GEOMICROBIOLOGY OF METAL AND MINERAL TRANSFORMATIONS IN THE ENVIRONMENT

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Summary

Microbes play key geoactive roles in the environment particularly regarding element biotransformations and biogeochemical cycling, metal, mineral and radionuclide transformations, decomposition, bioweathering, soil and sediment formation. All types of microbes, including prokaryotes and eukaryotes and their symbiotic associations with each other and “higher organisms”, can contribute to geological phenomena, and metals and mineral transformations are central to many. Microbes possess several properties that can effect changes in metal speciation, toxicity and mobility, as well as mineral formation or mineral dissolution. Such mechanisms are important components of natural biogeochemical cycles for metals as well as associated elements in biomass, soil, rocks and minerals, and metalloids, actinides and metal radionuclides. Apart from this, 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 and radionuclide pollutants. In addition, 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 structural, technological, environmental and antimicrobial purposes. In contrast, microbial metal and mineral transformations 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 significant social and economic consequences.

1. 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 affecting microbial growth, activity and survival. Furthermore, many minerals are biogenic in origin, and their formation is of global geological and industrial significance, as well as providing important structural components for important microbial groups such as diatoms, foraminifers and radiolarians (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). The term biomineralization refers to the collective processes by which organisms form minerals (Bazylinski, 2001; Dove et al., 2003), a phenomenon widespread in biology and which can be mediated by archaea, bacteria, protists, fungi, plants, and animals. Most biominerals are calcium carbonates, silicates, and iron oxides or sulfides (Baeuerlein 2000; Bazylinski 2001). Metal-mineral-microbe interactions are of key
importance within the framework of geomicrobiology and also fundamental to microbial biomineralization processes (Gadd, 2010; Benzerara et al., 2011).

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, geomorphology, and related disciplines (Banfield & Nealson, 1997; Warren & Haack, 2001; Macalady & Banfield, 2003; Bottjer, 2005; Gleeson et al., 2007; Konhauser, 2007; Gadd, 2008a, 2010; Uroz et al., 2009; Viles, 2011; Benzerara et al., 2011). 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 types 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, 2010), and most of these processes involve metal and mineral transformations. Examples of geomicrobiologically-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, 2010; Kim & Gadd, 2008; Gadd & Raven, 2010). Root-inhabiting rhizosphere microbes, including mycorrhizal fungi, have a major influence on plant nutrition by means of effects on phosphate availability but also metal circulation (Amundson et al., 2007). 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 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 affects 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 is 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 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 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. 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 requiring an interdisciplinary approach involving physical, chemical and biological disciplines. This contribution 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.

2. Metals and Minerals

Metals comprise about 75% of the known elements, 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 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), and originate from natural sources such as rocks and metalliferous minerals, and anthropogenic inputs from, e.g. agriculture, 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. 2005). 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 impact aquatic systems through runoff, leaching and transport via mobile colloids (Adriano 2001; Adriano et al. 2005). Metals are significant natural components of all soils where their presence in the mineral fraction comprises 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 may 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 all minerals contain metals, and there can be a multitude of mineral types for each metal element, of varying distribution in the environment and physico-chemical properties. For example, manganese is 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, e.g. silicates, sulfides, oxides, carbonates and phosphates. Regardless of their origin, whether geologic or biogenic, microbes can interact with minerals and affect their structure by mechanical and biochemical mechanisms, and affect the speciation and mobility of component metals (Ehrlich, 1996; Edwards et al., 2005; Landa, 2005; Gleeson et al., 2007; Lian et al., 2008; Gadd, 2008b; Brown et al., 2008; Uroz et al., 2009).

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 minerals produced by geochemical mechanisms. Biominalization may particularly refer to processes where biominal formation is highly-directed 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 CO$_2$, 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).

3. 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 influence metal speciation and therefore solubility, mobility, bioavailability, and toxicity (Gadd & Griffiths, 1978; Gadd, 1992a, 1993a, 2004, 2005, 2007). Many metals are essential, 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
Elevated concentrations of toxic metals and radionuclides can occur in the fruit bodies (basidiomata) of macrofungi in polluted environments. This is of significance in relation to the use of macrofungi as bioindicators of metal pollution, and because of toxicity to humans from the consumption of wild fungi. In general, levels of lead, cadmium, zinc and mercury found in macrofungi from urban or industrial areas are higher than from corresponding rural areas, although there are wide differences in uptake abilities between different species and metals (Tyler 1980; Bressa et al. 1988; Lepsova & Mejstrik 1989; Wondratschek & Roder 1993; Nasr & Arp, 2011). Macrofungi are also effective accumulators of radiocesium (Malinowska et al. 2006), silver and gold (Borovicka et al., 2010a,b).

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). Microbial resistance to toxic metals is widespread with frequencies ranging from a few percent in pristine environments to nearly 100% in heavily polluted environments (Silver & Phung, 2009).

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 (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, 2004a, 2005, 2006). Other microbial properties lead to metal solubilization from organic and inorganic sources (Gadd, 2007). Such metal transformations are central to metal biogeochemistry, and emphasize the link between microbial responses and geochemical cycles for metals (Ehrlich, 1997; Gilmour & Riedel, 2009). 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 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 enzymatic detoxification which can also result in release from cells, e.g. Hg\(^{2+}\) reduction to Hg\(^0\) (Silver & Phung 1996, 2009; Nies 1992a, 1995, 1999, 2003; Rosen, 2002; Osman & Cavet, 2008). Bacterial plasmids have resistance genes to many toxic metals and metalloids, e.g. Ag\(^+\), AsO\(_2\)^–, Cd\(^{2+}\), Co\(^{2+}\), CrO\(_4\)^{2–}, Cu\(^{2+}\), Hg\(^{2+}\), Ni\(^{2+}\), Sb\(^{3+}\), TeO\(_3\)^{2–}, Ti\(^+\) and Zn\(^{2+}\). Related systems are also frequently located on bacterial chromosomes, e.g. Hg\(^{2+}\) resistance in *Bacillus*, Cd\(^{2+}\) efflux in *Bacillus*, arsenic efflux in *E. coli* (Silver & Phung 1996; Rosen, 2002). The most detailed research exists for As, Hg, Cd, Cu, Co, Zn, Pb, Ag, Ni and Te for which genes have been sequenced and resistance 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 compartmentalization (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 also may synthesize a variety of metal-binding peptides and proteins, e.g. metallothioneins and phytochelatins, which regulate metal ion homeostasis (Eide, 2000; Avery, 2001). In eukaryotes, intracellular compartmentalization may also be significant in tolerance (Gadd, 1993a; Eide, 2000; Avery, 2001).

Many 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 component of acidic and neutral soils. Such metal oxides are ubiquitous and play a significant role in influencing soil behavior, e.g. mineral catalysis of humic substance formation, and influence on enzymatic stability and microbial activity, and, together with microbial activities in metal and mineral transformations have a great impact on soil processes (Huang et al., 2005).

4. 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. In addition, other excreted metabolites with metal-complexing properties, e.g. amino acids, phenolic compounds, and organic acids may also play a
Low molecular weight carboxylic acids can play an important role in chemical attack of minerals providing protons as well as a metal-chelating anion (Burgstaller and Schinner, 1993; Jacobs et al., 2002a,b; Huang et al., 2004; Lian et al., 2008). 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. chloropyromorphite (Pb₅(PO₄)₃Cl), contaminated soil and other solid wastes (Sayer et al., 1999; Fomina et al., 2004a,b, 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 & Watts, 2003; Schroder et al., 2003; Lloyd et al., 2003): Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II) respectively. Microbial reduction of Fe(III) and Mn(IV) may also be a means for releasing contaminant metals absorbed to Fe(III) and Mn(IV) oxides and this process may be enhanced by humic materials, or related compounds (Lovley and Coates 1997; Lloyd et al., 2003). Bacterial Fe(III) reduction resulted in release of, e.g. Mn and Co, from goethite (Bousserrhine et al. 1999). Pu from contaminated soils (Rusin et al. 1993) and Ra from uranium mine tailings (Landa and Gray 1995). Mercuric ion (Hg⁴⁺) can be enzymatically 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). Enzymatic reduction of plutonium(IV) to more soluble plutonium(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 enzymatically reduced to ferrous iron with a suitable electron donor (Schroder et al., 2003). Many Fe(III) reducers are heterotrophs and such Fe(III) respiration may be a more important mechanism of carbon source decomposition in some anaerobic environments than sulfate reduction (Ehrlich & Newman, 2009). Some ferric iron 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 enzymatically 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 Ti, Pd, Pt, Au and Cr but the involvement of microbial/abiotic components is unclear. Mercuric ion (Hg\(^{2+}\)) may be methylated by bacteria and fungi to methylmercury [(CH\(_3\))Hg\(^+\)] which is more toxic than the mercuric ion (Barkay & Wagner-Dobler, 2005). Some bacteria can methylate methylmercury, forming volatile dimethylmercury. Methylmercury as well as phenylmercury can be enzymatically reduced to volatile metallic mercury (Hg\(^0\)) by some bacteria. Phenylmercury can also be microbially converted to diphenylmercury (Barkay & Wagner-Dobler, 2005).

### 4.1. 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 10\(^{19}\)). These low-molecular weight 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 Fe\(^{3+}\) 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 of industrial waste treatment (Renshaw et al., 2002). Some siderophores can also promote reductive dissolution of certain Mn oxides (Duckworth & Sposito, 2007).

### 5. Metal Immobilization

Microbial biomass provides a metal sink, either by biosorption to cell walls, pigments and extracellular polymeric substances (EPS) including 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; Aguilera et al., 2008). All microbial material can be effective metal biosorbents 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 as clays 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, e.g. 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) and 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 or metal radionuclide to a lower redox state occurs, mobility and toxicity may be reduced for several elements (Lovley 2001; Lloyd & Lovley, 2001; Finneran et al. 2002; Lloyd et al., 2003; Holden & Adams, 2003; Wall & Krumholz, 2006; Simonoff et al., 2007), 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 (UO$_2$) (Lovley and Coates 1997; Lovley 2001; Finneran et al. 2002; Lloyd, 2003; Lloyd & Renshaw, 2005; Landa, 2005). Anaerobically, hexavalent uranium(VI) can be reduced to tetravalent uranium(IV) by a number of bacteria using either H$_2$ or one of a variety of organic electron donors (Lovley and 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), Te(V), and Pd(II) (Aubert et al. 1998; Lloyd et al. 1999a,b; Lloyd & Macaskie 1998; Lloyd, 2003; Lloyd & Renshaw, 2005). Some sulfate-reducing bacteria like 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 and Obraztsova 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 Fe$^{2+}$ and the produced sulfide. Elemental silver (Ag$^0$) and gold (Au$^0$) 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 Mo, V, 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, 2010, 2011).
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 (Fe(II)) may be biologically or abiotically oxidized to ferric iron at pH >5 under anaerobic or partial or fully aerobic conditions. Some bacteria can oxidize ferrous iron enzymatically with the generation of energy, e.g. acidophiles like Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans, Sulfolobus spp., Acidibacillus brierleyi, and Sulfoferribacillus thermosulfidooxidans. Fe(II) is least susceptible to autoxidation below pH 5. Some bacteria growing at circumneutral pH can also oxidize ferrous iron enzymatically under partially reduced conditions, e.g. the stalked bacterium Gallionella ferruginea and sheathed bacteria like Leptothrix spp. (Ehrlich & Newman, 2009). Ferrous iron can also be oxidized non-enzymatically by microbes when their metabolic activities alter the microenvironment to favor autoxidation. Some Fe(III) precipitation may also arise from the destruction of ferric iron chelates. Ferric iron 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).

6. 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, and, 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 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 elemental cycles.

Biodegradation of organometallic (and organometalloid) compounds, still widely used in agriculture and industry, can result from direct enzymatic action, or by microbial facilitation of abiotic degradation, e.g. by alteration of pH and excretion of metabolites (Gadd, 1993b, 2000b). Organotins, 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 less toxic, diffusible and volatile Hg$^{0}$ by mercuric reductase (Gadd, 1993b).

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Biographical Sketch

Professor Geoffrey M. Gadd is a microbiologist who works on the interactions of fungi, and other microorganisms, with toxic metals, metalloids and radionuclides. This work has lead to an understanding of the processes underlying accumulation, detoxification and tolerance, as well as mechanisms that alter metal mobility and fate in the environment. The environmental and biotechnological significance of these phenomena continues to be a focus, particularly in biogeochemical studies on mineral formation and dissolution, and in the bioremediation of polluted soil and water. He gained a B.Sc. (1975) and Ph.D. (1978) in Microbiology, University College Cardiff, Wales, and after an AFRC Postdoctoral Research Fellowship (1978) at the University of Dundee, with Professor Sir William Stewart FRS, was appointed to a Lectureship in Microbiology (1979). He was promoted to a Personal Chair in Microbiology in 1995 and became Head of the Division of Biological Sciences in 1999. From 2000, he was Head of the Division of Environmental and Applied Biology (until 2007) and Deputy Research Director (until 2006) in the School of Life Sciences, University of Dundee. He has served as Head of the Division of Molecular Microbiology within the College of Life Sciences in Dundee, and from 2010, was appointed to the Boyd Baxter Chair of Biology. Publications include over 200 refereed papers, 1 co-written book, 35 co-edited books (2 as sole editor), and over 50 invited book chapters, with invitations to speak at over 140 national/international venues in over 20 countries. He has served as the Chair of the Eukaryotic Microbiology Division of the Society for General Microbiology, and is the Treasurer and a past-President of the British Mycological Society. Geoff’s research has been recognized by the Berkeley Award of the British Mycological Society (1990), a D.Sc. from the University of Wales (1994), Fellowship of the Institute of Biology (1994), Fellowship of the American Academy of Microbiology (1995), Fellowship of the Linnean Society (2003), a Royal Society of Edinburgh – Scottish Office Education Department Research Fellowship (1994), and the Charles Thom Award of the Society for Industrial Microbiology (2004). He was awarded a Burroughs Welcome Fund (BWF) Visiting Professorship in the Microbiological Sciences to Guelph University in 2001-2, sponsored by the American Society for Microbiology, and from 2001, has been a Honorary Research Fellow at the Scottish Crop Research Institute (now the James Hutton Institute). In 2007 he was elected to Fellowship of the Royal Society of Edinburgh, and to the International
Union of Pure and Applied Chemistry (IUPAC). He was awarded the Colworth prize of the Society for General Microbiology in 2009 based on his research contributions to applied and environmental microbiology and in 2012 was awarded the Sir James Black Prize of the Royal Society of Edinburgh, the Life Science Senior Prize, for research contributions to geomicrobiology.