid retained in the surface ocean does not alter the acid-base stoichiometry of the ocean. Inorganic oxidation of DMS to  $\text{H}_2\text{SO}_4$  in the atmosphere—suspended water droplet system generated two  $\text{H}^+$  per mole DMS, which reach the surface ocean in rain. This cycle constitutes an atmospheric pathway for the transfer of acidity between parts of the surface ocean (Raven 1996). The quantitative significance of this transfer needs consideration in relation to other acidifying processes, i.e., anthropogenic inputs of  $\text{NO}_x$  and  $\text{SO}_x$  (Doney et al. 2007) and anthropogenic inputs of  $\text{CO}_2$  (Doney et al. 2009).

For the calcifying haptophytes, i.e., the coccolithophores, and the less common calcified, thyracosphaeroid dinophytes, the acidification caused by varying degrees of calcification partly offsets, or reverses, the alkalization of the medium caused by the assimilation of nitrate and sulfate, including the sulfate used to produce DMSP. The oxidation of DMS in the atmosphere ultimately yields  $\text{H}_2\text{SO}_4$ , which forms cloud condensation nuclei and hence has plausible effects on the geographical distribution of precipitation, with implications for weathering on land. Al-

though the CLAW hypothesis does not explain as much as was originally proposed, the basic idea seems qualitatively possible.

The acidification of atmospheric water droplets by the oxidation products of DMS might help to solubilize iron from aeolian dust particles that may make iron more available to phototrophic and saprotrophic organisms in the surface ocean after rain-out. However, it seems that anthropogenic  $\text{SO}_2$  inputs to the atmosphere are more important in solubilizing aeolian iron (Boyd et al. 2008; Mackie et al. 2008; Mahowald et al. 2009). DMS which remains in the surface ocean can, as DMS or DMSO, act as S source for saprotrophs, including those (with no known examples among eukaryotic microbes) that cannot use sulfate (Tripp et al. 2008).

Some microbial eukaryotes can oxidize sulfide in their mitochondria with oxygen as terminal electron acceptor, with energy conservation resulting from a proton gradient, which can be used in energizing solute transport or ADP phosphorylation (Teilens et al. 2002; Theissen et al. 2003). Sulfide oxidation in eukaryotic microbes is presumably coupled to energy conservation, although sulfide oxidation by mitochondria of eukaryotic microbes is not known to result in chemolithotrophic growth (Table 1). Some ciliates have (ecto-)symbiotic sulfide-oxidizing chemolithotrophic bacteria (Finlay et al. 1991; Ott et al. 2005; Roy et al. 2009) (Table 1). The fungus *Fusarium oxysporum* can, in culture, reduce elemental sulfur to sulfide (Abe et al. 2009), possibly related to energy conservation during organic matter oxidation in hypoxic or anoxic conditions, but dissimilatory sulfate reduction has not been reported for eukaryotes (Table 1).

### Iron Cycle

In oxygenated environments the essential element iron occurs as oxidized Fe(III) which is insoluble unless it is complexed with appropriate organic compounds. Soluble Fe(III) can be obtained from inorganic and organic colloids and particles by siderophores, Fe(III)-chelating organic compounds secreted by many bacteria (including cyanobacteria: Hunter and Boyd 2007) and many fungi, as well as by grasses (Raven et al. 2005b). The Fe(III)-siderophore complexes can be taken up, and used as an Fe source, by organisms other than those secreting the siderophores, as well as by the siderophore-secreters.

Saprotrophs and phototrophs that do not secrete siderophores obtain iron by reduction and acidification at the cell surface, converting Fe(III) to Fe(II) that is taken up before it has been re-oxidized (Raven et al. 2005b). Phagotrophs, including phagotrophs, can obtain iron from their particulate microbial food as well as from colloidal iron (Raven et al. 2005b, 2009; Raven and Knoll, 2010, this issue). Iron limits marine primary productivity in several parts of the surface ocean, by limiting  $\text{N}_2$  fixation by free living cyanobacteria and (presumably) cyanobacteria symbiotic with diatoms and, in the 'high nutrient (= nitrate, phosphate)—low chlorophyll (proxy for photosynthetic biomass)' areas, by limiting assimilation of combined nitrogen and phosphorus, the main beneficiaries of iron inputs

being diatoms (Raven et al. 2005b; Cullen and Boyd 2008; Watson et al. 2008). These iron enrichment experiments are considered again under “Biogeoengineering (Biogeo remediation)” The involvement of aeolian dust in providing iron to the distant, iron-deficient ocean has already been mentioned above under “Sulfur”. The advection of ocean waters is again being considered as a significant source of iron to some regions of the ocean (Ellwood et al. 2008).

### Halogen Cycles

The volatile organochlorine, organobromine and organoiodine compounds in the atmosphere have natural and anthropogenic sources. Although some of these compounds are purely anthropogenic (e.g., chlorofluorocarbons), the halomethanes have both natural and anthropogenic origins, with the natural sources predominating, and iodomethanes come entirely from marine organisms. The natural sources include marine bacteria and algae, coastal and inland vascular plants, and fungi, mainly, wood-rotting and mycorrhizal basidiomycetes (Watling and Harper, 1998; Moore 2003; Redeker et al. 2004; Itoh et al. 2009). The biogenic chloro- and bromo-methanes are the major natural catalysts of stratospheric ozone destruction. Biogenic halomethanes are the major vehicles of transfer of iodine, an essential element for vertebrates, from the sea to the land.

### Weathering of Rocks on Land

Biologically enhanced weathering depends on autotrophy. Before the evolution of embryophytic plants some of the required acids came from bacterial chemolithotrophs oxidizing reduced N (nitrifiers producing nitric acid) and S (sulfide-oxidizers producing sulfuric acid). These bacterial processes may have parallels in oxidation of sulfide and in non-autotrophic nitrification by fungi (Table 1). Photosynthesis using carbon dioxide from the atmosphere, percolation of organic carbon into crevices and fissures, and biological breakdown to form carbon dioxide and organic carboxylic acids which increase the rate of rock weathering. The development of embryophytes increased productivity and, through deeper-penetrating “root” structures, injecting respiratory carbon dioxide and organic carbon further into rocks (Raven and Edwards 2001).

Mycorrhizal fungi increase the spread of carbon dioxide and organic acids through the rocks, and increase weathering, as do the non-symbiotic archaea, bacteria and microbial eukaryotes that use organic matter from the plants, also producing carbon dioxide and organic acids. In some habitats inimical to embryophyte growth, lichens and some other microbes can live, again stimulating weathering though to a smaller extent than with embryophytes. Weathering supplies many of the nutrients required for photosynthetic organisms; combined (non-dinitrogen) nitrogen compounds are an exception, except in rare, biological, deposits derived from seabird nesting and roosting sites. Weathering also yields a range of non-nutrient inorganic solutes.

A special case of weathering is that of the marine rocky intertidal inhabited by micro- and macroalgae. Recent work has shown that the holdfasts of the two macroalgal species examined, a brown alga (Phaeophyceae) and a calcified coralline red alga (Rhodophyta) had significant chemical interaction with the rocky substrate (Morrison et al. 2009). There is no special nutritional role for the holdfast in these algae, but the weathering could increase the microtopographical relief and hence the area over which a given volume of holdfast interacts with the substratum, possibly decreasing the likelihood of detachment of the algae under the hydrodynamic stresses of the intertidal. Similar considerations presumably apply to the marine subtidal, where the extreme light-limited depth for macroalgal growth is 274 m below mean sea level (Raven et al. 2000).

### Production of Biominerals

Many clades of microbial eukaryotes produce one or more particulate minerals (Table 3), each with one or more possible functions, such as skeletal support, protection, restricting biophage (grazer, carnivore, parasite) damage, graviperception, magnetoperception, increased sinking rate, catalysis of certain biological important reactions, focussing, reflection or scattering of electromagnetic radiation, and so on (Raven and Waite 2004; Raven and Giordano 2009; Gadd 2010; Raven and Knoll 2010, this issue).

### Silicon

As is explained elsewhere in this paper, symbiotic fungi as mycorrhizas and, to a lesser extent, lichens are important in rock weathering on land that converts rock silicates into soluble silicic acid. Some of this silicic acid in soil is converted into internal silica bodies (phytoliths) by vascular plants such as *Equisetum* and many grasses and sedges (Raven 2003), and into silica in the tests (shells) of soil-dwelling testate amoebae from the euglyphid Rhizaria and, possibly, the testate amoebozoans (Aoki et al. 2007; Woodward 2008) (Table 3).

This biogenic silica is more readily weathered back to silicic acid than is silicate in rocks (Raven 2003). The silicic acid in some of the percolating groundwater that contributes to formation of surface inland water bodies is utilized by diatoms in constructing their silica frustules. Freshwater diatoms are more heavily silicified than their marine counterparts (Raven and Waite 2004) (Table 3). Much of the silicic acid from rock weathering eventually reaches the ocean, where planktonic diatoms (Raven and Waite 2004) and radiolarians (some symbiotically photosynthetic), in that order, are the main producers of biogenic silica (Tables 2, 3).

The cycle of silicon is completed by the incorporation of sinking biogenic silica into marine sediments and then subduction, deeper into the crust (Berner & Berner 1996), although the generally undersaturated state of silica with respect to dissolved silicic acid, in surface waters at least, means that silicified frustules and tests tend to dissolve despite a surface covering of

TABLE 3  
Distribution of skeletal and intracellular minerals among microbial eukaryotes

Higher Taxon	Phylum	Class	Skeletal and Intracellular Minerals
Opisthokonta: Fungi (including lichenized fungi)			Ca oxalate inside and outside cells; many other biominerals outside cells
Choanoflagellata Amoebozoa			Silica skeleton deposited inside and exocytosed Testate amoebozoans: various
Plantae	Rhodophyta	Floridiophyceae	CaCO <sub>3</sub> extracellular in walls of all Corallinales Intracellular Ca oxalate and silica
Plantae	Chlorophyta	Charophyceae	CaCO <sub>3</sub> extracellular in walls of oospores and vegetative cells many Charales BaSO <sub>4</sub> /SrSO <sub>4</sub> in intracellular vesicles in desmids, and as intracellular statoliths in rhizoid apices of Charales
Plantae	Chlorophyta	Prasinophyceae	SiO <sub>2</sub> scales (deposited internally and exocytosed) in a few
Plantae	Chlorophyta	Ulvophyceae	CaCO <sub>3</sub> in walls of Dasycladales, walls of Halimadales Intracellular Ca oxalate
Rhizaria		Acantharia	SrSO <sub>4</sub> deposited internally and exocytosed; also intracellular in some swimmers
Rhizaria		Radiolaria	SiO <sub>2</sub> deposited internally and exocytosed; SrSO <sub>4</sub> in some swimmers?
Rhizaria		Foraminifera	CaCO <sub>3</sub> deposited internally (usually) and exocytosed. Other minerals in shells made by agglutination
Rhizaria		Euglyphida	Silica deposited internally and exocytosed in a some; various minerals in some shells made by agglutination
Alveolata	Ciliata		SrSO <sub>4</sub> /BaSO <sub>4</sub> or CaCO <sub>3</sub> or Fe <sub>3</sub> O <sub>4</sub> intracellular in a few
Alveolata	Dinophyta		CaCO <sub>3</sub> extracellular in a few; Fe <sub>3</sub> O <sub>4</sub> intracellular in a few
Chromista	Ochista	Bacillariophyceae	SiO <sub>2</sub> in walls (deposited internally and exocytosed)
Chromista	Ochista	Chrysophyceae	SiO <sub>2</sub> in cysts (deposited internally and exocytosed)
Chromista	Ochista	Parmophyceae	SiO <sub>2</sub> in walls (deposited internally and exocytosed)
Chromista	Ochista	Phaeophyceae	CaCO <sub>3</sub> in walls of a few
Chromista	Ochista	Silicoflagellata	SiO <sub>2</sub> skeletons (deposited internally and exocytosed)
Chromista	Ochista	Synurophyceae	SiO <sub>2</sub> in scales, cysts (deposited internally and exocytosed)
Chromista	Haptophyta	Pavlovophyceae	Internal BaSO <sub>4</sub> /SrSO <sub>4</sub> in a few
Chromista	Haptophyta	Prymnesiophyceae	CaCO <sub>3</sub> in scales of coccolithophores, silica scales in a few (deposited internally and exocytosed)
Excavata/ Discicristata	Euglenophyta Bodonida		Fe <sub>3</sub> O <sub>4</sub> intracellular in a few Silica scales before exocytosis

Based on Raven and Giordano (2009) and Raven and Knoll (in press, this issue); see also Arnott (1995), Zettler et al. (1997), Gadd (2007, 2010). Intracellular polyphosphate is very widespread.

organic polymers (Raven and Giordano 2009) (Table 2). This means that a very significant fraction (97%) of the opal is recycled into silicic acid which, upon upwelling, is incorporated again into opal by diatoms and radiolaria (Raven and Giordano 2009) (Table 2).

Extant natural waters, with the exception of siliceous hot springs (Channing and Edwards 2009), are undersaturated with regard to silica in all crystal and amorphous forms, including the opal that is the mineral deposited by organisms. Precipitation of silica by organisms involves active transport of silicic acid from the medium into an endomembrane compartment; the deposited

silica is usually exocytosed to produce extracellular scales or more continuous skeletal structures such as occur in diatoms (Raven 1983; Raven and Waite 2004) and radiolarians. Since the endomembrane system only occurs in eukaryotes, biological silicification involving silica precipitation and exocytosis can only occur in eukaryotes (Raven and Knoll 2010, this issue). Skeletons built by accretion of pre-existing silica particles onto extracellular organic polymers could occur in Archaea and Bacteria as well, as could silica precipitation in an intracellular vesicle but without exocytosis, but there are no examples of this latter process (Raven and Knoll 2010, this issue).

## Calcium Carbonate

Although surface waters of the ocean, and many alkaline inland waters, are super-saturated with respect to aragonite, high magnesium calcite and calcite, many calcified microbial eukaryotes use intracellular precipitation of calcium carbonate involving the endomembrane systems, examples are coccolithophores and many foraminifera (Raven and Giordano 2009). In the present ocean some 0.092 Pmol C in  $\text{CaCO}_3$  is produced per year, mainly by coccolithophores and planktonic foraminifera. Of this a quarter (0.023 Pmol C in  $\text{CaCO}_3$ ) is buried long-term in sediments, while the rest is recycled to  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in the water column (Bernier and Bernier 1996; Feely et al. 2004; Langer 2008) (see Table 2).

Anthropogenic  $\text{CO}_2$  accumulation will lead to undersaturation of at least some surface ocean waters with respect to all biologically precipitated mineral forms of calcium carbonate by the end of the 21st century (Feely et al. 2004; Doney et al. 2009). Even before the anthropogenic increase in  $\text{CO}_2$  began in the 18th century, deep ocean waters were undersaturated with respect to all mineral phases of  $\text{CaCO}_3$ , as a result of the effect of hydrostatic pressure on the equilibrium between solid mineral phases and dissolved  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  (Bernier and Bernier 1996).

The organisms that have intracellular calcification may be expected to be more resistant to ocean acidification, since they could have more control, at an energy cost, of the chemistry of the site of calcification. However, available evidence on the effect of enhanced  $\text{CO}_2$  on marine calcification shows a diversity of responses, even within a single "species," the coccolithophore *Emiliania huxleyi*. This could be a result of differences among strains, differences in measurement methodology, or both (Doney et al. 2008; Hurd et al. 2009).

## Polyphosphates and Other Materials

Polyphosphates are commonly produced within cells of eukaryotic microbes, as well as by archaea and bacteria. They act as osmotically inactive stores of phosphate (Raven and Knoll 2010, this issue). They also play a significant role in immobilization of phosphorus in marine sediments (Raven and Knoll 2010, this issue) Minerals that are less commonly produced within the cells of eukaryotic microbes are barite (graviperception), celestite (skeletal, graviperception), calcium oxalate (which restricts grazing and is involved in acid-base regulation) and magnetite (magnetoperception) (Raven and Knoll 2010, this issue).

## Biogeoeengineering (Biogeoremediation) using Eukaryotic Microbes

Eukaryotic microbes have been proposed as agents of global scale alterations of the environment to mitigate anthropogenic change. The main emphasis has been on supplying a nutrient that is limiting photosynthetic primary productivity, with iron, (combined) nitrogen and phosphorus proposed for different oceanic regions. If this not only increases the rate of photosynthesis, but

also increases the rate of organic compound sedimentation to mid- or deep-ocean, then atmospheric carbon dioxide is drawn down and retained in the ocean for hundreds to thousands of years. Most of the effort has been on iron fertilization in the north-east subarctic Pacific, the eastern tropical Pacific and, especially, the Southern Ocean with mesoscale (square kilometers) experiments.

Although iron fertilization invariably increases primary productivity, the evidence for stimulated sedimentation is fragmentary. Furthermore, the expected maximum drawdown of atmospheric carbon dioxide is much less than that originally envisaged, and there could be a number of unintended adverse environmental consequences. The same goes for the addition of nitrogen (urea has been proposed) and phosphate to appropriate areas of the ocean. Woodward et al. (2009) presented a critique of ocean fertilization, and of three terrestrial possibilities, for global biogeoeengineering.

One topic not addressed by Woodward et al. (2009) is the albedo of blooms of calcified organisms (coccolithophores) in the surface ocean (Gondwe et al. 2001). If these organisms could be favoured, there would be a net cooling effect on the Earth even though the associated coccolith formation generates carbon dioxide. However, the effect only amounts to a percent or two in the bloom that in turn cover, at any one time, only a percent or two of the global ocean (Gondwe et al. 2009). Furthermore, the means by which stimulation of coccolithophore growth could be achieved is not clear, and ocean acidification is likely to have a strain-specific effect on coccolithophores (Doney et al. 2009; Hurd et al. 2009).

## Conclusions on Quantitative Global Aspects of Biogeoechemistry and of Biogeoremediation

Eukaryotic microbes have major roles in many biogeochemical cycles, including primary production in the ocean and in inland waters, and the assimilation of combined nitrogen and of phosphorus in the ocean, inland waters and on land. Some components of what are generally thought of as archaean or bacterial functions, e.g. sulfide oxidation (not resulting in chemolithotrophy), denitrification and (non-chemolithotrophic) nitrification, occur in eukaryotic microbes, whereas others, e.g., methanogenesis, diazotrophy and sulfide-oxidizing chemolithotrophy, are acquired by symbiosis with archaeans and bacteria. Microbial eukaryotes are also important in rock weathering on land, and production of the biominerals silica and calcium carbonate, with the endomembrane system playing a key role in intracellular production of silica and a major role for calcium carbonate. Biogeoremediation using microbial eukaryotes may have potential for mitigating global environmental change, but have limited possibilities and/or are likely to have undesired consequences.

## Fungi in Geomicrobiology

Particular attention is paid here to the fungi, which are chemoorganotrophic (heterotrophic) organisms, ubiquitous in aquatic and terrestrial environments, relying on organic carbon

sources for energy and metabolism (Gadd 2006). The most important environmental roles of fungi are as decomposer organisms, plant pathogens, symbionts (mycorrhizas, lichens), and in the maintenance of soil structure by their filamentous branching growth habit and exopolymer production (Frankland et al. 1996; Gadd 2006, 2007).

However, a broader appreciation of fungi within geomicrobiology seems to be lacking, and apart from obvious connections with the carbon cycle because of their degradative abilities, they are frequently neglected in contrast to bacteria. Clearly, a much wider metabolic capability is found among prokaryotes and while geochemical activities of bacteria and archaea receive considerable attention (Gadd et al. 2005; Gadd 2008a), especially in relation to the sub-surface environment, fungi are of great importance in aerobic environments (Sterflinger 2000; Gadd 2006, 2007, 2008a, 2010). Although fungi can be found in the deep subsurface and other anaerobic environments, rather less information is so far available about their biogeochemical roles in such locations (Gadd 2008a).

Although fungi are ubiquitous in aquatic ecosystems, the bulk of research in a biogeochemical context has been concerned with decomposition. It is within the terrestrial aerobic ecosystem that fungi exert their profound influence on biogeochemical processes in the biosphere, especially when considering soil, rock and mineral surfaces, and the plant root-soil interface (Sterflinger 2000; Gadd et al. 2007; Gadd 2008a, 2008b, 2010) (Table 4). For example, symbiotic mycorrhizal fungi are associated with ~80% of plant species (Ward and Qiu 2006; Smith and Read 2008) and are responsible for major mineral transformations and redistributions of inorganic nutrients, e.g. essential metals and phosphate, as well as carbon flow, while free-living fungi have major roles in decomposition of organic materials, including xenobiotics, as well as mineral and metal transformations (Fomina et al. 2005a, 2005b, 2005c; Gadd 2007, 2008a, 2008b).

Fungi are often dominant members of the soil microbiota, especially in acidic environments, and may operate over a wider pH range than many heterotrophic bacteria. They are also important components of rock-inhabiting microbial communities with significant roles in mineral dissolution and secondary mineral formation, and biodeterioration agents of wood, metals, stone, plaster, cement and other building materials (Burford et al. 2003a). The ubiquity and significance of lichens, a fungal growth form, as pioneer organisms in the early stages of mineral soil formation is well appreciated. Geomycology can be considered as a subset of geomicrobiology (Ehrlich 1998; Ehrlich and Newman 2009) and simply defined as the scientific study of the roles of fungi in processes of fundamental importance to geology (Burford et al. 2003b; Gadd, 2007).

### Fungi in Organic Matter Degradation and Biogeochemical Cycling

Most attention has been given to carbon and nitrogen cycles, and the ability of fungi to utilize a wide spectrum of organic

compounds is well known. These range from simple compounds such as sugars, organic acids, and amino acids to more complex molecules which are broken down to smaller molecules by extracellular enzymes before cellular entry. Such compounds include natural substances such as cellulose, pectin, lignin, lignocellulose, chitin and starch, and anthropogenic products like hydrocarbons, pesticides, and other xenobiotics. Some fungi have remarkable degradative properties. Lignin-degrading white rot fungi, such as *Phanerochaete chrysosporium*, can degrade, e.g. aromatic hydrocarbons, chlorinated organics, polychlorinated biphenyls, nitrogen-containing aromatics and many other pesticides, dyes and xenobiotics (Cerniglia and Sutherland 2001, 2006). Such activities have potential application in bioremediation where appropriate ligninolytic fungi have been used to treat soil contaminated with substances like pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs) (Singleton 2001; Gadd 2001, 2004a; Sutherland 2004).

Fungi are also important in the degradation of naturally-occurring complex molecules in the soil, and also in aquatic habitats. Since 95% of plant tissue is composed of carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur, the decomposition activities of fungi clearly are important in relation to redistribution of these elements between organisms and environmental compartments. As well as C, H, O, N, P, and S, another 15 elements are typically found in living plant tissues. These include K, Ca, Mg, B, Cl, Fe, Mn, Zn, Cu, Mo, Ni, Co, Se, Na, Si. However, all 90 or so naturally-occurring elements may be found in plants, most at low concentrations although this may be highly dependent on environmental conditions. These include Au, As, Hg, Pb and U, and there are some plants that accumulate relatively high concentrations of metals like Ni and Cd. Animals likewise contain a plethora of elements in varying amounts. For example, the human body is mostly water and so 99% of the body mass comprises oxygen, carbon, hydrogen, nitrogen, calcium and phosphorus. However, many other elements are present in lower amounts including substances taken up as contaminants in food and water. A similar situation occurs throughout the microbial world and therefore, any decomposition, degradative and pathogenic activities of fungi are linked to the redistribution and cycling of all constituent elements, both on local and global scales (Gadd 2004a, 2007) (Table 5).

Organometals (compounds with at least one metal-carbon bond) can also be attacked by fungi with the organic moieties being degraded and the metal compound undergoing changes in speciation (Gadd 1993a, 1993b, 2000a). Degradation of organometallic compounds can be carried out by fungi, either by direct biotic action (enzymes) or by facilitating abiotic degradation, for instance by alteration of pH and excretion of metabolites. Organotin compounds, such as tributyltin oxide and tributyltin naphthenate, may be degraded to mono- and dibutyltins by fungal action, inorganic Sn(II) being the ultimate degradation product (Gadd 2000a). Organomercury compounds may be detoxified by conversion to Hg(II) by fungal organomercury lyase, the Hg(II) being subsequently reduced to Hg(0) by

TABLE 4  
Summary of geomycological processes

Fungal Attribute or Activity	Geomycological Consequences
Growth	
Growth and mycelium development; fruiting body development; hyphal differentiation; melanization	Stabilization of soil structure Penetration of rocks and minerals Biomechanical disruption of solid substrates, building stone, cement, plaster, concrete etc. Plant, animal and microbial colonization, symbiosis and/or infection; mycorrhizas, lichens, pathogens Nutrient and water translocation Surfaces for bacterial growth, transport and migration Mycelium acting as a reservoir of N and/or other elements
Metabolism	
Carbon and energy metabolism	Organic matter decomposition and cycling of component elements, e.g. C, H, O, N, P, S, metals, metalloids, radionuclides Altered geochemistry of local environment, e.g., changes in redox, O <sub>2</sub> , pH Production of inorganic and organic metabolites, e.g., H <sup>+</sup> , respiratory CO <sub>2</sub> , organic acids, siderophores Exopolymer production Organometal formation and/or degradation Degradation of xenobiotics and other complex compounds Mineral formation or dissolution Biocorrosion of metals, glass, rock, minerals etc.
Inorganic nutrition	Altered distribution and cycling of inorganic nutrient elements, e.g., N, S, P, essential and inessential metals, metalloids, organometals and radionuclides Transport, accumulation, incorporation of elements into macromolecules Redox transformations of metal(loid)s and radionuclides Translocation of water, N, P, Ca, Mg, K etc. through mycelium and/or to plant hosts Fe(III) capture by siderophores MnO <sub>2</sub> reduction Element mobilization or immobilization including metals, metalloids, radionuclides, C, P, S, etc. Mineral formation or dissolution Biocorrosion of metals, glass, rock, minerals etc.
Mineral dissolution	Mineral and rock bioweathering Leaching/solubilization of metals and other components, e.g. phosphate Element redistributions including transfer from terrestrial to aquatic systems Altered bioavailability of, e.g., metals, P, S, Si, and Al Altered plant and microbial nutrition or toxicity Mineral formation, e.g., carbonates, oxalates, clays Altered metal and nutrient distribution, toxicity and bioavailability Mineral soil formation
Mineral formation	Biodeterioration of building stone, cement, plaster, concrete etc Element immobilization including metals and radionuclides, C, P, and S Mycogenic carbonate formation Limestone calcrete cementation Mycogenic metal oxalate formation Metal detoxification Contribution to patinas on rocks (e.g., "desert varnish") Mn(II) oxidation to Mn(IV)

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TABLE 4  
Summary of geomycological processes (*Continued*)

Physicochemical properties	
Sorption of soluble and particulate metal species, soil colloids, clay minerals etc.	Altered metal distribution and bioavailability Metal detoxification Metal-loaded food source for invertebrates Prelude to secondary mineral nucleation and formation
Exopolymer production	Complexation of cations Provision of hydrated matrix for mineral formation Enhanced adherence to substrate Clay mineral binding Stabilization of soil aggregates Matrix for bacterial growth Chemical interactions of exopolymers with mineral substrates
Symbiotic associations	
Mycorrhizas	Altered mobility and bioavailability of nutrient and inessential metals, N, P, S etc Altered C flow and transfer between plant, fungus and rhizosphere organisms Altered plant productivity Mineral dissolution and metal and nutrient release from bound and mineral sources Altered biogeochemistry in soil-plant root region Altered microbial activity in plant root region Altered metal distributions between plant and fungus Water transport to and from the plant
Lichens	Pioneer colonizers of rocks and minerals, and other surfaces Bioweathering Mineral dissolution and/or formation Metal accumulation by dry or wet deposition, particulate entrapment, metal sorption, transport, etc. Enrichment of C, N, P, etc. in thallus and alteration of elemental concentrations and distribution in local microenvironment Early stages of mineral soil formation Development and stimulation of geochemically-active microbial populations Mineral dissolution by metabolites including "lichen acids" Biomechanical disruption of substrate
Insects and invertebrates	Fungal populations in gut aid degradation of plant material Invertebrates mechanically render plant residues more amenable for decomposition Cultivation of fungal gardens by certain insects (organic matter decomposition and recycling) Transfer of fungi between plant hosts by insect vectors (aiding infection and disease)
Pathogenic effects	
Plant and animal pathogenicity	Plant infection and colonization Animal predation (e.g., nematodes) and infection (e.g., insects, etc) Redistribution of elements and nutrients Increased supply of organic material for decomposition Stimulation of other geochemically-active microbial populations

These processes may take place in aquatic and terrestrial ecosystems, as well as in artificial and man-made systems, their relative importance depending on the species and active biomass present and physicochemical factors. The terrestrial environment is the main site of fungal-mediated biogeochemical changes, especially in mineral soils and the plant root zone, decomposing vegetation, and on exposed rocks and mineral surfaces. There is rather a limited amount of knowledge on fungal geomicrobiology in freshwater and marine systems, sediments, and the deep subsurface. In this table, fungal roles have been arbitrarily split into categories based on growth, organic and inorganic metabolism, physicochemical attributes, and symbiotic relationships. It should be noted that many if not all of these are linked, and almost all directly or indirectly depend on the mode of fungal growth (including symbiotic relationships) and accompanying chemoorganotrophic metabolism, in turn dependent on a utilizable C source for biosynthesis and energy, and other essential elements, such as N, O, P, S and many metals, for structural and cellular components. Mineral dissolution and formation are detailed separately although these processes also depend on metabolic activity and growth form (adapted from Gadd 2007, 2008b).

TABLE 5  
Fungal roles in biogeochemical cycling of the elements

Element(s)	Fungal roles in elemental cycles
C	Decomposition of organic substances; respiration (CO <sub>2</sub> production); synthesis of polymers, organic metabolites etc.; humus formation; CN <sup>-</sup> production; carbonate formation; oxalate formation; oxalate-carbonate cycle; dissolution of carbonates
H, O	Uptake, assimilation, degradation and metabolism of organic and inorganic compounds; water uptake, transport, translocation and conduction; respiration (CO <sub>2</sub> ); organic and inorganic metabolite excretion
N	Decomposition of nitrogenous compounds; assimilation and transformation of organic and inorganic N compounds; fungal nitrification and denitrification; biosynthesis of N-containing biopolymers, e.g. chitin; production of N-containing metabolites and gases, e.g. N <sub>2</sub> O; ammonia fermentation under anaerobic conditions; mycorrhizal N transfer to plants
P	Dissolution of inorganic phosphates and P-containing minerals in soils and rocks; decomposition of organic P-containing organic compounds; formation of insoluble P, e.g. polyphosphate, secondary phosphate minerals; release of organically-bound P by phosphatases; assimilation and transformation of inorganic P species; oxidation of reduced forms of phosphate, e.g., phosphate; transformations of soil organic P; production of diphosphates and phosphonates; mycorrhizal P transfer to plants; precipitation of secondary metal phosphates
S	Degradation of organic S-containing compounds; organic-inorganic S transformations; uptake and assimilation of organic and inorganic S compounds; SO <sub>4</sub> <sup>2-</sup> reduction and assimilation; oxidation of reduced S compounds, e.g. S(0), thiosulfate, tetrathionate; sulfide production; oxidation of H <sub>2</sub> S to S(0); reduction of S(0) to H <sub>2</sub> S; dissolution of S-containing minerals in soils and rocks, e.g. sulfides, sulfates
Fe	Bioweathering of iron-containing minerals in rocks and soils; iron solubilization by siderophores, organic acids, metabolites etc.; Fe(III) reduction to Fe(II)
Mn	Mn(II) oxidation and immobilization as Mn oxides; Mn(IV) reduction; indirect Mn(IV)O <sub>2</sub> reduction by metabolites, e.g. oxalate; bioaccumulation of Mn oxides to surfaces, exopolymers; contribution to desert varnish formation; biosorption; accumulation; intracellular precipitation
Cr	Cr(VI) reduction to Cr(III); accumulation of Cr oxyanions
Mg, Ca, Co, Ni, Zn, Cd, Sr	Bioweathering of minerals in rocks and soil; biosorption; uptake and accumulation; bioprecipitation, e.g. oxalates, sulfides, phosphates, carbonates
Ag	Reduction of Ag(I) to Ag(0); biosorption; accumulation
K, Na, Cs	Uptake and accumulation; translocation through mycelium; concentration in fruit bodies; mobilization from clays and other minerals, and soil colloids
Cu	Mobilization from Cu-containing minerals in rocks and soils; CuS formation; biosorption; uptake and accumulation; bioprecipitation, e.g. oxalate
Se	Reductive transformation of Se oxyanions, e.g. Se(VI) to Se(IV) to Se(0); biomethylation of Se compounds; assimilation of organic and inorganic Se compounds
Te	Reductive transformation of Te oxyanions, e.g. Te(VI) to Te(IV) to Te(0); biomethylation of Te compounds; assimilation of organic and inorganic Te compounds
Pb	Biosorption; lead oxalate formation
Cl, Br, I	Methylation
Sn	Organotin degradation; sorption and accumulation of soluble Sn species
Au	Reduction of soluble Au species to Au(0)
As	Methylation of arsenic species, e.g., arsenite to trimethylarsine; reduction of As oxyanions, e.g. arsenate to arsenite; oxidation of As oxyanions, e.g., arsenite to arsenate
Hg	Hg methylation; reduction of Hg(II) to Hg(0); Hg volatilization as Hg(0); degradation of organomercurials; biosorption; accumulation
Al	Al mobilization from Al-containing minerals in soils and rocks; aluminosilicate dissolution; Al precipitation as oxides (early stage of bauxitization); biosorption
Si	Uptake of soluble Si species; organic Si complex formation from inorganic silicates; organic siloxane formation;

(Continued on next page)

TABLE 5  
Fungal roles in biogeochemical cycling of the elements (*Continued*)

Element(s)	Fungal roles in elemental cycles
	silica, silicate and aluminosilicate degradation; Si mobilization through production of chelators, acids, bases, exopolymers
U, Th	Biosorption; deposition of hydrolysis products; intracellular precipitation

Some of the major or representative roles of fungi in elemental cycles are indicated without reference to their global significance. Major elemental movements relate to decomposition activities reliant on metabolism and the hyphal mode of growth. Note only representative elements are shown here: virtually all elements in the Periodic Table (including actinides, lanthanides, radionuclides) can be associated with fungal biomass depending on the environment. Fungi possess transport systems for essential metals; inessential metal species can also be accumulated. Fungi are also capable of mediating metal bioprecipitation by, e.g., metabolite production, changing physicochemical conditions around the biomass, and indirect release of metal precipitating substances from other activities, e.g., phosphate. Fungal walls and exopolymers can sorb, bind or entrap many substances. Redox transformations are also widespread in fungal metabolism. While most roles occur in the terrestrial aerobic environment, similar transformations may occur in aquatic environments where fungal populations occur (adapted from Gadd 2008b).

mercuric reductase, a system analogous to that found in mercury-resistant bacteria (see Gadd 1993b).

### Fungi in Transformations of Rocks and Minerals

Minerals are naturally occurring inorganic solids of defined chemical composition with an ordered internal structure. Rocks can be considered to be any solid mass of mineral or mineral-like material and may therefore contain several kinds of minerals. The most abundant minerals are the silicates, with non-silicates constituting less than 10% of the Earth's crust, the most common being carbonates, oxides, sulfides and phosphates. Rocks and minerals represent a vast reservoir of elements, many of which are essential to life, and which must be released into forms that may be assimilated by the biota. These include essential metals as well as anionic nutrient species like sulfate and phosphate (Burford et al. 2003a; Gadd 2010).

### Bioweathering by Fungi

Bioweathering can be defined as the erosion, decay and decomposition of rocks and minerals mediated by living organisms (Burford et al. 2003a; Scheerer et al. 2009; Gadd 2010). Fungi are well suited as bioweathering agents since they can be highly resistant to extreme environmental conditions such as metal toxicity, UV radiation, and desiccation. They can adopt a variety of growth, metabolic and morphological strategies, exude protons and metal-complexing metabolites, and form mutualistic symbioses with plants, algae and cyanobacteria (Burford et al. 2003a; Gorbushina 2007). Most fungi exhibit a filamentous growth habit which gives them an ability to adopt either exploration or exploitation strategies. Some fungi are polymorphic occurring as filamentous mycelium and unicellular yeasts or yeast-like cells, e.g., the black meristematic or microcolonial rock-dwelling fungi (Gorbushina et al. 1993; Gorbushina 2007). The ability of fungi to translocate nutrients within the mycelial network is another important feature for exploiting heterogeneous environments like the soil (Boswell et al. 2002, 2003, 2006; Jacobs et al. 2002, 2004).

Sub-aerial rock surfaces may be thought to be an inhospitable habitat for fungi due to moisture deficit and nutrient limitation although many species are able to deal with varying extremes in such factors as light, salinity, pH, and water potential. Many oligotrophic fungi can scavenge nutrients from the air and rain-water which enables them to grow on rock surfaces. In the sub-aerial rock environment, they can also use organic and inorganic residues on mineral surfaces or within cracks and fissures, waste products of other microorganisms, decaying plants and insects, dust particles, aerosols and animal faeces as nutrient sources. Fungi may achieve protection by the presence of melanin pigments and mycosporines in their cell wall, and by embedding colonies in mucilaginous polysaccharide slime that may entrap clay particles providing extra protection (Gorbushina et al. 2003). It is likely that fungi are ubiquitous components of the microflora of all rocks and building stone and have been reported from a wide range of rock types including limestone, marble, granite, sandstone, basalt, gneiss, dolerite and quartz (Burford et al. 2003a).

The elements found in soil reflect the composition of the Earth's crust, though some modification occurs by weathering, biogenic and anthropogenic activities which on a local scale may be pronounced: chemical changes include dissolution of rock minerals. Elements and minerals that remain can also reorganize into secondary minerals. In the soil, fungus-mineral interactions are an integral component of environmental elemental cycling processes. Mycorrhizal fungi in particular are one of the most important ecological groups of soil fungi in terms of mineral weathering and dissolution (Landeweert et al. 2001). Fungi are also important components of lithobiotic communities (associations of microorganisms forming a biofilm at the mineral-microbe interface), where they interact with the substrate both geophysically and geochemically resulting in the formation of patinas, films, varnishes, crusts and stromatolites (Burford et al. 2003a; Gorbushina 2007).

Biomechanical deterioration of rocks can occur through hyphal penetration and burrowing into decaying material and along crystal planes in, e.g., calcitic and dolomitic rocks. Cleavage

penetration can also occur with lichens (Barker and Banfield 1998). Spatial exploration of the environment to locate and exploit new substrates is facilitated by a range of sensory responses that determine the direction of hyphal growth. Thigmotropism (or contact guidance) is a well-known property of fungi that grow on and within solid substrates with the direction of fungal growth being influenced by grooves, ridges and pores (Bowen et al. 2007a, 2007b). However, biochemical actions are believed to be more important processes than mechanical deterioration. Microbes and plants can induce chemical weathering of rocks and minerals through the excretion of, e.g.,  $H^+$ , organic acids and other metabolites (Gadd 1999; Adeyemi and Gadd 2005). Such biochemical weathering of rocks can result in changes in the mineral micro-topography through pitting and etching, and even complete dissolution of mineral grains. Fungi generally acidify their micro-environment via a number of mechanisms which include the excretion of protons via the plasma membrane proton translocating ATPase or in exchange for nutrients. They can also excrete organic acids (Gadd 1999), while respiratory activity may result in carbonic acid formation. In addition, fungi excrete a variety of other primary and secondary metabolites with metal-chelating properties (e.g., siderophores, carboxylic acids, amino acids and phenolic compounds). 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 (Burford et al. 2003a; Scheerer et al. 2009).

All kinds of rock- and mineral-based building and ceramic materials, including concrete and cement, can be attacked by microorganisms and in some environments, fungi dominate the microbiota and play an important role in biodeterioration (Gu et al. 1998; Nica et al. 2000; Warscheid and Braams 2000; Zhdanova et al. 2000; Scheerer et al. 2009). Cement and concrete are also used as barriers in all kinds of nuclear waste repositories. Fungal attack of concrete can be caused by protons and organic acids and the production of hydrophilic slimes leading to biochemical and biophysical/biomechanical deterioration (Fomina et al. 2007a). Microfungi from the genera *Aspergillus*, *Alternaria* and *Cladosporium* were able to colonize samples of the concrete used as the radioactive waste barrier in the Chernobyl reactor and leached iron, aluminium, silicon and calcium, and re-precipitated silicon and calcium oxalate in their micro-environment (Fomina et al. 2007a).

### Formation of Secondary Mycogenic Minerals

Formation of secondary organic and inorganic minerals by fungi can occur through metabolism-independent and -dependent processes (Table 6). Precipitation, nucleation and deposition of crystalline material on and within cell walls are influenced by such factors as pH and wall composition. This process may be important in soil as precipitation of carbonates, phosphates and hydroxides promote an increase in soil aggregation. Cations like  $Si^{4+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$  and  $Ca^{2+}$  (that may be released through dissolution mechanisms) stimulate precipi-

itation of compounds that may act as bonding agents for soil particles. Hyphae can enmesh soil particles, alter alignment and also release organic metabolites that enhance aggregate stability.

### Carbonates

In limestone, fungi and lichens are considered to be important agents of mineral biodeterioration (Ehrlich and Newman 2009). Many near-surface limestones (calcretes), calcic and petrocalcic horizons in soils are secondarily cemented with calcite ( $CaCO_3$ ) and whewellite (calcium oxalate monohydrate,  $CaC_2O_4 \cdot H_2O$ ) (Verrecchia 2000). The presence of fungal filaments mineralized with calcite ( $CaCO_3$ ), together with whewellite, has been reported in limestone and calcareous soils from a range of localities (Verrecchia et al. 2006). Calcium oxalate can also be degraded to calcium carbonate, e.g., in semi-arid environments, where such a process may again act to cement pre-existing limestones. During decomposition of fungal hyphae, calcite crystals can act as sites of further secondary calcite precipitation. Other work has demonstrated fungal precipitation of secondary calcite, whewellite, and glushkinskite ( $MgC_2O_4 \cdot 2H_2O$ ) (Burford et al. 2006; Gadd 2007).

### Oxalates

Fungi can produce metal oxalates with a variety of different metals and metal-bearing minerals (Ca, Cd, Co, Cu, Mn, Sr, Zn, Ni and Pb) (Fomina et al. 2005c). Calcium oxalate dihydrate (weddelite,  $CaC_2O_4 \cdot 2H_2O$ ) and the more stable calcium oxalate monohydrate (whewellite) are the most common forms of oxalate associated with various fungi (Arnott 1995; Gharieb et al. 1998; Gadd 1999; Braissant et al. 2004). Depending on physicochemical conditions, biotic fungal calcium oxalate can exhibit a variety of crystalline forms (tetragonal, bipyramidal, platelike, rhombohedral or needles). Precipitation of calcium oxalate can act as a reservoir for calcium in the ecosystem and also influences phosphate availability (Gadd 1999). The formation of toxic metal oxalates may provide a mechanism whereby fungi can tolerate high concentrations of toxic metals (Gadd and Griffiths 1978; Gadd 1993a).

### Reductive and Oxidative Precipitation

Reduced forms of metals and metalloids (e.g. elemental silver, selenium, tellurium) can be precipitated by many fungi. The reductive ability of fungi is manifest by black coloration of fungal colonies precipitating elemental Ag or Te, or red for those precipitating elemental Se (Kierans et al. 1991; Gharieb et al. 1999). An oxidized metal layer (patina) a few millimetres thick found on rocks and in soils of arid and semi-arid regions, called desert varnish, is also believed to be of microbial origin with some proposed fungal involvement (Gorbushina and Krumbein 2000). Soluble Mn(II) can be oxidized to  $Mn(IV)O_2$  by several fungi including *Acremonium* spp. (Miyata et al. 2004, 2006; Saratovsky et al. 2009). Fungi can also oxidize manganese and iron in metal-bearing minerals such as siderite ( $FeCO_3$ ) and rhodochrosite ( $MnCO_3$ ) and precipitate them as oxides and also

TABLE 6  
Some examples of biomineralization of fungal hyphae and lichen thalli

Mineral	Fungal Hyphae	Lichen Thalli	Organism(s)
Birnessite (Na,Ca,K) $Mn_7O_{14} \cdot 3H_2O$	Fungi on siderite boulder and Natraqualf soil		<i>Alternaria</i> spp. <i>Cladosporium</i> spp.
Cadmium oxalate ( $CdC_2O_4$ )	Fungi cultured with, e.g., cadmium phosphate, or other cadmium compounds and minerals		<i>Beauveria caledonica</i>
Calcite ( $CaCO_3$ )	Fungi on stalactites, Quaternary eolianites and calcretes; fungi grown in limestone cement microcosms and laboratory media containing insoluble calcium compounds, e.g., calcite, or other Ca-containing compounds and minerals	Lichens on roofing tiles, andesite, volcanoclastite and exposed caliche plates in weathered basaltic and rhyolitic rocks	<i>Caloplaca aurantia</i> <i>Cephalosporium</i> sp. <i>Penicillium coryliphilum</i> <i>Penicillium simplicissimum</i> <i>Verrucaria</i> spp.
Cobalt oxalate ( $CoC_2O_4$ )	Fungi cultured with Co compounds		<i>Aspergillus niger</i>
Desert Varnish (MnO and FeO)	Fungal action on siderite and rhodochrosite in desert regions and sandstone limestone and granite monuments; fungi grown with Mn compounds		<i>Acremonium</i> sp. <i>Alternaria alternata</i> <i>Cladosporium cladosporoides</i> <i>Lichenothelia</i> spp. <i>Penicillium frequentans</i> <i>Penicillium steckii</i> <i>Phoma glomerata</i> <i>Pertusaria coralline</i> <i>Stereocaulon vulcani</i>
Ferrihydrite ( $Fe_2HO_8 \cdot H_2O$ or $5Fe_2O_3 \cdot 9H_2O$ )		Lichen on recent lava flow, on olovine of basalt, gabbro and augite	<i>Lecanora atra</i> <i>Penicillium simplicissimum</i> <i>Parmelia conspersa</i> <i>Parmelia tiliacea</i>
Glushinskite ( $MgC_2O_4 \cdot 2H_2O$ )	Fungi cultured with hydromagnesite	Lichen/rock interface on serpentinite	
Goethite ( $FeO(OH)$ )		Lichen on metamorphic rocks, feldspars, granite and gneiss	
Halloysite ( $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ )	Fungal action on aluminosilicates	Action of lichens on cave deposits and waters	<i>Lasallia</i> spp. <i>Mucor</i> spp. <i>Parmelia</i> spp. <i>Penicillium</i> spp. <i>Rhizocarpon</i> spp. <i>Rhizopus</i> spp.
Humboldtine ( $FeC_2O_4 \cdot 2H_2O$ )		Lichens on Fe rich crystalline limestone and cupriferous rocks	<i>Acarospora smargdula</i> <i>Aspicila alpina</i> <i>Lecidea lactea</i> <i>Stereocaulon vesuvianum</i>
Hydrocerussite ( $Pb_3(CO_3)_2(OH)_2$ )		Mycobiont of lichen in ruins of a lead smelting mill	
Hydromagnesite ( $Mg_5(CO_3)_4(OH)_{2.4} \cdot$ $H_2O$ )	Fungi cultured with hydromagnesite		<i>Penicillium simplicissimum</i>
Lead oxalate, lead oxalate dihydrate ( $PbC_2O_4$ , $PbC_2O_4 \cdot 2H_2O$ )	Fungi cultured with pyromorphite, or in laboratory media containing Pb compounds		<i>Aspergillus niger</i> <i>Beauveria caledonica</i>

(Continued on next page)

TABLE 6  
Some examples of biomineralization of fungal hyphae and lichen thalli (*Continued*)

Mineral	Fungal Hyphae	Lichen Thalli	Organism(s)
Mn-oxalate ( $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ )	Fungi cultured in laboratory media containing Mn compounds	Lichen on Mn ore	<i>Aspergillus niger</i> <i>Pertusaria corallina</i>
Montmorillonite ( $\text{X}_{0.33}\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ) [X = $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$ ]	Fungal action on aluminosilicates	Action of lichens on cave deposits and waters	<i>Lasallia</i> spp. <i>Mucor</i> spp. <i>Parmelia</i> spp. <i>Penicillium</i> spp. <i>Rhizocarpon</i> spp. <i>Rhizopus</i> spp.
Moolooite ( $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ ( $n < 1$ ))	Fungi cultured with, e.g. copper phosphate, or other Cu-containing compounds and minerals	Lichens on cupriferous rocks	<i>Acarospora rugulosa</i> <i>Aspergillus niger</i> <i>Beauveria caledonica</i> <i>Lecidea inops</i> <i>Lecidea lactea</i> <i>Rhizopogon rubescens</i> <i>Serpula himantioides</i> <i>Penicillium simplicissimum</i> <i>Pseudallescheria boydii</i> <i>Serpula himantioides</i>
Strontium oxalate hydrate ( $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ; $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ )	Fungi cultured with strontianite ( $\text{SrCO}_3$ ), or other Sr-containing compounds and minerals		<i>Penicillium simplicissimum</i> <i>Pseudallescheria boydii</i> <i>Serpula himantioides</i>
Todorokite ( $(\text{Mn}, \text{Ca}, \text{Mg})\text{Mn}_3\text{O}_7 \cdot \text{H}_2\text{O}$ )	Fungi in cave deposits and waters		<i>Mucor</i> spp. <i>Penicillium</i> spp. <i>Rhizopus</i> spp.
Uramphite ( $\text{NH}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$ ) and Chernikovite ( $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ )	Fungi cultured with uranium oxides, metallic depleted uranium, or other U-containing compounds and minerals		<i>Beauveria caledonica</i> <i>Hymenoscyphus ericae</i> <i>Rhizopogon rubescens</i> <i>Serpula himantioides</i>
Weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ )	In leaf litter and soils; fungi grown on limestone cement microcosms, and laboratory media containing insoluble calcium compounds, e.g. calcite, or other Ca-containing compounds and minerals	On serpentinite, cupriferous rocks, andesite and volcanoclastite	<i>Acarospora rugulosa</i> <i>Aphylophorales</i> spp. <i>Aspicilia calcarea</i> <i>Caloplaca aurantia</i> <i>Caloplaca flavescens</i> <i>Geastrum</i> spp. <i>Hypogymnia physodes</i> <i>Hysterangium crassum</i> <i>Lecanora atra</i> <i>Lecanora rupicola</i> <i>Lecidea inops</i> <i>Lecidea lactea</i> <i>Ochrolechia parella</i> <i>Penicillium coryliphilum</i> <i>Penicillium simplicissimum</i> <i>Pseudallescheria boydii</i> <i>Serpula himantioides</i>
Whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ )	In Nari Limecrusts, Quaternary calcretes, forest leaf litter and soils; fungi grown on limestone cement	On basalt, serpentinite, cupriferous rocks, gabbro, dolerite, andesite and volcanoclastite	<i>Acarospora rugulosa</i> <i>Acarospora smargdula</i> <i>Aspicilia alpina</i>

(Continued on next page)

TABLE 6  
Some examples of biomineralization of fungal hyphae and lichen thalli (*Continued*)

Mineral	Fungal Hyphae	Lichen Thalli	Organism(s)
	microcosms, and laboratory media containing insoluble calcium compounds, e.g., calcite, or other Ca-containing compounds and minerals		<i>Aspicilia radiosa</i> <i>Caloplaca flavescens</i> <i>Cephalosporium</i> spp <i>Hypogymnia physodes</i> <i>Lecanora atra</i> <i>Lecanora rupicola</i> <i>Lecidea inops</i> <i>Lecidea lactea</i> <i>Ochrolechia parella</i> <i>Parmelia conspersa</i> <i>Parmelia subrudecta</i> <i>Penicillium coryliphilum</i> <i>Penicillium simplicissimum</i> <i>Pertusaria corallina</i> <i>Pseudallescheria boydii</i> <i>Serpula himantioides</i> <i>Xanthoria ectaneoides</i>
Zinc oxalate ( $ZnC_2O_4 \cdot 2H_2O$ )	Fungi exposed to, e.g., zinc oxide, zinc phosphate		<i>Aspergillus niger</i> ; <i>Beauveria caledonica</i> <i>Rhizopogon rubescens</i> <i>Suillus collinitus</i>

The hydration state of some minerals is unclear and only stated when this was specifically identified. The list is not exhaustive and many other mycogenic minerals are possible, as well as many other fungal species capable of mediating their formation (adapted from Burford et al. 2003a, 2003b and Gadd 2007, as well as a number of other sources including Grote and Krumbein 1992; de la Torre and Gomez-Alarcon 1994; Easton 1997; Verrecchia 2000; Haas and Purvis 2006; Burford et al. 2006).

mediate formation of dark Fe(III)- and Mn(IV)- patinas on glass surfaces (Grote and Krumbein 1992).

### Other Mycogenic Minerals

A specific combination of biotic and abiotic factors can lead to the deposition of a variety of other secondary minerals associated with fungi, e.g., birnessite, MnO and FeO, ferrihydrite, iron gluconate, calcium formate, forsterite, goethite, halloysite, hydroserussite, todorokite, moolooite, and montmorillonite (Burford et al. 2003a, 2003b). Secondary mycogenic uranium mineral precipitates on fungal mycelia growing in the presence of uranium oxides or depleted uranium were found to be uranyl phosphate minerals of the meta-autunite group, uramphite and/or chernikovite (Fomina et al. 2007c, 2008).

### Fungal-Clay Interactions: Clay Mineral Formation and Impact on Soil Properties

Silicon dioxide, when combined with Mg, Al, Ca and Fe oxides, forms the silicate minerals in rocks and soil. Silicates are the largest class of minerals comprising 30% of all minerals and making up 90% of the Earth's crust (Ehrlich and Newman 2009). These minerals are unstable and break down to form clays. Microorganisms, including fungi, play a fundamental role

in the dissolution of silicates in rock weathering, and therefore in the formation of clay minerals, and soil and sediment formation (Banfield et al. 1999). Their action is mainly indirect, either through the production of chelates or the production of acids, mineral or organic (including oxalic), or, as for certain bacteria, the production of ammonia or amines (Ehrlich and Newman 2009).

The presence of clay minerals can be a typical symptom of biogeochemically-weathered rocks, and this has been observed with symbiotic fungal associations (lichens and ectomycorrhizas) (Barker and Banfield 1998; Arocena et al. 1999). Some studies have shown that the transformation rate of mica and chlorite to 2:1 expandable clays was predominant in the ectomycorrhizosphere, likely to be a result of the high production of organic acids and direct extraction of K and Mg by the fungal hyphae (Arocena et al. 1999). Clay minerals are generally present in soil in larger amounts than organic matter and because of their adsorptive and ion-exchange capacity, they perform a significant buffering function in mineral soils and are important reservoirs of cations and organic molecules.

Fungal-clay mineral interactions play an important role in soil development, aggregation and stabilization (Burford et al. 2003a). Fungi entangle soil particles in their hyphae forming

stable microaggregates and also take part in exopolysaccharide-mediated aggregation. Interactions between hyphae and solid particles are subject to complex forces of both a physicochemical (electrostatic, ionic, hydrophobic effects, etc.) and biological nature (chemotropism, production of specific enzymes, polysaccharides, lectins and other adhesins, etc.) (Ritz and Young 2004). Interactions between clay minerals and fungi alter the adsorptive properties of both clays and hyphae (Morley and Gadd 1995; Fomina and Gadd 2002).

### Fungi in Metal Transformations

Fungi have many properties which influence metal toxicity and speciation including the production of metal-binding proteins, organic and inorganic precipitation, active transport and intracellular compartmentalization, while major constituents of fungal cell walls, e.g., chitin, melanin, have significant metal binding abilities (Gadd 1993a, 2004a,b, 2008c; Fomina et al., 2007b; Gadd 2010). Despite apparent toxicity, many fungi survive, grow and flourish in apparently metal-polluted locations and a variety of mechanisms, both active and incidental, contribute to tolerance (Gadd and Griffiths 1978; Gadd et al. 1984; Gadd 1992, 1993a, 2005).

### Metal Mobilization

Metal mobilization from rocks, minerals, soil and other substrates can be achieved by protonolysis, respiratory carbon dioxide resulting in carbonic acid formation, chelation by excreted metabolites and Fe(III)-binding siderophores, and methylation which can result in volatilization (Gadd 1999; Renshaw et al. 2002; Gadd 2007). In addition, other excreted metabolites with metal-complexing properties, e.g., amino acids, phenolic compounds, and organic acids may also be involved (Martino et al. 2003). Fungal-derived carboxylic acids can play an integral role in chemical attack of mineral surfaces and these provide a source of protons as well as a metal-chelating anion. Oxalic acid can act as a leaching agent for those metals that form soluble oxalate complexes, including Al and Fe (Strasser et al. 1994). Solubilization phenomena can also have consequences for mobilization of metals from toxic metal containing minerals, e.g. pyromorphite ( $Pb_5(PO_4)_3Cl$ ), contaminated soil and other solid wastes (Sayer et al. 1999). Fungi can also mobilize metals and attack mineral surfaces by redox processes because Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II) respectively. Reduction of Hg(II) to volatile elemental Hg(0) can also be mediated by fungi (see Gadd 1993b).

The removal of metals from industrial wastes and by-products, low grade ores and metal-bearing minerals by fungal "heterotrophic leaching" is relevant to metal recovery and recycling and/or bioremediation of contaminated solid wastes (Burgstaller and Schinner 1993; Strasser et al. 1994). Although fungi need a source of carbon and aeration, they can solubilize metals at higher pH values than thiobacilli and so could perhaps become important where leaching with such bacteria is not possible and in bioreactors (Brandl 2001). Other possible applica-

tions of fungal metal solubilization are the removal of unwanted phosphates, and metal recovery from scrap electronic and computer materials. The ability of fungi, along with bacteria, to transform metalloids has been utilized successfully in the bioremediation of contaminated land and water. Selenium methylation results in volatilization, a process which has been used to remove selenium from the San Joaquin Valley and Kesterson Reservoir, California, using evaporation pond management and primary pond operation (Thompson-Eagle and Frankenberger 1992).

### Metal Immobilization

Fungal biomass provides a metal sink, either by metal biosorption to biomass (cell walls, pigments and extracellular polysaccharides), intracellular accumulation and sequestration, or precipitation of metal compounds onto and/or around hyphae (Gadd 1993a). Fungi are effective biosorbents for a variety of metals including Ni, Zn, Ag, Cu, Cd and Pb and this can be an important passive process in both living and dead biomass (de Rome and Gadd 1987; Gadd 2009). The presence of chitin, and pigments like melanin, strongly influences the ability of fungi to act as sorbents (Gadd and Griffiths 1980; Fomina and Gadd 2002, 2007). In a biotechnological context, fungi and their by-products have received considerable attention as biosorbent materials for metals and radionuclides (Gadd and White 1989, 1990, 1992; White et al. 1995; Gadd 2009). Fungi can precipitate several inorganic and organic compounds, e.g., oxalates, oxides and carbonates and this can lead to formation of biogenic minerals (mycogenic precipitates) as discussed previously (Sayer and Gadd 1997; Jarosz-Wilkolazka and Gadd 2003; Gadd 2007).

### Fungi in Metalloid and Halide Transformations

Fungi can transform metals, metalloids (elements with properties intermediate between those of metals and non-metals, e.g., arsenic, selenium and tellurium) and organometallic compounds by reduction, methylation and dealkylation, again processes of environmental importance since transformation of a metal(loid) may modify its mobility and toxicity (Gharieb et al. 1995; Gadd 1993b). For example, methylated selenium derivatives are volatile and less toxic than inorganic forms while reduction of metalloid oxyanions, such as selenite or tellurite to amorphous elemental selenium or tellurium respectively, results in immobilization and detoxification.

Fungi have the ability to produce a variety of atmospheric methyl halides. This ability is widespread in both free-living and symbiotic fungi, and is dependent on substrate concentrations and community composition (Redeker et al. 2004). The production of chloromethane ( $CH_3Cl$ ) by wood-rotting fungi, e.g., *Phellinus* spp., may be particularly significant with one estimate of annual global input to the atmosphere from this source being 160,000 t, of which 75% is released from tropical and subtropical forests (Watling and Harper 1998). Filamentous fungi may also contribute to the global circulation of stable iodine and

also the long-lived radioiodine,  $^{129}\text{I}$  (half-life:  $1.6 \times 10^7$  years), released from nuclear facilities into the environment (Ban-nai et al. 2006).

### Fungal Symbioses in Mineral Transformations

A remarkable adaptation of fungi for exploitation of the terrestrial environment is their ability to form mutualistic partnerships with plants (mycorrhizas) and algae or cyanobacteria (lichens). Symbiotic fungi are provided with carbon by the photosynthetic partners (photobionts), while the fungi may protect the symbiosis from harsh environmental conditions (e.g., desiccation, metal toxicity), increase the absorptive area, and provide increased access to mineral nutrients.

### Lichens

Lichens are fungi that exist in facultative or obligate symbioses with one or more photosynthesizing partners, and play an important role in many biogeochemical processes (Easton 1997; Banfield et al. 1999; Haas and Purvis 2006). The symbiotic lichen association with algae and/or cyanobacteria, where photosynthetic symbionts provide a source of carbon and surface protection from light and other irradiation, is one of the most successful means for fungi to survive in extreme sub-aerial environments. Lichens are pioneer colonizers of fresh rock outcrops, and were possibly one of the earliest life forms. The lichen symbiosis formed between the fungal partner (mycobiont) and the photosynthesizing partner (algal or cyanobacterial photobiont) enables lichens to grow in practically all surface terrestrial environments. An estimated 6% of the Earth's land surface is covered by lichen-dominated vegetation. Globally, lichens play an important role in the retention and distribution of nutrient (e.g., C, N) and trace elements, in soil formation, and in rock weathering (Purvis, 1996; Purvis and Halls 1996). Lichens can readily accumulate metals such as lead (Pb), copper (Cu), and others of environmental concern, including radionuclides, and also form a variety of metal-organic biominerals, especially during growth on metal-rich substrates. On copper-sulfide bearing rocks, precipitation of copper oxalate (moolooite) can occur within the lichen thallus (Purvis 1996; Purvis and Halls 1996).

### Mycorrhizas

Nearly all land plants appear to depend on symbiotic mycorrhizal fungi (Smith and Read 2008). Two important types of mycorrhizas include endomycorrhizas where the fungus colonizes the interior of host plant root cells (e.g., ericoid and arbuscular mycorrhizas) and ectomycorrhizas where the fungus is located outside the plant root cells. Mycorrhizal fungi are involved in proton-promoted and ligand-promoted metal mobilization from mineral sources, metal immobilization within biomass, and extracellular precipitation of mycogenic metal oxalates (Jongmans et al. 1997; Leyval and Joner 2001; Landeweert et al. 2001; Fomina et al. 2004, 2005c, 2006).

Biogeochemical activities of mycorrhizal fungi lead to changes in the physico-chemical characteristics of the root environment and enhanced weathering of soil minerals resulting in metal cation release (Jongmans et al. 1997; Van Breemen et al. 2000; Leyval and Joner 2001; Landeweert et al. 2001). It has been shown that ectomycorrhizal mycelia may respond to the presence of different soil silicate and phosphate minerals (apatite, quartz, potassium feldspar) by regulating their growth and activity, e.g., colonization, carbon allocation and substrate acidification (Rosling et al. 2004a, 2004b). During their growth, mycorrhizal fungi often excrete low molecular weight carboxylic acids, e.g., malic, succinic, gluconic, oxalic (Van Breemen et al. 2000). In podzol E horizons under European coniferous forests, the weathering of hornblendes, feldspars and granitic bedrock has been attributed to oxalic, citric, succinic, formic and malic acid excretion by ectomycorrhizal hyphae (Landeweert et al. 2001). Ectomycorrhizal hyphal tips could produce micro- to millimolar concentrations of these organic acids, and such activities can release elements from a variety of solid substrates including wood ash, phosphates and other minerals (Wallander et al. 2003). Mobilization of phosphorus is generally regarded as one of the most important functions of mycorrhizal fungi (Wengel et al. 2006).

### CONCLUSIONS

Fungal populations are intimately involved in biogeochemical transformations at local and global scales, such transformations occurring in aquatic and terrestrial habitats. Within terrestrial aerobic ecosystems, fungi may exert an especially profound influence on biogeochemical processes, especially when considering soil, rock and mineral surfaces, and the plant root-soil interface (Gadd 2007, 2010). Of special significance in this regard are lichens and mycorrhizas. Key processes include organic matter decomposition and element cycling, rock and mineral transformations, bioweathering, metal and metalloid transformations, and formation of mycogenic minerals. Some fungal transformations have beneficial applications in environmental biotechnology, e.g., in metal leaching, recovery and detoxification, and xenobiotic and organic pollutant degradation (Gadd 2000b, 2001). They may also result in adverse effects when these processes are associated with the degradation of food-stuffs, natural products and building materials, including wood, stone and concrete.

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