

SGM Prize Lecture

Correspondence
Geoffrey Michael Gadd
g.m.gadd@dundee.ac.uk

Metals, minerals and microbes: geomicrobiology and bioremediation

Geoffrey Michael Gadd

Division of Molecular Microbiology, College of Life Sciences, University of Dundee, Dundee DD1 5EH, UK

Microbes play key geoactive roles in the biosphere, particularly in the areas of element biotransformations and biogeochemical cycling, metal and mineral transformations, decomposition, bioweathering, and soil and sediment formation. All kinds of microbes, including prokaryotes and eukaryotes and their symbiotic associations with each other and 'higher organisms', can contribute actively to geological phenomena, and central to many such geomicrobial processes are transformations of metals and minerals. Microbes have a variety of properties that can effect changes in metal speciation, toxicity and mobility, as well as mineral formation or mineral dissolution or deterioration. Such mechanisms are important components of natural biogeochemical cycles for metals as well as associated elements in biomass, soil, rocks and minerals, e.g. sulfur and phosphorus, and metalloids, actinides and metal radionuclides. Apart from being important in natural biosphere processes, metal and mineral transformations can have beneficial or detrimental consequences in a human context. Bioremediation is the application of biological systems to the clean-up of organic and inorganic pollution, with bacteria and fungi being the most important organisms for reclamation, immobilization or detoxification of metallic and radionuclide pollutants. Some biominerals or metallic elements deposited by microbes have catalytic and other properties in nanoparticle, crystalline or colloidal forms, and these are relevant to the development of novel biomaterials for technological and antimicrobial purposes. On the negative side, metal and mineral transformations by microbes may result in spoilage and destruction of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), acid mine drainage and associated metal pollution, biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment, all with immense social and economic consequences. The ubiquity and importance of microbes in biosphere processes make geomicrobiology one of the most important concepts within microbiology, and one requiring an interdisciplinary approach to define environmental and applied significance and underpin exploitation in biotechnology.

Microbes as geoactive agents

Microbes interact with metals and minerals in natural and synthetic environments, altering their physical and chemical state, with metals and minerals also able to affect microbial growth, activity and survival. In addition, many minerals are biogenic in origin, and the formation of such biominerals is of global geological and industrial significance, as well as providing important structural components for many organisms, including important microbial groups such as diatoms, foraminifera and radiolaria (Ehrlich, 1996; Gadd & Raven, 2010). Geomicrobiology can simply be defined as the roles of microbes in geological processes (Banfield & Nealson, 1997; Banfield *et al.*, 2005; Konhauser, 2007; Ehrlich & Newman, 2009). Metal–mineral–microbe interactions are of key importance within the framework of geomicrobiology and also fundamental to microbial biomineralization processes. The term biomi-

neralization represents the collective processes by which organisms form minerals (Bazylinski, 2001; Dove *et al.*, 2003), a phenomenon widespread in biology and mediated by bacteria, protists, fungi, plants and animals. Most biominerals are calcium carbonates, silicates and iron oxides or sulfides (Bauerlein, 2000; Bazylinski, 2001). Biomineralization is itself an important interdisciplinary research area, and one that overlaps with geomicrobiology (Banfield & Nealson, 1997; Dove *et al.*, 2003; Banfield *et al.*, 2005; Konhauser, 2007).

While the activities of microbes in transforming organic and inorganic substrates has long been appreciated by microbiologists, there is growing awareness of the geochemical significance of microbes among researchers in geology, mineralogy, geochemistry and related disciplines (Banfield & Nealson, 1997; Warren & Haack, 2001; Macalady & Banfield, 2003; Bottjer, 2005; Gleeson *et al.*,

Table 1. Microbial roles in key biogeochemical cycles of metals and other elements

Some of the major or representative microbial roles in metal and other elemental cycles are indicated without reference to their relative global significance. Only representative elements are shown: note that virtually all elements in the periodic table (including actinides, lanthanides, radionuclides) can be accumulated by or be associated with microbial biomass depending on the context and environment. Microbes possess transport systems for essential metals; inessential metal species can also be taken up. Microbes are also capable of mediating metal and mineral bioprecipitation, e.g. by metabolite production, by changing the physico-chemical microenvironmental conditions around the biomass, and also by the indirect release of metal-precipitating substances from other activities, e.g. phosphate from organic decomposition or phosphate mineral solubilization. Many different metal-containing minerals formed as a direct or indirect result of microbial activity, e.g. various carbonates, phosphates, etc., are omitted from the table. Microbial cell walls, outer layers, and exopolymers can sorb, bind or entrap many soluble and insoluble metal species as well as e.g. clay minerals, colloids, oxides, etc. which also have significant metal-sorption properties. Redox transformations are also widespread in microbial metabolism, some also mediated by the chemical activity of structural components.

Element(s)	Microbial roles in elemental cycles
C, H, O	Uptake, assimilation, degradation and metabolism of organic and inorganic compounds; respiration (CO ₂ production); photosynthesis; photorespiration; CO ₂ fixation; biosynthesis of polymers, organic and inorganic metabolite excretion; humus formation; CN ⁻ production; carbonate formation; oxalate formation; oxalate-carbonate cycle; dissolution of carbonates; methanotrophy; methanogenesis (archaea); hydrocarbon degraders; organometal(loid) degradation; metal(loid) biomethylation and demethylation; xenobiotic oxidation; CO utilization; water uptake; water transport, translocation and conduction (fungal mycelium); hydrogen oxidation and production
N	Decomposition of nitrogenous compounds; assimilation and transformations of organic and inorganic N compounds; N ₂ fixation (prokaryotes only); nitrification and denitrification; ammonia and nitrite oxidation; anaerobic nitrification; biosynthesis of N-containing biopolymers, e.g. chitin; production of N-containing metabolites and gases, e.g. N ₂ O; ammonia fermentation under anaerobic conditions; mycorrhizal N transfer to plants (fungi); fixed N transfer to plants (symbiotic N ₂ fixers)
P	Dissolution of inorganic phosphates and P-containing minerals in soils and rocks; decomposition of 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; P transfer to plants (mycorrhizas)
S	Degradation of S-containing organic compounds; organic-inorganic S transformations; uptake and assimilation of organic and inorganic S compounds; sulfidogenesis; S(0) accumulation; SO ₄ ²⁻ reduction and assimilation; S(0) reduction; oxidation of reduced S compounds, e.g. S(0), thiosulfate, tetrathionate; oxidation of H ₂ S to S(0); reduction of S(0) to H ₂ S; dissolution of S-containing minerals in soils and rocks, e.g. sulfides, sulfates
Fe	Bioweathering of Fe-containing minerals in rocks and soils; Fe solubilization by siderophores, organic acids, metabolites etc.; Fe(III) reduction to Fe(II); Fe(II) oxidation to Fe(III); Fe biomineralization, e.g. oxides, hydroxides, carbonates, sulfides; metal sorption to Fe oxides
Mn	Mn(II) oxidation and immobilization as Mn(IV) oxides; Mn(IV) reduction; indirect Mn(IV)O ₂ reduction by metabolites, e.g. oxalate; bioaccumulation of Mn oxides to surfaces and exopolymers; contribution to desert varnish formation; biosorption; accumulation; intracellular precipitation; Mn biomineralization, e.g. oxides, carbonates, sulfides, oxalates; metal sorption to Mn oxides
Cr	Cr(VI) reduction to Cr(III); Cr(III) oxidation; 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, carbonate; Co(III) reduction
Ag	Reduction of Ag(I) to Ag(0); biosorption; accumulation
K, Na, Cs	Uptake and accumulation; translocation through mycelium (fungi); concentration in fruit bodies (fungi); mobilization from minerals in soil
Cu	Mobilization from Cu-containing minerals in rocks and soils; CuS formation; biosorption; uptake and accumulation; bioprecipitation, e.g. oxalates
Se	Reductive transformation of Se oxyanions, e.g. Se(VI) to Se(IV) to Se(0); Se(0) oxidation; biomethylation and demethylation 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; assimilation of organic and inorganic Te compounds
Pb	Biosorption; lead oxalate formation; biomethylation
Cl, Br, I	Dehalorespiration; biomethylation; accumulation in biomass
Sn	Organotin degradation; sorption and accumulation of soluble Sn species; biomethylation
Au	Reduction of soluble Au species to Au(0); Au mineral dispersion and solubilization
As	Biomethylation of As species, e.g. arsenite to trimethylarsine; reduction of As oxyanions, e.g. arsenate to arsenite; oxidation of As oxyanions, e.g. arsenite to arsenate

Table 1. cont.

Element(s)	Microbial roles in elemental cycles
Hg	Hg biomethylation; reduction of Hg(II) to Hg(0); oxidation of Hg(0) to Hg(II); 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; silica, silicate and aluminosilicate degradation; Si mobilization through production of chelators, acids, bases, exopolymers; silicification; structural biomineralization (some algae and protozoa)
U, Th	Biosorption; deposition of hydrolysis products; intracellular precipitation; U(VI) reduction to U(IV); U(IV) oxidation to U(VI); U biomineralization, e.g. phosphates; UO ₂ formation
Tc	Per technetate accumulation; Tc(VII) reduction to Tc(IV); oxide formation
V	Vanadate accumulation; V(V) reduction to V(IV)

2007; Konhauser, 2007; Gadd, 2008a; Uroz *et al.*, 2009). Key topics within the geomicrobiology framework include biogeochemical cycling of the elements, mineral formation, mineral deterioration (which can include such subjects as bioweathering and processes leading to soil and sediment formation), and chemical transformations of metals, metalloids and radionuclides (Ehrlich, 1996). All kinds of microbes, including prokaryotes and eukaryotes and their symbiotic associations with each other and 'higher organisms', can contribute actively to geological phenomena (Macalady & Banfield, 2003; Bottjer, 2005; Chorover *et al.*, 2007; Konhauser, 2007; Gleeson *et al.*, 2007; Gadd, 2008a), and most of these processes involve metal and mineral transformations (Table 1, Fig. 1). Examples of geomicrobially important groups of microbes directly involved in geochemical transformations include iron-oxidizing and -reducing bacteria, manganese-oxidizing and -reducing bacteria, sulfate-reducing bacteria, sulfur-oxidizing and -reducing bacteria, and many other pro- and eukaryotes that can form or degrade silicates, carbonates, phosphates and other minerals (see Gadd, 2007; Kim & Gadd, 2008; Gadd & Raven, 2010). Root-inhabiting rhizosphere microbes, including mycorrhizal fungi, have a major influence on plant nutrition via effects on phosphate availability but also concomitant metal circulation (Amundson *et al.*, 2007). Indeed, during the early phases of soil formation the contribution of microbial activities (including the activities of lichens) to rock weathering, mineral dissolution and element cycling is also intimately related to metal movements and microbial strategies for metal transformations (Purvis & Pawlik-Skowronska, 2008; Gilmour & Riedel, 2009; Uroz *et al.*, 2009). It should also be emphasized that the general metabolic activities of all microbes affect metal distribution and bioavailability, not least because of the metabolic essentiality of many metals and the existence of specific biochemical mechanisms for their cellular accumulation, but also through the decomposition or biodeterioration of organic and inorganic substrates (Warren & Haack, 2001; Huang *et al.*, 2004; Gadd, 2007).

Apart from being important in natural biosphere processes, metal and mineral transformations can have beneficial or

detrimental consequences in a human context. Bioremediation refers to the application of biological systems to the clean-up of organic and inorganic pollution, with bacteria and fungi being the most important organisms in this context for reclamation, immobilization or detoxification of metallic pollutants. Some biominerals or metallic elements deposited by microbes may have catalytic and other properties in nanoparticle, crystalline or colloidal forms, and these are relevant to the development of novel biomaterials for structural, technological, environmental and antimicrobial purposes (Lloyd *et al.*, 2008; Theng & Yuan, 2008; Petkov *et al.*, 2009; Hennebel *et al.*, 2009). In contrast, metal and mineral transformations by microbes may result in degradation and spoilage of natural and synthetic materials, rock and mineral-based building materials, acid mine drainage and associated metal pollution, biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment, all with immense social and economic consequences. In view of the ubiquity and importance of microbes in biosphere processes, it can easily be argued that geomicrobiology is one of the most important concepts within microbiology, and requires an interdisciplinary approach involving physical, chemical and biological expertise. This review seeks to outline some of the main ways that microbes (chiefly bacteria and fungi) interact with metals and minerals, their importance in geological and environmental processes, and their applied significance.

Metals and minerals

Metals constitute about 75 % of the known elements; they are ubiquitous in the biosphere, and vital to our industry, infrastructure and daily life. Since the industrial revolution, metals have increasingly been redistributed in the environment, with accumulation in terrestrial and aquatic habitats being associated with adverse effects on the biota and human health. Thirteen trace metals and metalloids (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, Zn) are considered priority pollutants (Sparks, 2005); they originate from natural sources such as rocks and metalliferous minerals, and anthropogenic inputs from e.g. agriculture,

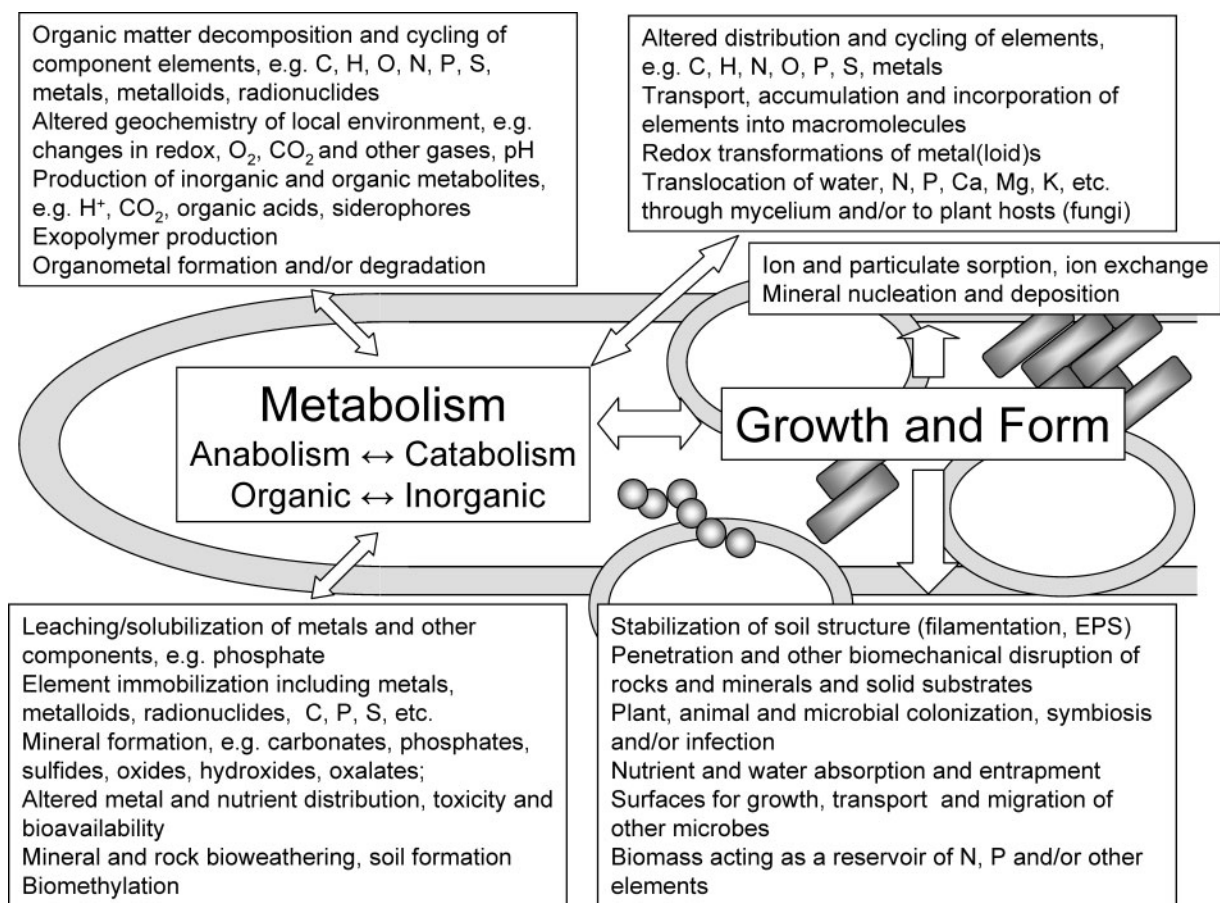


Fig. 1. Some of the important microbial roles and activities in biogeochemical processes leading to altered metal distributions and speciation. Such activities take place in aquatic and terrestrial ecosystems, as well as in artificial and man-made systems, their relative importance depending on the populations present and physico-chemical factors that affect activity. Most if not all of these roles are inter-linked, almost all directly or indirectly depending on the mode of growth, e.g. unicellular, filamentous, colonial, biofilm, and including symbiotic partnerships, and mode of metabolism, in turn dependent on nutrient and energy source(s) for biosynthesis and energy, essential elements, such as C, N, O, P, S and many metals, for structural and cellular components (adapted from Gadd, 2008a).

metallurgy, energy production, microelectronics, mining, sewage sludge and waste disposal (Landa, 2005; Gilmour & Riedel, 2009). Atmospheric deposition is a major mechanism for metal input to plants and soils. Volatile metal(loid)s such as As, Hg, Se and Sb can be distributed as gases or enriched in particles, while Cu, Pb and Zn are transported as particulates (Adriano, 2001; Adriano *et al.*, 2004a). In terrestrial ecosystems, soils are the major sink for metal contaminants, while sediments are the major sink for metals in aquatic systems. Metal contaminants can affect aquatic systems through runoff, leaching and transport via mobile colloids (Adriano, 2001; Adriano *et al.*, 2004a). Metals are significant natural components of all soils, where their presence in the mineral fraction constitutes a pool of potentially mobile metal species, many essential nutrients for plants and microbes, and important solid components that can have a fundamental

effect on soil biogeochemical processes, e.g. clays, minerals, iron and manganese oxides (Huang *et al.*, 2004). Metals are also present in organic fractions, frequently in bound forms, with some metal recycling occurring as a result of organic matter degradation. The aqueous phase provides a mobile medium for metal transfer and circulation through the soil and to organisms, and to the aquatic environment (Warren & Haack, 2001). The aquatic environment also contains a vast pool of metals in various chemical forms, with many accumulating in sediments (Warren & Haack, 2001; Gilmour & Riedel, 2009). Other contaminants related to metals are metalloids, organometals and organometalloids, while many radionuclides that enter the environment are metals.

Minerals are naturally occurring inorganic solids of definite chemical composition with an ordered internal structure;

rocks can be considered to be any solid mass of mineral or mineral-like material. Silicates are the most common minerals, with non-silicates constituting <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 essential for life, and such elements must be released in forms that can be assimilated by the biota. These include essential metals as well as nutrient elements like S and P (Gadd, 2007; Gadd *et al.*, 2005, 2007). Physical, chemical and biological mechanisms contribute to weathering and decay of rocks and minerals, and for the latter, metal-microbe interactions will be involved in the majority of cases. The activities of microbes (and other organisms) in rock and mineral deterioration can be termed bioweathering.

The vast majority of minerals contain metals, and there can be a bewildering plethora of mineral types for each metal element, of varying distribution in the environment and physico-chemical properties. For example, Mn is found as a major or minor component in more than 100 naturally occurring minerals, of which major accumulations are as oxides, carbonates and silicates (Ehrlich & Newman, 2009). In addition, metals may be common components of many minerals as impurities from natural and industrial sources: potentially toxic and other metals may be found in, for example, silicates, sulfides, oxides, carbonates and phosphates. Regardless of their origin, whether geological or biogenic, microbes can interact with minerals and affect their structure by mechanical and biochemical mechanisms, and affect the speciation and mobility of component metal elements (Ehrlich, 1996; Edwards *et al.*, 2005; Landa, 2005; Gleeson *et al.*, 2007; Lian *et al.*, 2008a, b; Gadd, 2008b; Brown *et al.*, 2008; Uroz *et al.*, 2009) (Table 1, Fig. 2).

In contrast to mineral deterioration, dissolution or fragmentation, all groups of microbes can mediate mineral formation by direct and indirect mechanisms. In such cases, the minerals can be termed biominerals, to emphasize the involvement of living organisms, although the chemical structure of the minerals so produced may be identical to that of minerals produced by geochemical mechanisms. Biomineralization may particularly refer to processes where biomineral formation is a highly directed process and fundamental to the formation of a cellular structure. Examples include magnetosomes composed of magnetite in magnetotactic bacteria (Bazylinski & Moskowitz, 1997; Bazylinski, 2001; Posfai & Dunin-Borkowski, 2009), silicaceous cell walls of diatoms (algae) and radiolarians (protozoa), and carbonate tests of various amoebae and algae (e.g. coccolithophores) (Banfield & Nealson, 1997; Dove *et al.*, 2003; Banfield *et al.*, 2005; Ehrlich & Newman, 2009; Gadd & Raven, 2010). Other biominerals may arise from redox transformations of metals, sorption phenomena and metabolic activities, where organic and inorganic metabolites, e.g. oxalate, respiratory CO₂ and sulfide, may precipitate metals in the cellular microenvironment, or effect chemical changes in the substrate which also lead to secondary mineral

formation (Ehrlich, 1996; Hamilton, 2003; Glasauer *et al.*, 2004; Konhauser, 2007; Ehrlich & Newman, 2009).

Microbes, metals and minerals

Metals are directly and/or indirectly involved in all aspects of microbial growth, metabolism and differentiation (Gadd, 1992a). Metals and their compounds interact with microbes in various ways depending on the metal species, organism and environment, while structural components and metabolic activity also influence metal speciation and therefore solubility, mobility, bioavailability and toxicity (Gadd & Griffiths, 1978; Gadd, 1992a, 1993a, 2004, 2005, 2007) (Table 1, Fig. 2). Many metals are essential for life, e.g. Na, K, Cu, Zn, Co, Ca, Mg, Mn and Fe, but all can exert toxicity when present above certain threshold concentrations. Other metals, e.g. Cs, Al, Cd, Hg and Pb, have no known essential metabolic functions but all can be accumulated. Microbes are intimately associated with the biogeochemical cycling of metals, and associated elements, where their activities can result in mobilization and immobilization depending on the mechanism involved and the microenvironment where the organism(s) are located (Gadd, 2004, 2007; Violante *et al.*, 2008; Ehrlich & Newman, 2009).

Metals exhibit a range of toxicities towards microbes, and while toxic effects can arise from natural geochemical events, toxic effects on microbial communities are more commonly associated with anthropogenic contamination or redistribution of toxic metals in aquatic and terrestrial ecosystems. Such contamination can arise from aerial and aquatic sources, as well as agricultural and industrial activities, and domestic and industrial wastes. In some cases, microbial activity can result in remobilization of metals from waste materials and transfer into aquatic systems (Gadd, 2009a; Violante *et al.*, 2008). It is commonly accepted that toxic metals, their chemical derivatives, metalloids and organometals can have significant effects on microbial populations and, under toxic conditions, almost every index of microbial activity can be affected (Giller *et al.*, 2009). However, metal toxicity is greatly affected by the physico-chemical nature of the environment and the chemical behaviour of the metal species in question (Gadd & Griffiths, 1978). Despite apparent toxicity, many microbes grow and even flourish in apparently metal-polluted locations, and a variety of mechanisms, both active and incidental, contribute to resistance (Gadd & Griffiths, 1978; Mowll & Gadd, 1984; Gadd *et al.*, 1984; Avery, 2001; Holden & Adams, 2003; Fomina *et al.*, 2005c) (Fig. 3). Microbial resistance to toxic metals is widespread, with frequencies ranging from a few per cent in pristine environments to nearly 100% in heavily polluted environments (Silver & Phung, 2009).

It seems that most survival mechanisms depend on some change in metal speciation leading to decreased or increased mobility. These include redox transformations, the production of metal-binding peptides and proteins

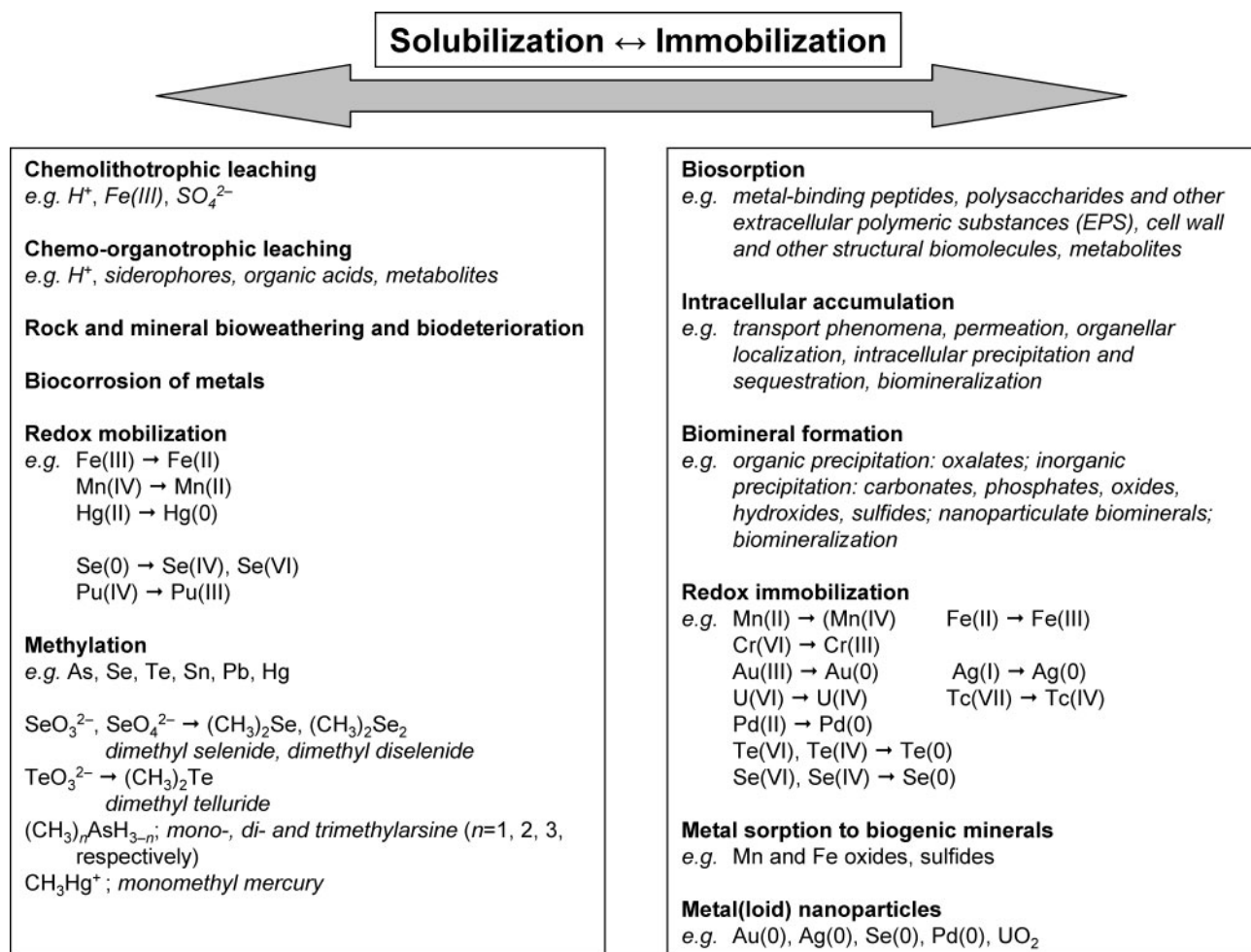


Fig. 2. Diagram depicting the major mechanisms of microbial metal transformations between soluble and insoluble metal species. The relative balance between such processes depends on the environment and associated physico-chemical conditions and the microbe(s) involved as well as relationships with plants, animals and anthropogenic activities. Chemical equilibria between soluble and insoluble phases are influenced by abiotic components, including dead biota and their decomposition products, as well as other physico-chemical components of the environmental matrix, e.g. pH, water, inorganic and organic ions, molecules, compounds, colloids and particulates. Solubilization can occur by chemolithotrophic (autotrophic) and chemo-organotrophic (heterotrophic) leaching; siderophores and other complexing agents; redox reactions; methylation and demethylation; and biodegradation of organo-radionuclide complexes. Immobilization can occur by biosorption to cell walls, exopolymers, other structural components and derived/excreted products; precipitation can be a result of metabolite release (e.g. sulfide, oxalate) or reduction; transport, accumulation, intracellular deposition, localization and sequestration; and adsorption and entrapment of colloids and particulates. The overall scheme is also affected by reciprocal interactions between biotic and abiotic components of the ecosystem such as abiotic influence on microbial diversity, numbers and metabolic activity; ingestion of particulates and colloids (including bacteria) by phagotrophs; and biotic modification of physico-chemical parameters including redox potential, pH, O_2 , CO_2 , other gases and metabolites, temperature, and nutrient depletion.

(e.g. metallothioneins, phytochelatins), organic and inorganic precipitation, active transport, efflux and intracellular compartmentalization, while cell walls and other structural components have significant metal-binding abilities (Mowll & Gadd, 1984; White & Gadd, 1998; Gadd, 2004, 2005, 2006) (Figs 2 and 3). Other microbial properties lead to metal solubilization from organic and inorganic sources (Gadd, 2007). Such metal transforma-

tions are central to metal biogeochemistry, and emphasize the link between microbial responses and geochemical cycles for metals (Ehrlich, 1997; Gilmour & Riedel, 2009). Such metal–mineral–microbe interactions are especially important in the so-called terrestrial ‘critical zone’, defined as ‘the heterogeneous, near-surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine

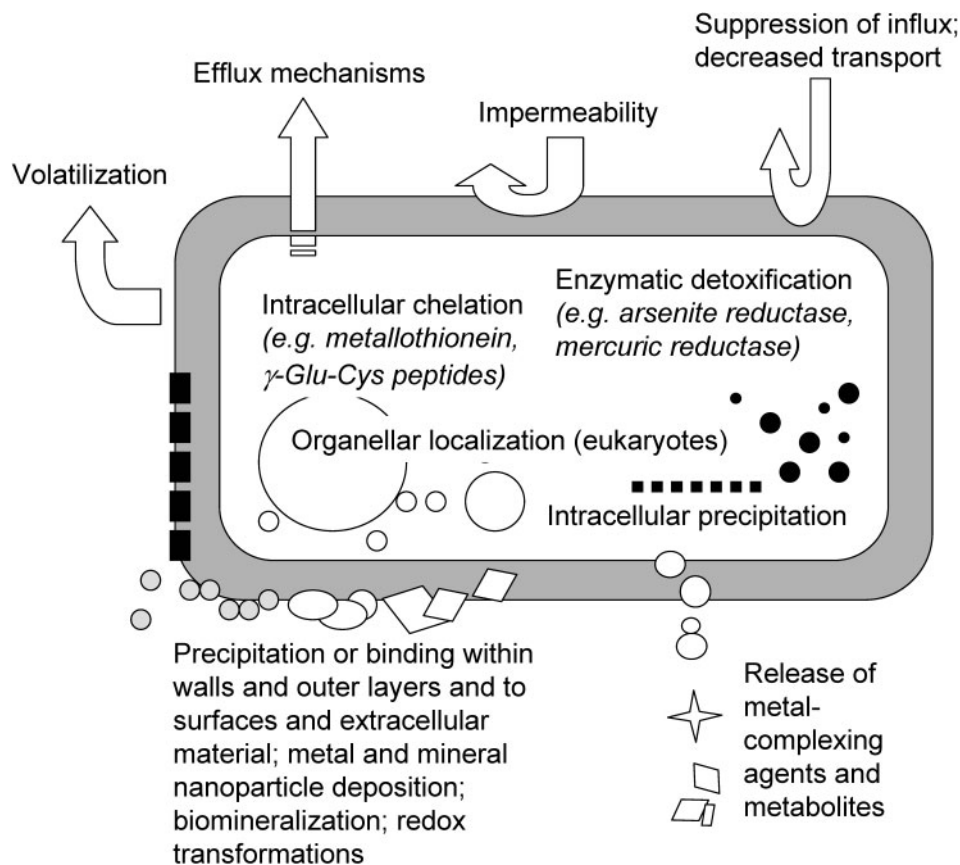


Fig. 3. Mechanisms involved in the detoxification and transformation of metals, including mechanisms that restrict entry into the cell and intracellular detoxification or organellar compartmentation, the latter occurring in some eukaryotes, e.g. algae and fungi. Operation of a number of mechanisms is possible depending on the organism and the cellular environment; mechanisms may be dependent on and/or independent of metabolism. A variety of mechanisms may be involved in transport phenomena contributing to decreased uptake and/or efflux. A variety of specific or non-specific mechanisms may also effect redox transformations, intracellular chelation and intracellular precipitation. Biomineral formation (biomineralization) may be biologically induced, i.e. caused by physico-chemical environmental changes mediated by the microbes, or biologically controlled (solid rectangles) (adapted from Gadd, 2009a).

the availability of life sustaining resources' (Sparks, 2005; Chorover *et al.*, 2007; Amundson *et al.*, 2007; Brantley *et al.*, 2007).

Bacterial resistance mechanisms generally involve efflux or enzymic detoxification, which can also result in release from cells, e.g. Hg(II) reduction to Hg(0) (Silver & Phung, 1996, 2009; Nies, 1992a, 1999, 2003; Nies & Silver, 1995; Rosen, 2002; Osman & Cavet, 2008). Bacterial plasmids have resistance genes to many toxic metals and metalloids, e.g. Ag^+ , AsO_2^- , AsO_4^{3-} , Cd^{2+} , Co^{2+} , CrO_4^{2-} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Sb^{3+} , TeO_3^{2-} , Tl^+ and Zn^{2+} . Related systems are also frequently located on bacterial chromosomes, e.g. Hg²⁺ resistance in *Bacillus*, Cd²⁺ efflux in *Bacillus* and arsenic efflux in *Escherichia coli* (Silver & Phung, 1996; Rosen, 2002). The most detailed research has been done for As, Hg, Cd, Cu, Co, Zn, Pb, Ag, Ni and Te, for which resistance genes have been sequenced and mechanisms proposed (Osman & Cavet, 2008; Silver &

Phung, 2009). As with bacteria, intracellular metal concentrations in fungi may be regulated by transport, including efflux mechanisms and internal compartmentation (Gadd, 1993a; Macreadie *et al.*, 1994; Blaudez *et al.*, 2000; Eide, 2000; Van Ho *et al.*, 2002) as well as the direct and indirect mechanisms listed above. Microbes may also synthesize a variety of metal-binding peptides and proteins, e.g. metallothioneins and phytochelatins, which regulate metal ion homeostasis and affect toxic responses (Eide, 2000; Avery, 2001). In eukaryotes, intracellular compartmentation may also be significant in tolerance (Gadd, 1993a; Eide, 2000; Avery, 2001) (Fig. 3).

Many important microbial processes can be influenced by minerals, including energy generation, nutrient acquisition, cell adhesion and biofilm formation (Hochella, 2002; Brown *et al.*, 2008). Essential nutrients may be acquired from mineral surfaces, and this concentrates these substances above surrounding environmental levels, e.g.

C, N, P, Fe, essential metals, and various organic compounds (Vaughan *et al.*, 2002). Environmental contaminants, including metals, may also be sorbed to mineral surfaces and these can be displaced by microbial activity (Kraemer *et al.*, 1999; Huang *et al.*, 2004; Chorover *et al.*, 2007; Theng & Yuan, 2008). Potentially toxic metals released from minerals as a result of physico-chemical and biological processes may also affect microbial communities (Fomina *et al.*, 2005c; Gadd, 2005). Such properties of mineral surfaces as microtopography, surface composition, surface charge and hydrophobicity play an important role in thigmotropism, microbial attachment and detachment, and are therefore critical for colonization and biofilm formation, and the ecology of microbial populations associated with mineral substrates (Vaughan *et al.*, 2002; Gleeson *et al.*, 2005, 2006, 2010; Bowen *et al.*, 2007; Brown *et al.*, 2008). Interactions of soil minerals with organic substances and microbes also have an enormous impact on the formation and transformation of metal oxides. Al and Fe oxides, especially in their nanoparticulate forms, are among the most reactive components of acidic and neutral soils. Such metal oxides are ubiquitous and play a significant role in influencing soil behaviour, e.g. mineral catalysis of humic substance formation, and influence on enzymic stability and microbial activity, and together with microbial activities in metal and mineral transformations they have a great impact on soil physical, chemical and biological processes (Huang *et al.*, 2005).

Metal mobilization

Metal mobilization from rocks, minerals, soil and other substrates can be achieved by protonolysis, complexation by excreted metabolites and Fe(III)-binding siderophores, chemical oxidation or reduction, indirect Fe(III) attack, and methylation, which can result in volatilization (Fig. 2). In addition, other excreted metabolites with metal-complexing properties, e.g. amino acids, phenolic compounds and organic acids, may play a role. Low-molecular-mass carboxylic acids can play an important role in chemical attack of minerals, providing protons as well as a metal-chelating anion (Burgstaller & Schinner, 1993; Jacobs *et al.*, 2002a, b; Huang *et al.*, 2004; Lian *et al.*, 2008a, b). Oxalic acid can leach metals that form soluble oxalate complexes, including Al and Fe (Strasser *et al.*, 1994). Such activity may be involved in the weathering of silicate minerals such as feldspars (Drever & Stillings, 1997). Solubilization mechanisms may have adverse consequences when metals are mobilized from toxic-metal-containing minerals, e.g. pyromorphite [Pb₅(PO₄)₃Cl]-contaminated soil and other solid wastes (Sayer *et al.*, 1999; Fomina *et al.*, 2004, 2005a, b). Degradation of persistent carbon sources, such as charcoal and black shale, can be accelerated by fungal activity, which in turn may accelerate release of toxic metals as organic metal complexes (Wengel *et al.*, 2006). It has been shown that microbes and their extracellular products can influence the mobility of metals, e.g. Cu, from waste-disposal sites, even under the relatively low

nutrient fluxes that dominate subsurface systems (Boult *et al.*, 2006).

Microbes can also mobilize metals and attack mineral surfaces by redox processes (Ehrlich, 1996; Lloyd & Lovley, 2001; Holden & Adams, 2003; Schröder *et al.*, 2003; Lloyd *et al.*, 2003): Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II) respectively (Table 1, Fig. 2). Microbial reduction of Fe(III) and Mn(IV) may also be a means for releasing contaminant metals adsorbed to Fe(III) and Mn(IV) oxides, and this process may be enhanced by humic materials or related compounds (Lovley & Coates, 1997; Lloyd *et al.*, 2003). Bacterial Fe(III) reduction resulted in release of Mn and Co from goethite (Bousserrhine *et al.*, 1999), Pu from contaminated soils (Rusin *et al.*, 1993) and Ra from uranium mine tailings (Landa & Gray, 1995). Mercuric ion, Hg²⁺, can be enzymically reduced to metallic mercury by bacteria and fungi, which serves as a resistance and detoxification mechanism as Hg⁰ is volatile (Gadd, 1993b; Lloyd *et al.*, 2003; Barkay & Wagner-Dobler, 2005). Metallic mercury may also be oxidized to Hg²⁺ as a result of interaction with metabolic by-products (Barkay & Wagner-Dobler, 2005; Ehrlich & Newman, 2009). Enzymic reduction of Pu(IV) to the more soluble Pu(III) under anaerobic conditions was demonstrated for *Geobacter metallireducens* GS-15 and *Shewanella oneidensis* MR-1 (Boukhalfa *et al.*, 2007). Ferric iron, Fe(III), can be enzymically reduced to ferrous iron, Fe(II), with a suitable electron donor (Schröder *et al.*, 2003). Many Fe(III) reducers are heterotrophs and in some anaerobic environments such Fe(III) respiration may be a more important mechanism of carbon source decomposition than sulfate reduction (Ehrlich & Newman, 2009). Some Fe(III) reduction can be the result of metabolic products such as H₂S or formate, or other secondary metabolites. Naturally occurring microbially produced metal chelators that may solubilize Fe(III) include oxalate, citrate, humic acids and tannins.

Methylated derivatives of several elements naturally arise in the environment as a result of chemical and biological methylation, microbes playing significant roles in the latter process (Thayer, 1989; Gadd, 1993b). Methylation of Hg, Sn and Pb, and the metalloids As, Se and Te (see later), can be mediated by a range of microbes, including clostridia, methanogens and sulfate-reducing bacteria under anaerobic conditions, and principally fungi under aerobic conditions, such as *Penicillium* and *Alternaria* spp., as well as a variety of bacteria, including pseudomonads. There is also evidence for methylation of Sb by diatoms. Methyl groups are enzymically transferred to the metal, and a given species may transform a number of different metal(loid)s. Methylated metal compounds formed by these processes differ in their solubility, volatility and toxicity. Volatile methylated species are often lost from the soil. There are examples of methyl-accumulating reactions for Tl, Pd, Pt, Au and Cr but the involvement of microbial/abiotic components is unclear. Mercuric ion (Hg²⁺) may be methylated by bacteria and fungi to the more toxic

methylmercury [(CH₃)₂Hg⁺] (Barkay & Wagner-Dobler, 2005). Some bacteria can methylate methylmercury, forming volatile dimethylmercury. Methylmercury as well as phenylmercury can be enzymically reduced to volatile metallic mercury, Hg⁰, by some bacteria. Phenylmercury can also be microbially converted to diphenylmercury (Barkay & Wagner-Dobler, 2005).

Siderophores

Siderophores are the largest class of known compounds that can bind and transport, or shuttle, Fe. They are highly specific Fe(III) ligands (formation constants often greater than 10³⁰). These low-molecular-mass coordination molecules are excreted by a wide variety of fungi and bacteria to aid Fe assimilation. Although the mechanism could be used to acquire other metals, Fe is the only known essential element for which these specific organic shuttles operate. This is probably because Fe is needed in larger amounts by cells than other poorly soluble metals, and given the low solubility-product constant of ferric hydroxide (less than 10⁻³⁸), the concentration of free Fe³⁺ is too low to support microbial growth at pH values where most life exists. Organisms have most likely evolved mechanisms to ensure that Fe demand is met through the production of species-specific siderophores, or by attachment to a solid Fe mineral, e.g. Fe oxides, to shorten the pathway between the Fe substrate and cellular site of uptake (Kalinowski *et al.*, 2000; Glasauer *et al.*, 2004). Siderophores can complex other metals apart from iron, in particular actinides. Because of such metal-binding abilities, there are potential applications for siderophores in medicine, reprocessing of nuclear fuel, bioremediation of metal-contaminated sites and treatment of industrial wastes (Renshaw *et al.*, 2002).

Metal immobilization

Microbial biomass provides a metal sink, by biosorption to cell walls, pigments and extracellular polysaccharides, intracellular accumulation, or precipitation of metal compounds in and/or around cells, hyphae or other structures (Gadd, 1986, 1993a, 2000a, 2001a, b, 2007; Baldrian, 2003; Fomina *et al.*, 2007a, b) (Table 1, Figs 2 and 4). All microbial materials can be effective biosorbents for metals except for mobile alkali metal cations like Na⁺ and K⁺, and this can be an important passive process in living and dead organisms (Gadd, 1993a, 2009b; Sterflinger, 2000; Wang & Chen, 2009).

In natural systems, metal bioavailability is determined by interactions with environmental components, such components including clay and other minerals, humic substances, soil colloidal materials, biogenic debris and exudates, and living organisms. Sorption is one of the most important reactions that influences bioavailability, and metal sorption to cells is likely to play an important role in all microbe–metal–mineral interactions (Burford *et al.*, 2003a), taking place over a massive range of

timescales from milliseconds to years (Borda & Sparks, 2008; Theng & Yuan, 2008). Metal interactions with specific cell-surface groups may also enhance or inhibit metal transport, metal transformations and biomineralization processes (Barkay & Schaefer, 2001).

The major biosphere compartments, such as soil and the oceans, contain a vast amount of metal-sorbing material with high surface area to volume ratios: bacteria have the highest surface area : volume ratios of any living organisms. Microbes are major components of the soil while biogenic particles dominate oceanic detrital phases (Stumm & Morgan, 1996). Many studies have shown that microbial cells, on a specific unit area basis, can exhibit higher sorption values for metals than even clay minerals (Garnham *et al.*, 1993; Morley & Gadd, 1995). It is possible that biosorption phenomena have a more significant role in metal/radionuclide speciation, bioavailability and mobility in the biosphere than has previously been supposed (Krantz-Rulcker *et al.*, 1993, 1996; Ledin *et al.*, 1996; McLean *et al.*, 2002); it should be emphasized that this may also accompany or precede nucleation, precipitation and biomineral formation (Burford *et al.*, 2003a; Gadd, 2007, 2009a, b).

Where microbial reduction of a metal to a lower redox state occurs, mobility and toxicity may be decreased for several elements (Lovley, 2001; Lloyd & Lovley, 2001; Finneran *et al.*, 2002a, b; Lloyd *et al.*, 2003; Holden & Adams, 2003; Wall & Krumholz, 2006), e.g. U(VI) to U(IV) and Cr(VI) to Cr(III) (Phillips *et al.*, 1995; Smith & Gadd, 2000). U(VI) reduction to U(IV) can be the basis of U removal from contaminated waters and leachates as well as the formation of uranium ores such as uraninite (UO₂) (Lovley & Coates, 1997; Lovley, 2001; Finneran *et al.*, 2002a, b; Lloyd, 2003; Lloyd & Renshaw, 2005; Landa, 2005). Anaerobically, hexavalent U(VI) can be reduced to tetravalent U(IV) by a number of bacteria using either H₂ or one of a variety of organic electron donors (Lovley & Coates, 1997; Landa, 2005; Wall & Krumholz, 2006). Aerobic or anaerobic microbial reduction of Cr(VI) to Cr(III) is widespread (Smith & Gadd, 2000; McLean & Beveridge, 2001). Sulfur- and sulfate-reducing bacteria are particularly important in reductive precipitation of e.g. U(VI), Cr(VI), Tc(VII) and Pd(II) (Aubert *et al.*, 1998; Lloyd *et al.*, 1999a, b; Lloyd & Macaskie, 1998; Lloyd, 2003; Lloyd & Renshaw, 2005). Some sulfate-reducing bacteria such as *Desulfotomaculum reducens* share physiological properties of both sulfate- and metal-reducing groups of bacteria, and can use Cr(VI), Mn(IV), Fe(III) and U(IV) as sole electron acceptors (Tebo & Obratzsova, 1998). Such direct processes may accompany indirect mechanisms of reductive metal precipitation, e.g. in sulfate-reducing bacterial systems, where reduction of Cr(VI) can be a result of indirect reduction by Fe²⁺ and the produced sulfide. Elemental silver (Ag⁰) and gold (Au⁰) species result during microbial reduction of ionic silver and gold species (Kierans *et al.*, 1991; Holden & Adams, 2003; Southam *et al.*, 2009). Other redox transformations of metals such as

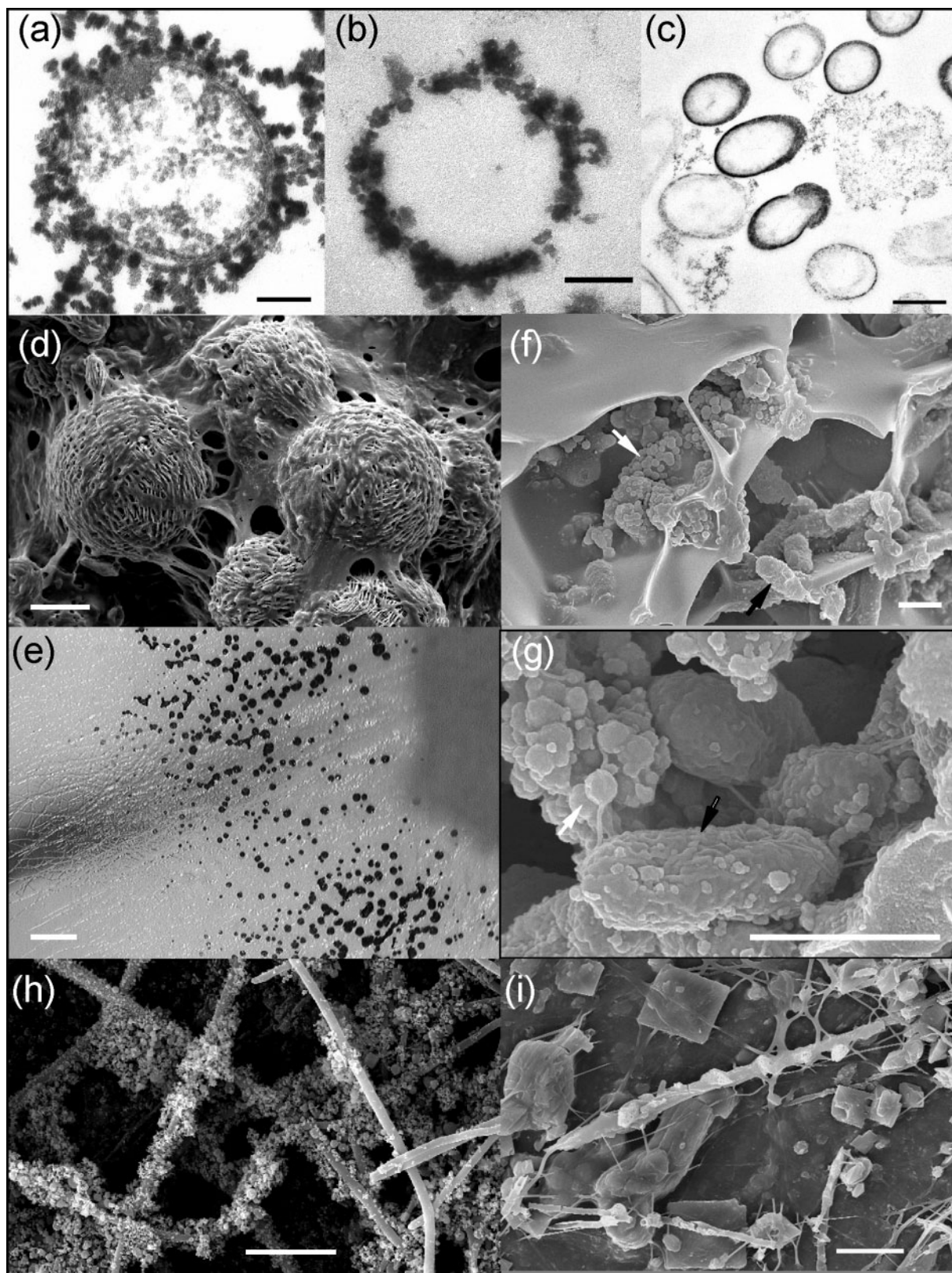


Fig. 4. Some examples of metal(loid) and metal mineral deposition by microbes. (a) Transmission electron microscopy (TEM) thin section showing abiotically precipitated goethite nano-crystals sorbed to the cell wall of *Shewanella putrefaciens*. Bar, 150 nm. (b) TEM thin section of an unknown bacterial cell, taken from a Yellowstone hot spring, embedded in a sample of metal-rich precipitates. Bar, 150 nm. (c) TEM thin section showing uranium precipitates formed in the periplasmic space of *Geobacter metallireducens* cells during dissimilatory reduction of U(VI). Bar, 150 nm. (a, b, c adapted from Glasauer *et al.*, 2004.) (d) Moolooite (copper oxalate) deposition within fungal biofilm consisting of aggregated hyphae and exopolymeric matrix. Bar, 20 μm (M. Fomina & G. M. Gadd, unpublished). (e) MnO_x deposition in agar media around a colony of *Acremonium strictum* growing in the presence of MnSO_4 . Bar, 0.5 cm (Z. Wei & G. M. Gadd, unpublished) (f, g) Precipitation of selenium-sulfur granules within a sulfate-reducing biofilm matrix. Individual cells of *Desulfomicrobium norvegicum* (black arrows) form colonies within the matrix, with abundant Se-S nanoparticles (white arrows) precipitated beneath the biofilm canopy. Bars, 1 μm (adapted from Hockin & Gadd, 2003). (h) Uranium biomineralization of fungal hyphae with uranium phosphates after growth in the presence of U_3O_8 . Bar, 10 μm (adapted from Fomina *et al.*, 2007a). (i) A crust of calcium oxalate (weddelite and whewellite) crystals and tubular crystalline sheath around fungal hyphae formed on medium containing CaCO_3 and $\text{Cu}_3(\text{PO}_4)_2$. Bar, 20 μm (adapted from Gadd *et al.*, 2007; M. Fomina & G. M. Gadd, unpublished).

Mo, V and Sb are also known, which must play a role in their speciation, although rather less is known about such rarer elements. Microbes can also mediate formation of several inorganic and organic biominerals, e.g. oxalates, phosphates, sulfides, oxides and carbonates, which lead to metal immobilization (Gadd, 2007) (Table 1, Figs 2 and 4).

Weathering of iron-containing minerals in rocks, soils and sediments is promoted partly by bacterial and fungal action and partly by chemical activity (Lovley, 2000). Mobilized ferrous iron, Fe(II), may be biologically or abiotically oxidized to Fe(III) at $\text{pH} > 5$ under anaerobic or partially or fully aerobic conditions. Some bacteria can oxidize ferrous iron enzymically with the generation of energy, e.g. acidophiles such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Sulfolobus* spp., *Acidianus brierleyi* and *Sulfobacillus thermosulfidooxidans*. Fe(II) is least susceptible to autoxidation below pH 5. Some bacteria growing at circumneutral pH can also oxidize Fe(II) enzymically under partially reduced conditions, e.g. the stalked bacterium *Gallionella ferruginea* and sheathed bacteria such as *Leptothrix* spp. (Ehrlich & Newman, 2009). Fe(II) can also be oxidized non-enzymically by microbes when their metabolic activities alter the microenvironment to favour autoxidation. Some Fe(III) precipitation may also occur as a result of the destruction of ferric iron chelates. Fe(III) may also be locally concentrated by adsorption to microbial surfaces and metal oxides. Microbial formation of hydrous iron oxides in aqueous environments may cause accumulation of other metal ions by coprecipitation or adsorption: such adsorbed metals may be remobilized by reduction of the iron oxides or acidification (Ehrlich & Newman, 2009).

Organic matter decomposition and metal cycling

Organic matter decomposition is one of the most important microbial activities in the biosphere, and the ability of microbes, mainly bacteria and 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 may be broken down by extracellular enzymes before

cellular uptake and metabolism. These latter compounds include cellulose, pectin, lignin, lignocellulose, chitin and starch, and also hydrocarbons, pesticides and other xenobiotics that may be anthropogenically produced. Degradation of such substances results in redistribution of component elements between organisms and environmental compartments. The vast majority of elements in plant, animal and microbial biomass (>95%) comprise carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur; as well as these, several other elements are typically found in living organisms, most with essential biochemical and structural functions, e.g. K, Ca, Mg, B, Cl, Fe, Mn, Zn, Cu, Mo, Ni, Co, Se, Na and Si. However, all 90 or so naturally occurring elements may be found in plants, animals and microbes, including Au, As, Hg, Pb, Cd and U. Some of these elements will be taken up as contaminants in food and from the environment. Therefore, it should be stressed that all decomposition, degradative and pathogenic microbial activities are linked to the cycling of these constituent elements, most of which are metals and some of which may be radionuclides accumulated from anthropogenic sources. This simple perspective on organic matter decomposition illustrates the global involvement of microbes in almost all elemental cycles.

Biodegradation of organometallic (and organometalloid) compounds, still widely used in agriculture and industry, can result from direct enzymic action, or by microbial facilitation of abiotic degradation, e.g. by alteration of pH and excretion of metabolites (Gadd, 1993b, 2000b). Organotin, such as tributyltin oxide and tributyltin naphthenate, may be degraded to mono- and dibutyltins, inorganic Sn(II) being the ultimate product (Gadd, 2000b). Organomercury compounds may be detoxified by organomercury lyase, the resultant Hg^{2+} being subsequently reduced to the less toxic, diffusible and volatile Hg^0 by mercuric reductase (Gadd, 1993b).

Metalloid transformations

Microbes can transform certain metalloids (elements with properties intermediate between those of metals and non-metals). Elements included in the chemical classification of

metalloids are B, Si, Ge, As, Sb, Te and Po. Se is also often considered under this heading. Microbial oxidation, reduction and methylation influence the bioavailability and toxicity of many metalloids. For example, methylated Se derivatives are volatile and less toxic than inorganic forms while reduction of metalloid oxyanions, such as selenite or tellurite, to amorphous elemental Se or Te respectively, results in immobilization and detoxification. As and Se are readily metabolized by prokaryotes, participating in a full range of metabolic functions including assimilation, methylation, detoxification and anaerobic respiration. The speciation and mobility of As are affected by microbes through oxidation/reduction reactions as part of resistance and respiratory processes (Stolz *et al.*, 2006).

For Se, some bacteria can use selenate (SeO_4^{2-}) as a terminal electron acceptor in dissimilatory reduction and also reduce and incorporate Se into organic components, e.g. selenoproteins. SeO_4^{2-} and selenite (SeO_3^{2-}) can be reduced to Se^0 , with SeO_3^{2-} reduction appearing more ubiquitous than SeO_4^{2-} reduction. However, only SeO_4^{2-} can support bacterial growth under anaerobic conditions: SeO_4^{2-} reduction to Se^0 is a major sink for Se oxyanions in anoxic sediments (Oremland *et al.*, 1989; Stolz & Oremland, 1999; Oremland & Stolz, 2000). Reduction to Se^0 can be considered a detoxification mechanism (Dungan & Frankenberger, 1999; Yee & Kobayashi, 2008). The opposite process of Se^0 oxidation can also occur in soils and sediments (Dowdle & Oremland, 1998; Losi & Frankenberger, 1998).

Methylation of Se is a ubiquitous microbial property and can occur in soils, sediments and water (Gadd, 1993b). Bacteria and fungi are the most important Se-methylators in soil (Karlson & Frankenberger, 1988), with the most frequently produced volatile being dimethyl selenide [$(\text{CH}_3)_2\text{Se}$; DMSe] (Karlson & Frankenberger, 1988, 1989; Thompson-Eagle *et al.*, 1989). Other volatiles produced in smaller amounts include dimethyl diselenide [$(\text{CH}_3)_2\text{Se}_2$; DMDSe] (Dungan & Frankenberger, 1999). The opposite process of demethylation can also occur in soil and water systems (Oremland *et al.*, 1989). Te may also be transformed by reduction and methylation (Chasteen & Bentley, 2003). Reduction of tellurite (TeO_3^{2-}) to Te^0 results in grey to black coloration of microbial colonies and extracellular and intracellular precipitation (Gharieb *et al.*, 1999). Dimethyl telluride (DMTe) is the main product of Te methylation (Chasteen & Bentley, 2003). Methylation of As can be mediated by many organisms, with compounds having the general structure $(\text{CH}_3)_n\text{AsH}_{3-n}$ and mono-, di- and trimethylarsine ($n=1, 2, 3$ respectively) being major volatile compounds (Bentley & Chasteen, 2002). Methylation pathway(s) involve a series of steps in which the reduction of the pentavalent form of As is followed by the oxidative addition of a methyl group (Dombrowski *et al.*, 2005), generating a growing methylated series of methyl arsenite (MMA), dimethyl arsenate (DMA-V), dimethyl arsenite (DMA-III) and trimethyl arsine oxide (TMAO). Two different As reduction activities have been found in

bacteria. One is the dissimilatory reduction for anaerobic respiration, which involves arsenate as the terminal electron acceptor. The second detoxifies As by converting arsenate to arsenite, the substrate of the As efflux pumps and a determinant of As resistance (Bentley & Chasteen, 2002; Paez-Espino *et al.*, 2009). Microbial oxidation of arsenite to arsenate by arsenite oxidase enzymes could be a detoxification mechanism (Tamaki & Frankenberger, 1992; Lebrun *et al.*, 2003), with arsenite oxidation serving as an electron donor.

Mineral transformations

Microbes are involved in the formation and deterioration of minerals, including those produced biogenically. The majority of such interactions are probably accompanied by changes in metal speciation and mobility.

Mineral formation

Biomineralization refers to the collective processes by which organisms form minerals. Mineral synthesis can be categorized into biologically induced mineralization (BIM) and biologically controlled mineralization (BCM). Biologically induced mineralization occurs when an organism modifies its local microenvironment creating conditions such that there is extracellular chemical precipitation of mineral phases (Bazyliński, 2001; Hamilton, 2003; Dupraz *et al.*, 2009) (Fig. 4). The organism does not appear to control the biomineralization process in BIM while a great degree of control over biomineralization is exerted by the organism in BCM, e.g. magnetosome formation in magnetotactic bacteria, and complex cellular biomineral structures in certain eukaryotes (Bazyliński & Schubbe, 2007; Posfai & Dunin-Borkowski, 2009; Gadd & Raven, 2010). Organomineralization has also been used as a term encompassing biomineralization processes (Dupraz *et al.*, 2009). The term 'organomineral' has been used to refer to minerals that are affected by organic substances, mostly life-related, but not directly produced by living cells. Biominerals are defined as being directly produced by an organism, while organominerals are formed under the influence of adjacent organic matter (Perry *et al.*, 2007). However, such definitions are not universally accepted because of the obvious imprecision of almost all such terms (Altermann *et al.*, 2009).

Most biomineralization examples referred to in this article relate to biologically induced mineralization. This can result from microbial oxidation or reduction of a metal species, metabolite excretion (e.g. sulfide, oxalate) and other metabolism-dependent transformations of metal species, with microbial surfaces providing chemically reactive sites for sorption (\equiv biosorption), which can also lead to the nucleation and formation of mineral precipitates around biomass (Beveridge, 1989; Fortin *et al.*, 1997; McLean *et al.*, 2002; Lloyd *et al.*, 2008; Gadd, 2009b).

Highly reactive bacterial cell surfaces can bind metal ions (Beveridge, 1989), inorganic anions (e.g. silicates; Urrutia & Beveridge, 1994) and even pre-formed nanominerals (Glasauer *et al.*, 2001), leading to fine-grained mineral phases on cell surfaces (Lloyd *et al.*, 2008). This reactivity arises from the array of ionizable groups, such as carboxylates and phosphates, present in the lipopolysaccharides of Gram-negative cell walls and the peptidoglycan, teichuronic acids and teichoic acids of Gram-positive bacteria (Beveridge, 1989). Sometimes nanomineral phases can form directly in cytoplasmic components of bacteria, such as magnetite and greigite (Bazylinski & Moskowitz, 1997) or amorphous iron hydroxide (Glasauer *et al.*, 2002). External metal precipitation and biomineralization may also result from indirect effects of bacterial metabolism on microenvironmental geochemistry (Lee & Beveridge, 2001; McLean *et al.*, 2002; Lloyd *et al.*, 2008). Precipitation can also be due to the production of reactive components which either bind metals or catalyse precipitation (Macaskie *et al.*, 1994; Mossman *et al.*, 1999; Wang *et al.*, 2001; Hockin & Gadd, 2003, 2006, 2007; Gadd, 2007) (Fig. 4). The nature of the resultant mineral(s) may depend on the nature of the cell surface, the cellular microenvironment, and the presence of reactive anions, e.g. sulfide, carbonate and phosphate. However, such biomineralization can also occur independent of microbial activity and on dead biomass. Mineral phases may undergo further changes in crystallinity with time, and some minerals may incorporate other metals into their structure (Watson *et al.*, 1995, 2000; Brown *et al.*, 1999; McLean *et al.*, 2002; Lloyd *et al.*, 2008). The formation of solid mineral phases by bacterial processes may result in mineral deposition over geological timescales (Beveridge *et al.*, 1983). Oxidative and reductive reactions mediated by microbes play important roles in the iron cycle, and the formation of some sedimentary iron deposits has been attributed directly to microbial iron oxidation. Bacterial iron reduction has been associated with the formation of magnetite and siderite (Ehrlich & Newman, 2009).

While much work on microbial mineral formation has been carried out using bacteria, it should be stressed that all major microbial groups have roles in metal immobilization and mineral formation, e.g. cyanobacteria, microalgae, protozoa and fungi. While cyanobacterial and microalgal processes are generally of greater significance in aquatic environments, fungi have especially important roles in the terrestrial environment regarding mineral dissolution, metal and anion cycling, and also mineral formation in free-living and symbiotic forms (see later) (Fig. 4). As in bacteria, formation of secondary minerals by fungi can occur through metabolism-independent and -dependent processes (Gadd, 2007). Precipitation, nucleation and deposition of crystalline material on and within cell walls are influenced by factors such as pH and wall composition. Cationic species of Si(IV), Fe(III), Al(III) and Ca(II), which may be released through dissolution mechanisms, stimulate precipitation of compounds that may bond soil

particles: precipitation of carbonates, phosphates and hydroxides increases soil aggregation. Hyphae and any associated exopolymeric material can enmesh soil particles, and also release organic metabolites that enhance aggregate stability (Bronick & Lal, 2005). Apart from the more detailed biomineral examples that follow, a variety of other secondary minerals have been recorded associated with fungal biomass, e.g. birnessite, ferrihydrite, iron gluconate, calcium formate, forsterite, goethite, halloysite, hydrocerussite, todorokite, moolooite, montmorillonite and uranium phosphates (Burford *et al.*, 2003a, b; Gadd, 2007; Fomina *et al.*, 2007a, b, 2008) (Fig. 4).

Mineral biodeterioration

Direct and indirect physical, chemical and biochemical mechanisms are involved in mineral biodeterioration by microbes (Sand, 1997; Edwards *et al.*, 2005; Amundson *et al.*, 2007; Lian *et al.*, 2008a, b; Uroz *et al.*, 2009) (Figs 1 and 2). Biomechanical deterioration of rocks and minerals can occur through penetration, boring and burrowing into decaying material and along crystal planes in e.g. calcitic and dolomitic rocks (Sterflinger, 2000; Golubic *et al.*, 2005; Smits, 2006; Gadd, 2007; Cockell & Herrera, 2008). Cleavage penetration can also occur with lichens (Banfield *et al.*, 1999; Chen *et al.*, 2000; Adamo & Violante, 2000). However, biochemical actions are believed to be more important processes than mechanical degradation. Biochemical weathering of rocks and minerals can occur through excretion of e.g. H⁺, organic acids and other metabolites. This can result in changes in the mineral microtopography through pitting and etching of surfaces to complete dissolution (Drever & Stillings, 1997; Ehrlich, 1998; Gharieb *et al.*, 1998; Kumar & Kumar, 1999; Adamo & Violante, 2000; Adeyemi & Gadd, 2005; Edwards *et al.*, 2005; Uroz *et al.*, 2009). Mineral dissolution may result in release of toxic (Sayer *et al.*, 1999) or essential metals like K (Lian *et al.*, 2008a, b). Fungi generally acidify their microenvironment via a number of mechanisms, which include the excretion of protons and organic acids, while respiratory CO₂ can result in carbonic acid formation. In addition, fungi excrete a variety of other metal-complexing metabolites (e.g. siderophores, carboxylic acids, amino acids and phenolic compounds) (Burgstaller & Schinner, 1993). The origin of fungal tunnels within soil minerals has been explained as a result of dissolution and 'burrowing' within the mineral matrix – the 'rock-eating fungi' hypothesis (Jongmans *et al.*, 1997; Landeweert *et al.*, 2001; Golubic *et al.*, 2005; Cockell & Herrera, 2008). An additional 'rock-building fungi' hypothesis has also been presented which explains how fungal tunnels may occur inside minerals (Fomina *et al.*, 2010). The 'rock-building fungi' hypothesis particularly highlights fungal involvement in mineral formation. It is likely that fungi explore and burrow within pre-existing cracks, fissures, pores and weak points in weatherable minerals and, during colonization and mineral dissolution, build a matrix of secondary minerals often of the same chemical composition as the

host rock, e.g. secondary CaCO_3 precipitation in calcareous soil and rock (Verrecchia, 2000). As a result, fissures and cracks become secondarily cemented with mycogenic minerals. In less easily weathered silicate minerals such as feldspars, fungal-mediated precipitation of amorphous aluminosilicates (Van Breemen *et al.*, 2000) may modify the appearance of pre-existing cracks and fissures in an analogous manner. After death and degradation of fungal hyphae, tunnels may be left within surficial patinas and crusts representing distinct signatures of previous biogeochemical fungal activity.

Common mineral and biomineral transformations by microbes

Bauxite

Aluminium is the third most abundant element in the Earth's crust after silicon and oxygen. Various microbes are involved in the formation of some aluminium-containing minerals through bioweathering. The formation of bauxite (bauxitization) involves two stages where microbes are involved. The major constituents of bauxite are Al_2O_3 , Fe_2O_3 and SiO_2 or aluminosilicate in various forms, and the source material for bauxitization may be volcanic and other aluminosilicate rocks, limestone and alluvium. Weathering of source rock (formation of protobauxite) is promoted by those activities of bacteria and fungi that mobilize aluminium, iron and silicon, which are then subsequently precipitated as oxides, silica and silicate minerals. Maturation of protobauxite to bauxite is promoted by iron-reducing and fermentative bacteria under anaerobic conditions, which selectively mobilize iron oxides and silica or silicate, and enrich the bauxite in aluminium (Ehrlich & Newman, 2009).

Carbonates

A significant portion of insoluble carbonate at the Earth's surface is of biogenic origin. Certain bacteria, cyanobacteria and fungi can deposit calcium carbonate extracellularly (Verrecchia *et al.*, 1990; Chafetz & Buczynski, 1992). Mineralized carbonate precipitates are also found in association with bacterial biofilms (Glasauer *et al.*, 2002). Some algae, including certain green, brown and red algae, and chrysophytes, such as coccolithophores, deposit calcium carbonate as cell-surface structures, while some protozoa (foraminifera) use it for tests or shells. Calcium, as well as some magnesium ions, can combine with carbonate ions of biogenic origin sometimes to massive scales; e.g. the White Cliffs of Dover, UK, is a biogenic carbonate deposit in the form of chalk. Carbonate precipitation is possibly the most important process that influences global carbon cycling (Dupraz *et al.*, 2009).

Calcium carbonate associated with stromatolites, originating from types of cyanobacterial mats, may be a result of calcium carbonate entrapment or deposition as well as

cyanobacterial photosynthesis and bacterial activities. Calcium carbonate associated with travertine (a porous limestone) and lacustrine carbonate crusts and nodules can result from cyanobacterial photosynthesis in freshwater environments. Calcareous nodules are formed around rounded rocks, stones, pebbles, shells, etc., to which calcium-carbonate-depositing cyanobacteria are attached. Most bacteria, including cyanobacteria, and some algae cause precipitation of CaCO_3 close to or at their cell surface. In contrast, some algae and protozoa form CaCO_3 intracellularly and then export it to the cell surface to become support structures. These include the coccolithophores (green algae) and foraminifera (Protozoa, Sarcodinae), the mineral form of calcium carbonate deposited being calcite or aragonite. Apart from calcium and magnesium carbonates, others that may have a microbial involvement in their formation include hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], SrCO_3 , siderite (FeCO_3), rhodochrosite (MnCO_3) and sodium carbonate (natron, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) (Ehrlich & Newman, 2009). The range of composition and crystallography of carbonate precipitates produced by microbial communities is influenced by environmental conditions and community species composition (Dupraz & Visscher, 2005). Key components of carbonate biomineralization in microbial mat systems are the 'alkalinity' engine (microbial metabolism and environmental conditions which affect the calcium carbonate saturation index) and microbially produced extracellular polymeric substances which provide a template for carbonate nucleation (Dupraz *et al.*, 2009). Alkalinity produced by sulfate-reducing bacteria has a prominent role in such carbonate deposition (Dupraz *et al.*, 2009).

Insoluble carbonates may be broken down by microbial attack. This is usually the result of organic and inorganic acid formation but may also involve physical processes (Lian *et al.*, 2008a). Various bacteria, fungi, lichens, cyanobacteria and even algae have been implicated (Schneider & Le Campion-Alsumard, 1999; Adamo & Violante, 2000; Hoppert *et al.*, 2004; Cockell & Herrera, 2008; Lian *et al.*, 2008a). Such activity is evident on limestones and marble used in building construction, and also in natural limestone formations such as coral reefs, where limestone-boring cyanobacteria, algae and fungi are active in the breakdown process (Golubic *et al.*, 2005; Cockell & Herrera, 2008). Bacteria and fungi contribute to the discoloration and destruction of structural limestone and marble and are also involved in patina formation. Fungal attack on carbonate substrates (dolomites and limestones) can result in significant microbial diagenesis of these substrates to neo-dolomite, glushinskite, weddellite, whewellite and possibly struvite, as well as intense substrate 'de-micritization' and 'micritization' with oxalates, grain bridging and cementation, open space filling, formation of intergranular and intragranular porosity, and permeability enhancement. Advanced stages of diagenesis were characterized by dissolution and replacement of the original minerals by the new substrates

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

Oxalates

Calcium oxalate is the most common form of oxalate encountered in the environment, mostly occurring as the dihydrate (weddellite) or the more stable monohydrate (whewellite) (Gadd, 1999). Calcium oxalate crystals are commonly associated with free-living, pathogenic and plant symbiotic fungi, and lichens, and are formed by the precipitation of solubilized calcium as the oxalate (Gadd, 1999; Gharieb *et al.*, 1998; Adamo & Violante, 2000; Adamo *et al.*, 2002). Biotic fungal calcium oxalate can exhibit a variety of crystalline forms (tetragonal, bipyramidal, plate-like, rhombohedral or needles) (Arnott, 1995). Calcium oxalate precipitation has an important influence on biogeochemical processes in soils, acting as a reservoir for calcium, and also influencing phosphate availability. Fungi can also produce other metal oxalates on interacting with a variety of different metals and metal-bearing minerals, e.g. Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (White *et al.*, 1997; Gadd, 1999; Sayer *et al.*, 1999; Sayer & Gadd, 1997; Gadd, 2007) (Fig. 4). The formation of toxic metal oxalates may also provide a mechanism enabling fungi to tolerate high concentrations of toxic metals (Gadd, 1993a; Jarosz-Wilkolazka & Gadd, 2003).

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

Oxides

A good example of microbial oxide formation is provided by manganese. Many bacterial species can oxidize this metal, which is then deposited on cells, sheaths or spores as oxides (Tebo *et al.*, 2005). Some species promote oxidation non-enzymically, others enzymically, with possible involvement of a multicopper oxidase system; they include spore-forming and non-spore-forming rods, sheathed and appendaged bacteria as well as the usual morphological forms of Gram-

positive and -negative bacteria from a diverse range of freshwater, marine and terrestrial ecosystems (Tebo *et al.*, 2005). Several fungi can also promote Mn(II) oxidation to Mn(IV)O_2 , including *Acremonium* spp. (Miyata *et al.*, 2004, 2006, 2007; Saratovsky *et al.*, 2009) (Fig. 4). In many cases, fungal oxidation is probably non-enzymic and due to interaction with a metabolic product (e.g. a hydroxy acid) or a cellular component (Ehrlich & Newman, 2009), although the involvement of laccase and/or multicopper oxidases has been shown in ascomycetes, which are ubiquitous in natural environments (Miyata *et al.*, 2004, 2007; Tebo *et al.*, 2005). For some basidiomycete white-rot fungi such as *Phanerochaete chrysosporium*, redox transformations of manganese occur during lignin degradation but this oxidation is thought to be of minor significance regarding manganese redistribution in the environment (Ehrlich & Newman, 2009). The MnO_x material produced by *Acremonium* KR21-2 is manifest as small crystalline particles which adopt a todorokite-like tunnel structure; this is in striking contrast to previously reported microbial MnO_x materials, which adopt layered birnessite-type structures (Saratovsky *et al.*, 2009). Non-enzymic microbial Mn(II) oxidation may be effected through production of metabolites, e.g. hydroxycarboxylic acids such as citrate, lactate, malate, gluconate or tartrate. Some microbes can oxidize Mn(II) and Fe(II) in metal-bearing minerals such as siderite (FeCO_3) and rhodochrosite (MnCO_3) and precipitate them as oxides (Grote & Krumbein, 1992).

Manganese and iron oxides are major components (20–30 %) along with clay (~60 %) and various trace elements in the brown-to-black veneers known as desert varnish or rock varnish (Grote & Krumbein, 1992; Gorbushina, 2007). The prevalence of manganese oxidizers in desert varnish implies a role for these bacteria in its formation (Ehrlich & Newman, 2009). Manganese-oxidizing and -reducing bacteria also play an important role in the manganese cycle in freshwater and marine environments through the accumulation of manganese oxides in sediments. The oxides they form may be deposited as concretions formed around sediment grains, pebbles, mollusc shells, coral fragments, or other debris. Manganese oxide phases have high sorption capacities for numerous metal cations (e.g. Ni, Zn, Cu, Co, Mn, Pb and Cd), and also serve as strong oxidants for inorganic [e.g. As(III) to As(V); Cr(III) to Cr(IV)] and organic compounds such as humic substances (Tebo *et al.*, 2004; Miyata *et al.*, 2007). Furthermore, in anoxic environments, manganese oxides as well as Fe(III) (hydr)oxides become terminal electron acceptors for microbial metal respiration, potentially controlling the fates of a wide variety of organic compounds such as organic acids, fatty acids and aromatics in the environment (Lovley, 2000).

Conversely, manganese-reducing microbes may mobilize oxidized or fixed manganese, releasing it into the aqueous phase. A number of different, taxonomically unrelated bacteria can reduce manganese enzymically or non-enzymically. The bacteria that reduce manganese enzymically often do so as a form of respiration where oxidized

manganese serves as a terminal electron acceptor and is reduced to Mn(II) (Lovley, 2000). Some bacteria can reduce the oxidized manganese aerobically or anaerobically, whereas others can reduce it only anaerobically. Microbial reduction of oxidized manganese can also be enzymic or non-enzymic. Some bacteria and most of those fungi that reduce Mn(IV) oxides such as MnO₂ reduce them indirectly (non-enzymically), with the likely mechanism being the production of metabolic products that can act as reductants for Mn(IV) oxides such as formic acid, pyruvate, H₂S, sulfite, Fe(II) (bacteria) and oxalate (fungi) (Ehrlich & Newman, 2009). Microbial reduction of manganese oxides may also lead to the formation of manganous carbonate. Ferromanganese nodules on parts of the ocean floor are inhabited by manganese-oxidizing and -reducing bacteria, and these are likely to contribute to nodule formation (Ehrlich & Newman, 2009).

Many bacteria can precipitate and deposit Fe(III) oxides and hydroxides (e.g. FeOOH, Fe₃O₄) around their cells by enzymic, e.g. *Gallionella* sp., and non-enzymic processes, e.g. *Leptothrix* sp. (Ehrlich & Newman, 2009).

Phosphates

Phosphorus occurs primarily as organic phosphate esters and as inorganic forms, e.g. calcium, aluminium and iron phosphates. Organic phosphates are hydrolysed by phosphatases, which liberate orthophosphate during microbial decomposition of organic material. Microbes also liberate free orthophosphate from insoluble inorganic phosphates by producing organic or mineral acids or chelators, e.g. gluconate and 2-ketogluconate, citrate, oxalate and lactate, which complex the metal resulting in dissociation or, for iron phosphates, by producing H₂S. Phosphate-solubilizing activity is very important in the plant rhizosphere (Whitelaw *et al.*, 1999).

Microbes can also play a role in the formation of phosphate minerals such as vivianite [Fe₃(PO₄)₂·8H₂O], strengite (FePO₄·2H₂O) and variscite (AlPO₄·2H₂O). Here, the orthophosphate may arise from organic phosphate degradation while Fe or Al may arise from microbial solubilization of other minerals. Such formation of phosphate minerals is probably most common in soil (Ehrlich & Newman, 2009). Secondary mycogenic uranium mineral precipitates on fungal mycelia growing in the presence of uranium oxides or depleted uranium were found to be uranyl phosphate minerals of the meta-autunite group, uramphite and/or chernikovite (Fomina *et al.*, 2007a, 2008) (Fig. 4).

Silicates

Silica, silicates and aluminosilicates in rocks are weathered by biological, chemical and physical processes (Brehm *et al.*, 2005). Silicon liberated as soluble silicate can be assimilated by several microbial groups in order to fabricate cell-support structures. These groups include diatoms, some chrysophytes, silicoflagellates, some xantho-

phytes, radiolaria, and actinopods. Silicon-assimilating microbes such as diatoms and radiolaria are important in the formation of oceanic siliceous oozes, while diatoms are important in forming such oozes in lakes. Such 'cellular' silicon may later be returned to solution by weathering processes. Biosilicification of natural microbial mats has been shown to be a microbially mediated geochemical process, with a requirement for colloidal silica, an acidic pH and exposed organic surfaces, both of which favour colloidal silica sorption (Amores & Warren, 2007).

Silicon dioxide, when combined with oxides of magnesium, aluminium, calcium and iron, forms the silicate minerals in rocks and soil (Bergna, 1994). Silicates are the largest class of minerals, comprising 30 % of all minerals and making up 90 % of the Earth's crust (Ehrlich, 1998; Ehrlich & Newman, 2009). Silicate minerals are unstable in the biosphere and break down readily to form clays (Adamo *et al.*, 2002; Tazaki, 2006). Many kinds of bacteria, fungi and lichens play an important role in the dissolution of silicates, and therefore in the genesis of clay minerals, and in soil and sediment formation (Barker & Banfield, 1996, 1998; Rodriguez Navarro *et al.*, 1997; Banfield *et al.*, 1999; Adamo & Violante, 2000; Arocena *et al.*, 1999, 2003; Tazaki, 2006; Theng & Yuan, 2008; Cockell *et al.*, 2009a, b; Ehrlich & Newman, 2009). Even silicates of great physical and chemical resistance can be attacked, e.g. quartz sand, crystalline quartz and commercial glass (Brehm *et al.*, 2005). Microbial action is mainly indirect, through either the production of chelates or the production of acids (mineral or organic) or other metabolites, together with biomechanical effects (Cromack *et al.*, 1979; De La Torre *et al.*, 1992; Mandal *et al.*, 2002). In bioweathering of rock silicates and aluminosilicates, cleavage of Si–O–Si (siloxane) or Al–O bonds or removal of cations from the silicate crystal lattice may cause collapse of the silicate lattice structure. The mechanisms of attack may include microbially produced (1) ligands of cations; (2) organic or inorganic acids (a source of protons); (3) alkali (ammonia or amines); or (4) extracellular polysaccharides that act at acidic pH. Such agents may be excreted into the bulk phase but may also involve attached biofilm microbes on surfaces of silica or silicates resulting in etching (Bennett *et al.*, 1996, 2001). Such mechanisms of silicate dissolution may be instrumental in releasing limiting nutrients such as bound phosphorus and iron (Rogers & Bennett, 2004). For several bacteria, dissolution of silicates results from complexation of cationic components by 2-ketogluconate. Quartz (SiO₂) can be subject to slow dissolution by organic acids such as citric and oxalic acid (Bennett *et al.*, 1988), the mechanism of action being chelation rather than protonation. Hydration of respiratory or fermentative CO₂ to give the weak carbonic acid H₂CO₃ can also result in solubilization of silicates. Alkaline conditions can mobilize silicon from silicates, ammonia production from urea hydrolysis being one bacterial mechanism (Ehrlich & Newman, 2009).

In lichen weathering of silicate minerals, calcium, potassium, iron clay minerals and nanocrystalline aluminous

iron oxyhydroxides become mixed with fungal organic polymers (Barker & Banfield, 1998), while biotite was interpenetrated by fungal hyphae along cleavages, partially converting it to vermiculite (Barker & Banfield, 1996). The fungal partner has also been reported to be involved in the formation of secondary silicates, such as opal and forsterite, in lichen thalli (Gorbushina *et al.*, 2001). The transformation rate of mica and chlorite to 2 : 1 expandable clays was pronounced in ectomycorrhizosphere soil and was probably a result of the high production of organic acids and direct extraction of K^+ and Mg^{2+} by fungal hyphae (Arocena *et al.*, 1999).

Silicon compounds in the form of clays (aluminosilicates) can exert many effects on microbes in soil and stimulate or inhibit metabolism (Marshall, 1971; Marshman & Marshall, 1981a, b; Weaver & Dugan, 1972; Theng & Yuan, 2008). Effects of clays are mostly indirect and arise from physico-chemical effects of clays on the microenvironment, e.g. action as buffers, and as sorptive agents for cells, metabolites, ions and enzymes (Tazaki, 2006; Ehrlich & Newman, 2009). Clay minerals (bentonite, palygorskite and kaolinite) can also influence the size, shape and structure of fungal mycelial pellets in liquid culture (Fomina & Gadd, 2002a).

Sulfides

Most non-ferrous sulfides are formed abiotically but some sedimentary deposits are of biogenic origin. Sulfate-reducing bacteria play an important role in some sedimentary environments in mediating the formation of certain sulfide minerals, especially iron pyrite (FeS_2). Microbial roles in the biogenesis of sulfide deposits arise from the generation of H_2S , usually from bacterial reduction of sulfate (Ehrlich & Newman, 2009), and reaction of metal ions with the biogenic sulfide, although some sulfide may also result from decomposition of sulfur-containing organic compounds.

Metal sulfides are subject to oxidation by bacteria such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Sulfolobus* spp. and *Acidianus brierleyi*. The bacterial action may involve direct oxidative attack of the crystal lattice of a metal sulfide or indirect oxidative attack by generation of acid ferric sulfate, which oxidizes the metal sulfide chemically. The indirect mechanism is of primary importance in the solubilization of uraninite (UO_2). Microbial oxidation of metal sulfides is exploited industrially in extracting metals from low-grade metal sulfide ores and uraninite (see later). In bituminous coal seams that are exposed as a result of mining activity, pyrite oxidation by these bacteria is an environmentally deleterious process and the source of acid mine drainage (Rawlings *et al.*, 2003; Ehrlich & Newman, 2009; Jerez, 2009).

Fungal symbioses in mineral transformations

One of the most remarkable adaptations of fungi for exploitation of the terrestrial environment is their forma-

tion of mutualistic partnerships with plants (mycorrhizas) and algae or cyanobacteria (lichens). The 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 inorganic nutrients.

Lichens

Lichens are fungi that exist in facultative or obligate symbioses with one or more photosynthesizing partners; they play an important role in many biogeochemical processes. The symbiosis 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 (Haas & Purvis, 2006). Lichens are pioneer colonizers of fresh rock outcrops. Globally, they 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. Alteration of bedrock minerals and synthesis of biominerals in the proximity of lichens gives rise to different chemical microenvironments and emphasizes their participation in mineral nutrient cycling (Banfield *et al.*, 1999; Chen *et al.*, 2000; Adamo & Violante, 2000). Lichens can accumulate metals such as lead, copper, and many other elements of environmental concern, including radionuclides, to high levels (Purvis & Pawlik-Skowronska, 2008). They can also form a variety of metal-organic biominerals, e.g. oxalates, especially during growth on metal-rich substrates (Chen *et al.*, 2000; Adamo *et al.*, 2002). For example, on copper-sulfide-bearing rocks, precipitation of copper oxalate (moolooite) can occur within the lichen thallus (Purvis, 1996; Purvis & Halls, 1996).

Mycorrhizas

Nearly all land plants depend on symbiotic mycorrhizal fungi (Smith & Read, 1997). Two main types of mycorrhizas are 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 (Fomina *et al.*, 2004, 2005b). 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 release. 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, b).

During growth, mycorrhizal fungi often excrete low-molecular-mass carboxylic acids (Martino *et al.*, 2003; Fomina *et al.*, 2004). The weathering of hornblendes, feldspars and granitic bedrock in certain soils has been attributed to oxalic, citric, succinic, formic and malic acid excretion by ectomycorrhizal hyphae, which can produce micro- to millimolar concentrations of these organic acids in their microenvironments. Weathering and the supply of nutrients derived from minerals to plants is known to be stimulated by plant-symbiotic mycorrhizal fungi. Ectomycorrhizal fungi can form narrow cylindrical pores in weatherable minerals in podzol E horizons, probably by exuding low-molecular-mass organic acids at their hyphal tips, causing local dissolution of aluminium silicates (Jongmans *et al.*, 1997; Van Breemen *et al.*, 2000).

Ectomycorrhizal fungi (*Suillus granulatus* and *Paxillus involutus*) can release elements from apatite and wood ash (K, Ca, Ti, Mn, Pb) and accumulate them in the mycelia (Wallander *et al.*, 2003). Ericoid mycorrhizal and ectomycorrhizal fungi can dissolve a variety of cadmium, copper, zinc and lead-bearing minerals, including metal phosphates (Leyval & Joner, 2001; Martino *et al.*, 2003; Fomina *et al.*, 2004, 2005b). Mobilization of phosphorus from inorganic phosphate is generally regarded as one of the most important functions of mycorrhizal fungi; this will also result in movement and redistribution of associated metals, and also the formation of other secondary minerals, including phosphates.

Environmental and applied significance of metal–mineral–microbe interactions

Biocorrosion of metals

The deterioration of metal due to microbial activity is termed biocorrosion or microbially influenced corrosion (Beech & Sunner, 2004). The main types of microbes associated with metals in terrestrial and aquatic habitats are sulfate-reducing bacteria (SRB), sulfur-oxidizing bacteria, iron-oxidizing/reducing bacteria, manganese-oxidizing bacteria, bacteria secreting organic acids and slime, and various algae and fungi, and many develop complex biofilm communities on surfaces of materials (Beech & Sunner, 2004; Gu, 2009). Mechanisms of corrosion are complicated; they include depolarization of metals, biomineral formation, complexation by exopolymeric materials, H₂ embrittlement, acidic attack and electron shuttling (Gu, 2009). A proposed unifying hypothesis of electron transfer from zero-valent metal to oxygen as ultimate electron acceptor for microbially influenced corrosion of ferrous metals has been proposed as a model system for the study of metal–microbe interactions in wider contexts (Hamilton, 2003). Adhesion of microbes onto metal surfaces establishes microelectrochemical concentration cells where electron flow can be initiated from anode to cathode. During aerobic corrosion, the area of a metal beneath colonies acts as an anode, while the area further

away from the colonies, where oxygen concentrations are relatively higher, serves as a cathodic site. Electrons flow from anode to cathode and corrosion reactions take place, resulting in the dissolution of metal. For iron, dissociated metal ions may form ferrous and ferric hydroxides, and a series of iron-containing minerals in the solution phase, depending on the species present and chemical conditions. SRB have been studied extensively in biocorrosion. The hydrogenase system of these bacteria can remove the adsorbed film of H₂ on surfaces of iron and steel, depolarizing the system. Electron removal as a result of hydrogen utilization results in cathodic depolarization and forces more iron to be dissolved at the anode. Under anaerobic conditions, production of H₂S by SRB by SO₄²⁻ reduction can also lead to precipitation of FeS on metal surfaces. Other microbes in the genus *Acidithiobacillus* oxidize sulfur compounds to sulfuric acid, which can attack metals and alloys. Under natural conditions, alternation of aerobic and anaerobic conditions is common and is accelerated greatly when sulfur is present. Here, sulfate can be reduced to H₂S by SRB under anaerobic conditions, but oxidized to elemental S, SO₄²⁻ and other sulfur species, generating acidity. Such a process can occur continuously, resulting in significant deterioration (Gu, 2009). Exopolymers and organic acids produced by microbes are also involved in biocorrosion by metal complexation as well as acid effects.

Biorecovery of metals from ores

Solubilization mechanisms provide a route for removal of metals from industrial wastes and by-products, low-grade ores and metal-bearing minerals, which is relevant to bioremediation of soil matrices and solid wastes, metal recovery and recycling (Burgstaller & Schinner, 1993; Gadd, 2000a; Gadd & Sayer, 2000; Brandl, 2001; Suzuki, 2001; Rawlings, 2002; Kartal *et al.*, 2006). Chemolithotrophic leaching has been used to remove metals from contaminated solids such as sewage sludge (Sreekrishnan & Tyagi, 1994), soil (White *et al.*, 1998) and red mud, the latter being the main waste product of aluminium extraction from bauxite (Vachon *et al.*, 1994). Extracellular ligands excreted by fungi, e.g. *Aspergillus* and *Penicillium* spp., have been used to leach metals such as zinc, copper, nickel and cobalt from a variety of materials, including low-grade mineral ores (Brandl, 2001; Mulligan & Galvez-Cloutier, 2003; Santhiya & Ting, 2005). Of the several mechanisms involved in such chemo-organotrophic (=heterotrophic) leaching, the production of low-molecular-mass organic acids is of major significance (Gadd, 1999, 2007).

Industrial-scale biorecovery of metals is used to extract metals such as copper, gold, uranium and others from their ores (Suzuki, 2001; Rawlings, 2002; Rawlings *et al.*, 2003; Jerez, 2009). This process, also termed biomining, employs chemolithoautotrophic microbes, with the most common leaching bacteria belonging to the genus *Acidithiobacillus*,

e.g. *A. ferrooxidans* and *A. thiooxidans*. Thermophilic archaea capable of oxidizing sulfur and Fe(II), including *Sulfolobus*, *Acidianus*, *Metallosphaera* and *Sulfurisphaera* spp., as well as mesophilic archaea have also been described, e.g. *Ferroplasma* spp. Most bioleaching operations for gold or copper use some kind of irrigation process involving percolation of leaching solutions through the crushed ore contained in a column, heap or dump (Rawlings, 2002; Rawlings *et al.*, 2003). The leachate containing e.g. copper sulfate generated by microbial solubilization of insoluble copper sulfides in the ore is subjected to solvent extraction to produce a highly concentrated copper sulfate solution from which the copper is recovered in an electrowinning plant to generate electrolytic copper of high purity. Bioleaching bacteria can also be used for gold recovery. Gold is usually associated with minerals containing arsenic and pyrites (arsenopyrites) (Rawlings *et al.*, 2003). During gold bioleaching, iron- and sulfur-oxidizers attack the arsenopyrite, releasing the gold particles. Following release, the gold is complexed with cyanide prior to recovery using standard gold-mining procedures. Most leaching bacteria grow as a biofilm attached to the surface of solid substrates such as elemental sulfur and metal sulfides, and can 'pit' the surface of mineral ores such as pyrite (FeS₂) (Suzuki, 2001), although other studies have shown that attachment is not necessary for pitting to occur with pyrite (Edwards *et al.*, 2001). Cells are embedded in a matrix of extracellular polymeric substances in which an indirect mechanism generates Fe(II) and thiosulfate, which is finally oxidized to sulfuric acid, with elemental sulfur being a side product. The oxidation of some metal sulfides, such as chalcopyrite (CuFeS₂), generates elemental sulfur as a side product instead of thiosulfate. Insoluble metal sulfides are oxidized to soluble metal sulfates by the chemical action of Fe(III) (Edwards *et al.*, 2001), the main role of the microbes being the reoxidation of generated Fe(II) to additional Fe(III). In an environmental context, acidophilic microbes can mobilize metals from waste ores, abandoned mines and dumps, and generate acid mine drainage, itself a serious environmental problem (Jerez, 2009).

Bioweathering of rocks and minerals: soil formation

Weathering, which leads to soil formation, is a process in which rock is eroded or broken down into smaller particles and finally to constituent minerals, and this ultimately leads to mineral soil formation (Tazaki, 2006; Ehrlich & Newman, 2009). Physical, chemical and biological processes are involved: bioweathering can be defined as the erosion and decay of rocks and minerals mediated by living organisms, and in microbes it is mediated by the direct and indirect physical and chemical mechanisms detailed previously. Some researchers prefer the term biodeterioration to bioweathering (Gorbushina & Krumbein, 2005). Microbes are effective biological weathering agents and many can tolerate extremes of light, salinity, pH and water potential as well as adopting a variety of growth, metabolic

and morphological strategies (Gorbushina *et al.*, 1993; Sterflinger, 2000; Verrecchia, 2000; Burford *et al.*, 2003a, b; Gadd, 2007; Gorbushina & Broughton, 2009). Many organisms can scavenge nutrients from the atmosphere and rainwater, and also use organic and inorganic residues on surfaces or within cracks and fissures, waste products of other microbes, decaying plants and insects, dust particles, aerosols and animal faeces as nutrient sources (Sterflinger, 2000; Gorbushina & Broughton, 2009). Many organisms receive protection from the presence of pigments in their cell walls, e.g. melanins in fungi, and by the production of extracellular polymeric materials (EPS) during adhesion, with biofilm formation providing extra protection (Gadd, 1993a; Gorbushina, 2007). Microbes are probably associated with all rocks and minerals, building stone and concrete (Burford *et al.*, 2003a, b; Gleeson *et al.*, 2005, 2006, 2010; Gorbushina, 2007; Gorbushina & Broughton, 2009). Such ubiquitous endolithic rock ecosystems offer an ideal model system for studying the complex interactions between microbes and minerals that drive the biosphere; they provide tractable model systems for microbial ecology, geobiology and astrobiology, and form biosignatures that can be preserved in the geological record (Walker & Pace, 2007; Gorbushina & Broughton, 2009). As mentioned previously, lichens, a fungal growth form, are highly significant bioweathering agents (Adamo & Violante, 2000; Adamo *et al.*, 2002). Lithobiotic biofilm communities can interact with mineral substrates both geophysically and geochemically: as well as deterioration this can also result in the formation of patinas, films, varnishes, crusts and stromatolites (Gadd, 2007; Gorbushina, 2007; Fomina *et al.*, 2010). Elements found in soil therefore largely reflect the composition of the Earth's crust, although some modification occurs by further weathering, biogenic and anthropogenic activities: chemical changes include mineral dissolution while biological activity causes enrichment of carbon, nitrogen and sulfur. Elements and minerals that remain can re-form as secondary minerals. Mycorrhizal fungi are also very important in mineral weathering and dissolution of insoluble metal compounds in the soil, along with free-living bacteria and fungi. Bioweathering is a primary source of essential elements, except nitrogen and carbon, for organisms (Hoffland *et al.*, 2004). Acidification is an important fungal bioweathering mechanism, with low-molecular-mass organic anions (LMWOAs) being especially significant (Gadd, 1999; Hoffland *et al.*, 2004). Because production of LMWOAs has a carbon cost, symbiotic mycorrhizal fungi that are provided with organic carbon compounds by the plant host may have an advantage over free-living saprotrophic organisms (Hoffland *et al.*, 2004).

Many microbes can attack silicates, thus playing a role in the genesis of clay minerals, and in soil and sediment formation. Microbe–clay mineral interactions are therefore important in soil evolution, as well as aggregation and stabilization (Burford *et al.*, 2003a; Tazaki, 2006; Theng & Yuan, 2008). The production of EPS by cyanobacteria,

bacteria and fungi is significant, while filamentous fungi entangle soil particles in their hyphae, forming stable microaggregates, and also take part in polysaccharide aggregation (Lunsdorf *et al.*, 2000). Direct biophysical effects have been shown where fungal hyphae attracted and oriented clay platelets because of surface charge phenomena, and acted as nucleation zones for the formation of narrow clay-lined channels (Ritz & Young, 2004). Interactions between clay minerals and microbes alter the adsorptive properties of both clays and biomass (Fomina & Gadd, 2002b). Under certain conditions, the sorption abilities of microbe–clay aggregates can be decreased due to blocking and masking of binding sites or increased due to modification of binding sites and emergence of new ones (Fomina & Gadd, 2002b; Tazaki, 2006). As well as being important in stages of mineral soil and sediment formation and development, bioweathering mechanisms also effect structural decay of rock and mineral-based building materials, monuments and other structures. It should be stressed that the activities of all groups of microbes and interactions between them should be considered in bioweathering, and indeed other geomicrobiological, studies. Fungal–bacterial interactions in the root environment are likely to be significant in mineral weathering and plant nutrition for example (Balogh-Brunstad *et al.*, 2008; Koele *et al.*, 2009).

Bioweathering of rocks and minerals: structural decay of stone

Deterioration of stone monuments represents a permanent loss of cultural heritage (Ranalli *et al.*, 2009; Scheerer *et al.*, 2009). The most common stone types affected are marble, limestone, sandstone and granite, with many overlaps between calcareous and siliceous rocks. Materials used to stabilize building blocks (mortar) and to coat surfaces prior to painting (plaster or stucco) are generally also extremely susceptible to degradation. External stone surfaces are a complex ecosystem, including not only cyanobacteria, algae, bacteria, fungi and protozoa but also ‘higher’ organisms such as small animals and plants (Scheerer *et al.*, 2009). Stone-inhabiting microbes may grow on the surface (epilithic), in more protected habitats such as crevices and fissures (chasmolithic), or may penetrate some millimetres or even centimetres into the rock pore system (endolithic). Microbial colonization is generally initiated by phototrophic cyanobacteria and algae, usually in a biofilm, probably followed by lichens, and then general heterotrophs (Hoppert *et al.*, 2004), although establishment of heterotrophic rock communities is possible without initial phototroph involvement (Roeselers *et al.*, 2007). Highly deteriorated stone surfaces provide appropriate conditions (a ‘proto-soil’) for colonization by mosses, ferns and higher plants.

Mechanisms of stone deterioration are complex and include most of the direct and indirect mechanisms previously discussed for mineral decay (Sand, 1997;

Ranalli *et al.*, 2009; Scheerer *et al.*, 2009). The weathering of sandstone monuments by fungi has been attributed to the production of e.g. acetic, oxalic, citric, formic, fumaric, glyoxylic, gluconic, succinic and tartaric acids. The common formation of biofilms is significant, aiding colonization and survival, with the EPS also capable of e.g. metal complexation, and weakening the mineral lattice through repeated wetting and drying cycles and subsequent expansion and contraction (Warscheid *et al.*, 1996). The production of efflorescences (‘salting’) involves secondary minerals produced through reaction of anions from excreted acids with cations from the stone. Such secondary minerals can cause physical damage leading to blistering, flaking, scaling and granular disintegration, which may often be the main mechanism of stone decay (Wright, 2002). Physical damage may be caused by penetration of filamentous microbes (particularly fungal hyphae) into the stone (Hirsch *et al.*, 1995a; Cockell & Herrera, 2008). Many cyanobacteria, not necessarily filamentous, have also been shown to have this ability. Weakened areas of the stone will be affected first. Lichens cause mechanical damage due to penetration of their rhizines, composed of fungal filaments, and the expansion/contraction of the thallus on wetting/drying, which can lift grains of stone from the surface (De los Rios *et al.*, 2004; Gaylarde & Morton, 2002). ‘Lichen acids’, principally oxalic acid, cause damage at the stone/lichen interface, and lichen thalli may accumulate 1–50 % calcium oxalate, depending on the substrate (Cameron *et al.*, 1997; Seaward, 2003; Lisci *et al.*, 2003). In addition, carbonic acid formed in the lichen thallus can solubilize calcium and magnesium carbonates in calcareous stone (Tiano, 2002).

Concrete biodeterioration

All types of building and ceramic materials, concrete and cement can deteriorate as a result of microbial action, and in some environments, fungi dominate the microbiota and play an important role in biodeterioration of concrete (Gu *et al.*, 1998; Nica *et al.*, 2000; Zhdanova *et al.*, 2000; Gu, 2009; Scheerer *et al.*, 2009). Apart from structural uses, cement and concrete are used as barriers in all kinds of nuclear waste repositories. Despite the theoretical service life of such concrete materials reaching up to one million years, biocorrosion is an important factor to take into account over such time periods. Microbial attack on concrete is mediated by protons, inorganic and organic acids and the production of hydrophilic slimes, leading to biochemical and biophysical/biomechanical deterioration (Sand, 1997; Fomina *et al.*, 2007c; Scheerer *et al.*, 2009). Fungal degradation may proceed more rapidly than bacterial degradation, with complexation suggested as the main mechanism of calcium mobilization. Microfungi from the genera *Aspergillus*, *Alternaria* and *Cladosporium* were able to colonize samples of the concrete used as radioactive waste barrier in the Chernobyl reactor and leached iron, aluminium, silicon and calcium, and reprecipitated silicon and calcium oxalate in their micro-

environment (Fomina *et al.*, 2007c). Fungi are also important members of the microbial communities (including lichens) that colonize and cause deterioration of 'normal' concrete and cement used in buildings and other structures.

Bioremediation, biotechnology and bioprocessing

Many microbial metal and mineral transformations have potential for the treatment of environmental pollution, and some processes are in commercial operation (Gadd, 2004, 2005; Lloyd & Lovley, 2001; Pumpel & Paknikar, 2001; Lloyd & Renshaw, 2005). However, many processes are still at the laboratory scale and yet to be tested in a rigorous applied and/or commercial context. The bioremediation literature is huge and only selected examples employing the kinds of mechanisms detailed earlier can be provided here. The reader is referred to several detailed reviews (e.g. Gadd, 2001a, b; Pumpel & Paknikar, 2001; Barkay & Wagner-Dobler, 2005; Hockin & Gadd, 2007; Gadd, 2009b). Some of the processes described below could be combined or improved through genetic manipulation. In other cases, appropriate detailed knowledge of microbe-metal-related reactions may allow further optimization of the desired process by altering the physico-chemical conditions of the contaminated area. A combination of genetic engineering with appropriate eco-engineering of polluted sites may be relevant to some future bioremediation strategies (Valls & de Lorenzo, 2002) although subject to significant legal and socio-political barriers. In addition to bioremediation, microbe-metal-mineral transformations have applications in other areas of biotechnology and bioprocessing, including biosensors, biocatalysis, electricity generation and nanotechnology.

Bioleaching

Microbiological solubilization of metals from solid minerals (bioleaching) is a well-established process in the mining industry (see previously). In addition, other metal and mineral wastes, including contaminated soil, may be subject to microbial bioleaching for metal recovery, recycling and bioremediation purposes (White *et al.*, 1998). Metals such as Cd, Cu, Ni and Zn can be solubilized from fly ash (originating from incineration of municipal solid waste) by bacterial and fungal activity (Brandl, 2001; Brandl & Faramarzi, 2006). HCN-forming bacteria, e.g. *Chromobacterium violaceum* and *Pseudomonas fluorescens*, can mobilize Ni, Au, Pt and Cu as various cyanide complexes and compounds from solid materials such as copper-containing ores, electronic scrap, and spent automobile catalytic converters (Brandl & Faramarzi, 2006).

Bioprecipitation

In the context of bioremediation, precipitation of metal species by reduction is generally limited to anaerobic processes and is ineffective against single-oxidation-state

metals. Precipitation by other means has the advantage of producing chemically stable forms of metal, and its use is not limited to reducible metals. In this context, bioprecipitation by both sulfides and phosphates has been investigated because of the low solubility of many of their metal compounds. Release of phosphate via the hydrolysis of an organic phosphate has been shown to be an effective method for precipitation of metals, which precipitate on the surface of cells as insoluble metal phosphates (Macaskie, 1991). In addition, metal precipitation by secreted phosphate generated from polyphosphate hydrolysis has been suggested as a mechanism to remove metals and actinides from aqueous waste streams. *Acinetobacter johnsonii* was effective in removing lanthanum from solution (Boswell *et al.*, 1999, 2001). A mixed bacterial consortium, enriched for its ability to cycle phosphate, was able to remove over 98% of the uranium from a 1.5 mmol l⁻¹ solution of uranyl nitrate, to loadings of over 0.5 g of uranium per g of dry-cell weight (Renninger *et al.*, 2001). Another two-stage system utilized *Pseudomonas aeruginosa*, chosen for its metal tolerance and ability to accumulate large amounts of polyphosphates. Metal binding occurred after the degradation of the polyphosphate and concomitant release of phosphate from the cells. This system removed uranyl ions from solution as uranyl phosphate but in a manner that did not require an organic phosphate source, a chelation system, or living cells (Renninger *et al.*, 2004).

Sulfide produced from sulfate reduction plays a major role in metal sulfide immobilization in sediments but has also been applied to bioremediation of metals in waters and soil leachates (White & Gadd, 1998, 2000; White *et al.*, 2003). One process used sulfur- and iron-oxidizing bacteria to liberate metals from soils in the form of an acidic sulfate solution that enabled almost all the metals to be removed by bacterial sulfate reduction (White *et al.*, 1998). Large-scale commercial bioreactors have in fact been developed using bacterial sulfate reduction for treating metal-contaminated waters (Barnes *et al.*, 1992; Gadd, 1992b; <http://www.paques.nl/>).

Biosorption and bioaccumulation

Biosorption is a physico-chemical process, simply defined as 'the removal of substances from solution by biological material'; it is a property of both living and dead organisms (and their components), and has been heralded as a promising biotechnology for removal (and/or recovery) of metals, radionuclides and organic pollutants for many years because of its simplicity, analogous operation to conventional ion-exchange technology, apparent efficiency and availability of biomass and waste bio-products (Macaskie, 1991; Gadd, 1986, 2001a, b, 2009b; Volesky, 1990; Garnham *et al.*, 1992; Gadd & White, 1990, 1993; Wang & Chen, 2009). Most biosorption studies are carried out on microbial systems, chiefly bacteria, microalgae and fungi, and with toxic metals and radionuclides, particularly

actinides and lanthanides. The term is now applied to all manner of organic and inorganic pollutants, and biosorption can describe 'any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a biosorbent (i.e. a solid surface of a biological matrix) resulting in an accumulation at the sorbate–biosorbent interface, and therefore a reduction in the solution sorbate concentration' (Gadd, 2009b). Biosorption also has application for recovery and use of precious metals, e.g. gold (Volesky, 1990; Gadd, 2009b; Wang & Chen, 2009). However, despite dramatic increases in published research on biosorption there has been little or no exploitation in an industrial context. In recent years, modification of biomass has been attempted to improve the efficiency or selectivity of microbial biosorbents. For example, the metalloregulatory protein MerR, which exhibits high affinity and selectivity for mercury, was used to construct microbial biosorbents specific for mercury removal (Bae *et al.*, 2001, 2002, 2003). The presence of surface-exposed MerR on engineered strains of *E. coli* enabled sixfold higher Hg^{2+} biosorption than that found in the wild-type. Hg^{2+} binding via MerR was very specific, with no observable decline even in the presence of 100-fold excess Cd^{2+} and Zn^{2+} (Bae *et al.*, 2003). Since metalloregulatory proteins are available for a variety of toxic metals, these results suggest that microbial biosorbents overexpressing metalloregulatory proteins may be used for clean-up of other important metals (Bae *et al.*, 2000, 2003). Fungal–clay biomineral sorbents combine the sorptive advantages of the individual components, i.e. the high density of metal-binding sites per unit area and high sorption capacity of the fungal biomass, and the high sorption affinity, high surface area per unit weight, mechanical strength and efficient sorption at high metal concentrations of the clay minerals (Fomina & Gadd, 2002b). *Saccharomyces cerevisiae* mutants (*pmr1Δ*) hypersensitive to heavy metals due to increased metal uptake have been investigated for the ability to remove Mn^{2+} , Cu^{2+} , Co^{2+} or Cd^{2+} from synthetic effluents by a combination of biosorption and continuous metabolic uptake after physical adsorption (Ruta *et al.*, 2010).

Biosorptive processes are a component of varying significance in any form of primary or secondary biological treatment process for process streams including domestic, municipal and industrial wastes, and solid wastes. Sewage treatment, activated sludge plants, biofilters, biofilm reactors, fixed and suspended film systems, lagoon treatments, stream meanders, nitrification and denitrification treatments, biological phosphate removal processes, wetlands and reed-bed technologies, composting, and *in situ* and *ex situ* bioremediation processes all rely on the activities of microbes to break down organic substances. Many wastes contain metals in addition to organics and therefore biosorption of metals must play a part in the overall process, although the significance of such a role is difficult to establish. In biological treatment processes, a clear advantage is that metabolic activities contribute to the degradation of organic substances. Several examples have

been described where organic and inorganic transformations are closely linked to biosorptive removal, e.g. rotating biological contactors for treatment of dilute metal-containing mine waste streams (Gadd & White, 1993).

Phytochelatin (PCs) are metal-binding cysteine-rich peptides, enzymically synthesized in plants and certain fungi from glutathione in response to heavy metal stress. In an attempt to increase the ability of bacterial cells to accumulate heavy metals, the *Arabidopsis thaliana* PC synthase gene (*AtPCS*) was expressed in *E. coli*. When the bacterial cells expressing *AtPCS* were exposed to e.g. cadmium or arsenic, cellular metal contents were increased 20- and 50-fold, respectively. Overexpression of PC synthase in bacteria could be a means of improving the metal content of organisms for use in bioremediation (Valls *et al.*, 2000; Sauge-Merle *et al.*, 2003).

Metalloid bioremediation

Microbial responses to arsenic with potential in bioremediation include chelation, compartmentalization, exclusion and immobilization. Attempts to engineer an arsenic-accumulating microbe have involved modification of natural resistance mechanisms and development of novel or hybrid pathways into one easily manipulated organism. For example, the bacterial ArsC (arsenate reductase) and γ -ECS (GSH synthase) were expressed in *Arabidopsis thaliana*, resulting in accumulation of As(V) as GSH–As complexes (Dhankher *et al.*, 2002), while yeast YCF1 was expressed in *A. thaliana* for enhanced As storage in the vacuole (Song *et al.*, 2003). PC synthase from *Schizosaccharomyces pombe* (SpPCS) has been expressed in *E. coli*, resulting in higher arsenic accumulation, these steps being combined in an arsenic efflux deletion *E. coli* strain to achieve the highest reported arsenic accumulation in *E. coli* of 16.8 μmol per g cells (Tsai *et al.*, 2009). Anaerobically, sulfate-reducing bacteria can precipitate As(V) as insoluble sulfide complexes, while a yeast strain coexpressing *AtPCS* and cysteine desulfhydrase, an aminotransferase that converts cysteine into hydrogen sulfide under aerobic conditions, was used to elevate arsenic accumulation by formation of PC–metal–sulfide complexes (Tsai *et al.*, 2009). The ability of fungi, along with bacteria, to transform metalloids has been utilized successfully in the bioremediation of contaminated land and water. Selenium methylation results in volatilization, a process 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 & Frankenberger, 1992).

Mycoremediation and the mycorrhizosphere

Mycorrhizal associations may also be used for metal clean-up in the general area of phytoremediation (Van der Lelie *et al.*, 2001; Rosen *et al.*, 2005; Gohre & Paszkowski, 2006). Mycorrhizas may enhance phytoextraction directly or indirectly by increasing plant biomass, and some studies have shown increased plant accumulation of metals,

especially when the plants were inoculated with mycorrhizas isolated from metalliferous environments. However, many complicating factors affect successful exploitation (Meharg, 2003). The potential impact of mycorrhizal fungi on bioremediation may be conditional and dependent on the metal tolerance of fungal strains, their mycorrhizal status, and the nutritional status of contaminated soils (Meharg, 2003). In addition, several studies have shown that mycorrhizas can reduce metal uptake by plants (Tullio *et al.*, 2003). Arbuscular mycorrhizas (AM) depressed translocation of zinc to shoots of host plants in soils moderately polluted with zinc by binding of metals in mycorrhizal structures and immobilization of metals in the mycorrhizosphere (Christie *et al.*, 2004). It is generally concluded that local conditions in metal-contaminated sites may determine the cost–benefit relationship between the plant and the AM fungus, since detrimental, neutral or beneficial interactions have all been documented (Meharg & Cairney, 2000). A protective metal-binding effect of ectomycorrhizal fungi (EcM) has been postulated (e.g. Leyval *et al.*, 1997). A copper-adapted *Suillus luteus* isolate provided protection against copper toxicity in pine seedlings exposed to elevated copper. Such a metal-adapted *Suillus–Pinus* combination might be suitable for large-scale land reclamation at phytotoxic metalliferous and industrial sites (Adriaensen *et al.*, 2005). Ectomycorrhizal fungi persistently fixed Cd(II) and Pb(II), and formed an efficient biological barrier that reduced movement of these metals in birch tissues (Krupa & Kozdroj, 2004). Such mycorrhizal metal immobilization around plant roots, including biomineral formation, may also assist soil remediation and revegetation. Naturally occurring soil organic compounds can stabilize potentially toxic metals such as copper, cadmium, lead and manganese. The insoluble glycoprotein glomalin, produced in copious amounts on hyphae of arbuscular mycorrhizal fungi, can sequester such metals, and could be considered a useful stabilization agent in remediation of polluted soils (Gonzalez-Chavez *et al.*, 2004). Phytostabilization strategies may be suitable to reduce the dispersion of uranium (U) and the environmental risks of U-contaminated soils. *Glomus intraradices* increased root U concentration and content, but decreased shoot U concentrations. AM fungi and root hairs improved not only P acquisition but also root uptake of U, and the mycorrhiza generally decreased U translocation from plant root to shoot (Rufyikiri *et al.*, 2004; Chen *et al.* 2005a, b).

For ericaceous mycorrhizas, clear host protection has been observed, e.g. in *Calluna*, *Erica* and *Vaccinium* spp. growing on Cu- and Zn-polluted and/or naturally metalliferous soils, the fungus preventing metal translocation to plant shoots (Bradley *et al.*, 1981, 1982). Further, ericaceous plants are generally found on nutrient-deficient soils and it is likely that the mycorrhiza could additionally benefit the plants by enhanced nutrient uptake (Smith & Read, 1997). The development of stress-tolerant plant–mycorrhizal associations may therefore be a promising

strategy for phytoremediation and soil amelioration (Schutzendubel & Polle, 2002). Because of the symbiosis with ericoid mycorrhizal fungi, ericaceous plants are able to grow in highly polluted environments, where metal ions can reach toxic levels in the soil substrate (Perotto *et al.*, 2002; Martino *et al.*, 2003). Ericoid mycorrhizal fungal endophytes, and sometimes their plant hosts, can evolve toxic metal resistance which enables ericoid mycorrhizal plants to colonize polluted soil. This seems to be a major factor in the success of ericoid mycorrhizal taxa in a range of harsh environments (Cairney & Meharg, 2003).

Free-living and symbiotic microbial populations associated with plant roots significantly alter the physico-chemical characteristics of the rhizosphere, which may have consequences for the biogeochemical mobility of metals and associated elements (Wenzel *et al.*, 1994; Olsson & Wallander, 1998; Whitelaw *et al.*, 1999). The importance of mycorrhizas in plant phosphorus nutrition has been appreciated for a long time and their ability to dissolve and transform calcium-containing insoluble compounds and minerals (calcium phosphates, carbonate and sulfate) has been widely studied (Callot *et al.*, 1985a, b; Lapeyrie *et al.*, 1990, 1991; Gharieb & Gadd, 1999). However, toxic metal mineral solubilization has received little attention, although this should be considered in any revegetation, natural attenuation or phytoremediation strategies. The ectomycorrhizal fungi *Suillus granulatus* and *Pisolithus tinctorius* can promote the release of cadmium and phosphorus from rock phosphate (Leyval & Joner, 2001) while the ericoid mycorrhizal fungus *Oidiodendron maius* can solubilize zinc oxide and phosphate (Martino *et al.*, 2003). Our experimental studies on ericoid mycorrhizal and ectomycorrhizal fungi showed that many species were able to solubilize zinc, cadmium, copper phosphates and lead chlorophosphate (pyromorphite), releasing phosphate and metals (Fomina *et al.*, 2004). Both non-mycorrhizal *Pinus sylvestris* and pines infected with the ectomycorrhizal *Paxillus involutus* were able to enhance zinc phosphate dissolution, withstand metal toxicity, and acquire the mobilized phosphorus, increasing the amount of phosphorus in shoots when zinc phosphate was present in the growth matrix (Fomina *et al.*, 2006).

Phytoremediation

Phytoremediation is the use of plants to remove or detoxify environmental pollutants (Baker & Brooks, 1989; Salt *et al.*, 1998). Although free-living and symbiotic microbes influence plant productivity, metal bioavailability and interactions, there have been few integrated studies, and many phytoremediation studies are carried out without reference to contributory microbial processes. Phytoremediation can be divided into phytoextraction (pollutant removal from soil into shoots and leaves), phytodegradation (pollutant degradation by plant–microbe systems), rhizofiltration (absorption of pollutants by plant roots), phytostabilization (plant-mediated reduction of

pollutant bioavailability), phytovolatilization (plant-mediated volatilization of pollutants) and phytoscrubbing (plant removal of atmospheric pollutants). Most attention has focussed on metals, with two remediation strategies being chelate-assisted and continuous phytoextraction. Application of various synthetic chelates can enhance plant metal accumulation (Huang *et al.*, 1997; Salt *et al.*, 1998). Chelate-assisted phytoextraction has been developed because plants do not naturally accumulate important toxic elements, e.g. Pb, Cd, As, and many radionuclides, to levels that would be significant in a remediative context. Continuous phytoextraction of metals relies on properties of plants that lead to accumulation in aerial plant tissues. However, many natural 'hyperaccumulators' often exhibit low biomass and slow growth rates, and none are known for important elements such as Pb, Cd, As and U (Salt *et al.*, 1998). Ni, Zn and Se appear to be the elements accumulated to the highest levels (Salt *et al.*, 1998). Plants possess metal resistance mechanisms analogous to those of microbes, i.e. chelation, intracellular compartmentation, transformations, etc., although plants may be relatively metal sensitive. Manipulation of metal tolerance may provide a means for phytoremediation: bacterial Hg²⁺ reductase has been expressed in *Arabidopsis thaliana* (Rugh *et al.*, 1996). Recombinant heavy-metal-resistant endophytic bacteria have also been examined for effects on metal uptake by their host plants (Lodewyckx *et al.*, 2001).

Reductive transformations, nanoparticle formation and nano-biotechnology

Microbial activities in anaerobic, subsurface environments also offer possibilities for metal and radionuclide bioremediation (Lloyd, 2003; Lloyd *et al.*, 2003; Lloyd & Renshaw, 2005). Metal(loid)s that form insoluble precipitates when reduced include Se(0), Cr(III), Tc(IV) and U(IV) (Lovley & Coates, 1997; Stolz & Oremland, 1999; Thompson-Eagle & Frankenberger, 1992; Hockin & Gadd, 2003, 2006; Wall & Krumholz, 2006; Yee & Kobayashi, 2008). Microbial reduction of U(VI) to U(IV) has been proposed as a bioremediation strategy for uranium-contaminated groundwaters (Lovley *et al.*, 1991; Lovley, 1995; Lloyd *et al.*, 2003), as reduction of U(VI) under anaerobic conditions produces U(IV), which precipitates as the insoluble mineral uraninite (Wall & Krumholz, 2006). It has also been suggested that anaerobic oxidation of U(IV) to U(VI) with nitrate serving as the electron acceptor may provide a novel strategy for solubilizing and extracting microbial U(IV) precipitates from the subsurface (Finneran *et al.*, 2002a). Biogenic uraninite is an important nanoscale biogeological material and crucial to the viability of microbial bioremediation strategies for subsurface uranium contamination by stimulated uranium reduction because it is orders of magnitude less soluble than most other uranium species. Such approaches utilize electron donors such as ethanol and acetate to establish anoxia in an aquifer (by injection), which is followed by microbial reduction of electron acceptors such as NO₃,

U(VI), Fe(III) and SO₄²⁻. U(VI) reduction can be catalysed by many microbes, the majority being metal- or sulfate-reducing bacteria. Successful uranium bioremediation requires continued strictly anaerobic conditions, with the biomass-associated nanoparticles tending to aggregate, making it unlikely that they will be transported in groundwater (Bargar *et al.*, 2008).

The hydrogenase activity of bacteria such as *Desulfovibrio desulfuricans* and *E. coli* can be linked to the recovery of precious metals from wastes, e.g. by reducing Pd(II) to Pd(0) [Bio-Pd]. Biosynthesis of precious metal nanoparticles may be an alternative way to manufacture fuel cell catalysts using precious metal wastes as the source. A bio-PM (precious metals) catalyst made directly from an industrial reprocessing solution by *E. coli* FS1 was also made into electrodes and tested successfully in a fuel cell, indicating that such catalysts could be made directly from 'waste' solutions containing precious metals without pre-purification (Yong *et al.*, 2009).

Metal micro-/nano-particles, with appropriate chemical modification, have applications as new ceramic-metal (cermet) or organic-metal (orgmet) composites or structured materials for a variety of applications. The use of metal-accumulating microbes for the production of nanoparticles, and their assembly, may allow control over the size, morphology, composition and crystallographic orientation of the particles. The potential of such biomimetic materials appears great and is relevant to production of new advanced materials, with applications in metal and radionuclide bioremediation, antimicrobial treatments (e.g. nano-silver), solar energy and electrical battery applications, and microelectronics (Dameron *et al.*, 1989; Klaus-Joerger *et al.*, 2001). Because of their high specific surface area and high catalytic properties, biogenic metal products also offer potential for sorption and degradation of organic contaminants, as well as a variety of other applications, e.g. electricity generation in fuel cells, novel catalysts and sensors. Biogenic Mn oxides can sequester metals such as Pb, Zn, Co, Ni, As and Cr and also oxidize certain organic pollutants (Hennebel *et al.*, 2009). Biogenic Fe oxides have larger specific surface areas than chemically synthesized Fe oxides and may be more efficient adsorbents for metals. Biological Fe(II) and Mn(II) oxidation with subsequent As(III) adsorption has gained recent interest (Hennebel *et al.*, 2009). Biogenic Fe oxides, such as nanoscale magnetite (Fe₃O₄), are also reactive in dehalogenation reactions, which may be several orders of magnitude faster than enzymic degradation (Hennebel *et al.*, 2009). Magnetotactic bacteria biomineralize either magnetite (Fe₃O₄) or greigite (Fe₃S₄) within their magnetosomes (Bazylinski & Schubbe, 2007; Posfai & Dunin-Borkowski, 2009). Cells of magnetotactic bacteria and their magnetic inclusions have novel magnetic, physical and perhaps optical properties that can be and have been exploited in a variety of scientific, commercial and other applications, including nanoproboscopes and biosensors. Cells of magnetotactic bacteria have been examined

for Cd recovery using magnetic separation, while magnetosomes have been used in drug delivery, separation of cells, nucleic acids and other substances, and many other applications (Bazylinski & Schubbe, 2007). Several environmental pollutants have been detected by using monoclonal antibodies immobilized on such bio-magnets (Hennebel *et al.*, 2009).

Metal reduction resulting in immobilization has applications in the production of novel biomaterials and catalysts as well as bioremediation. Bacterial reduction of Pd(II) to Pd(0) (Bio-Pd) can be carried out by e.g. *Desulfovibrio desulfuricans* and *Shewanella oneidensis*, and the application of Bio-Pd nanoparticle catalysts for dehalogenation, reduction and (de-)hydrogenation reactions for the treatment of contamination is well documented (Hennebel *et al.*, 2009). Microbial reduction of silver is of interest because of the antimicrobial properties of this metal. Applications of nanosilver particles include their use as antimicrobial agents, catalysts in chemical synthesis, biosensors and electrodes (Hennebel *et al.*, 2009). A wide range of microbes can reduce precious metals, e.g. soluble gold, Au(III), to insoluble Au(0). In fact, bacteria and archaea are involved in every step of the biogeochemical cycle of gold, from primary mineralization in hydrothermal and deep subsurface systems to its solubilization, dispersion and reconcentration as secondary gold under surface conditions (Reith *et al.*, 2006, 2007; Southam *et al.*, 2009). Biomineralization of gold nanoparticles in *Cupriavidus metallidurans* CH34 is the result of gold-regulated gene expression leading to reductive precipitation of toxic Au(III) complexes which are accumulated from solution. Cellular gold accumulation is coupled to the formation of Au(I)-S complexes, which induces detoxification responses involving efflux, reduction and possible methylation of Au complexes, leading to formation of Au(I)-C-compounds and nanoparticulate Au(0). Similar particles have been observed in bacterial biofilms on gold grains (Reith *et al.*, 2006). Identification of these specific genetic responses to gold has potential for the development of bioexploration and bioprocessing techniques (Reith *et al.*, 2009; Southam *et al.*, 2009).

Soil treatment processes and microbial influence

Application to soils of certain amendments that immobilize metals, e.g. lime or phosphate treatment, have demonstrated, under field conditions, enhanced natural remediation resulting in improved vegetation growth, increased microbial activity and diversity, and reduced offsite metal transport. However, while long-term stability of certain metal complexes and compounds has been shown in model systems (Adriano *et al.*, 2004b), the influence of plant roots and their microbial and mycorrhizal associations on such stability has often been neglected. For example, pyromorphite [Pb₅(PO₄)₃Cl], which can form in urban and industrially contaminated soils, can be solubilized by phosphate-solubilizing fungi,

with concomitant production of lead oxalate (Sayer *et al.*, 1999; Fomina *et al.*, 2004). The ability of free-living and mycorrhizal fungi to transform pyromorphite (and other minerals containing toxic metals) should clearly be taken into account in risk assessments of the long-term environmental consequences of *in situ* chemical remediation techniques, revegetation strategies or natural attenuation of contaminated sites. The bioweathering potential of fungi has been envisaged as a possible means for the bioremediation of asbestos-rich soils. Several fungi could extract iron from asbestos mineral fibres (e.g. 7.3% from crocidolite and 33.6% from chrysotile by a *Verticillium* sp.), thereby removing the reactive iron ions responsible for DNA damage (Daghino *et al.*, 2006).

Conclusions

All kinds of microbes, including prokaryotes and eukaryotes and their symbiotic associations with each other and 'higher organisms', play a remarkably wide diversity of geoactive roles in the biosphere. Microbial transformations of metals and minerals are a vital part of natural biosphere processes and can also have beneficial or detrimental consequences for human society. Increasing our understanding of this important area of microbiology and exploiting it in applications such as bioremediation and other areas of biotechnology will clearly require a multidisciplinary approach.

Acknowledgements

The author gratefully acknowledges research support from the Biotechnology and Biological Sciences Research Council, the Natural Environment Research Council, the Royal Societies of London and Edinburgh, CCLRC Daresbury SRS, and British Nuclear Fuels plc. I would also like to thank key members of my research group, who contributed immensely to several aspects of the research reviewed here, especially the late Dr Chris White, and Drs Jacqueline Sayer (now Sugden), Euan Burford, Mohammed Gharieb, Simon Hockin, Helen Jacobs and Marina Fomina. Thanks are also due to Martin Kierans for invaluable assistance with electron microscopy, and Euan Starke for technical support over many years. I also acknowledge the inspiration and friendship of the late Joe Cooney (UMASS, Boston, USA), the late Terry Beveridge (Guelph, Canada), and Harry Eccles (BNFL, Springfields) for many years of advice, support and education. Thanks are also due to the late Alan Griffiths (Cardiff) for first kindling my interest in metals and microbes, and Sir William (Bill) Stewart FRS for enabling me to initiate metal-microbe research in Dundee. Finally, the support of the Society for General Microbiology and the British Mycological Society is gratefully acknowledged as is the inspiration from many friends and colleagues in microbiology, mycology and biogeochemistry around the world.

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