Front. Earth Sci. China 2010, 4(2): 127–147
DOI 10.1007/s11707-010-0022-8

FEATURE ARTICLE

Mineral-microbe interactions: a review

Hailiang DONG (✉)[1,2,3]

1 Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, China University of Geosciences,
Wuhan 430074, China
2 Geomicrobiology Laboratory, State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences,
Beijing 100083, China
3 Department of Geology, Miami University, Oxford, OH 45056, USA

© Higher Education Press and Springer-Verlag Berlin Heidelberg 2010

Abstract The studies of mineral-microbe interactions lie at the heart of the emerging field of Geomicrobiology, as minerals and rocks are the most fundamental earth materials with which microbes interact at all scales. Microbes have been found in a number of the Earth's extreme environments and beyond. In spite of the diverse geological environments in which microbes are found and diverse approaches taken to study them, a common thread, mineral-microbe interactions, connects all these environments and experimental approaches under the same umbrella, i.e., Geomicrobiology. Minerals and rocks provide microbes with nutrients and living habitats, and microbes impact rock and mineral weathering and diagenesis rates through their effects on mineral solubility and speciation. Given a rapid growth of research in this area in the last two decades, it is not possible to provide a comprehensive review on the topic. This review paper focuses on three area, i.e., microbial dissolution of minerals, microbial formation of minerals, and certain techniques to study mineral-microbe interactions. Under the first area, three subjects are reviewed; they include siderophores as important agents in promoting mineral dissolution, microbial oxidation of reduced minerals (acid mine drainage and microbial leaching of ores), and microbial reduction of oxidized minerals. Under the second topic, both biologically controlled and induced mineralizations are reviewed with a special focus on microbially induced mineralization (microbial surface mediated mineral precipitation and microbial precipitation of carbonates). Under the topic of characterization, the focus is on transmission electron microscopy (TEM) and electron energy loss spectroscopy. It is the author's hope that this review will promote more focused research on mineral-microbe interactions and encourage more collaboration between microbiologists and mineralogists.

Keywords interaction, microbe, mineral, oxidation, reduction, siderophores, transmission electron microscopy (TEM)

1 Introduction

The last decade has seen an extraordinary growth of Geomicrobiology, the interdisciplinary field of Geology and Microbiology. The studies of mineral-microbe interactions lie at the heart of Geomicrobiology, as minerals and rocks are the most fundamental earth materials with which microbes interact at all scales, from macroscopic to microscopic. Microbes have been found in a number of the Earth's extreme environments (Dong and Yu, 2007), ranging from crystalline rocks of the deep subsurface (Boone et al., 1995; Stevens and McKinley, 1995; Fredrickson and Onstott, 1996; Fredrickson et al., 1997; Krumholz et al., 1997; Pedersen, 1997; Chapelle et al., 2002; Fredrickson and Balkwill, 2006), frozen ice from thousands of meters under Antarctic ice sheets (Priscu and Christner, 2004), acid mine drainage (Edwards et al., 2000b; Baker and Banfield, 2003; Johnson and Hallberg, 2009a), hot springs (Reysenbach et al., 2000a; Kashefi et al., 2002; Meyer-Dombard et al., 2005; Costa et al., 2009), and deep ocean hydrothermal vent systems (Zierenberg et al., 2000; Reysenbach et al., 2000b; Reysenbach and Shock, 2002). Even signatures of ancient life in Mars are being revealed (Thomas-Keprta et al., 2000; Friedmann et al., 2001; Thomas-Keprta et al., 2002), although the subject has been hotly debated (Buseck et al., 2001). In spite of the diverse geological environments in which microbes are found and diverse approaches taken to study them, a

Received December 7, 2009; accepted February 1, 2010

E-mail: dongh@muohio.edu

common thread, i.e., mineral-microbe interactions, connects all these studies under the same umbrella, i.e., Geomicrobiology. Minerals and rocks provide microbes with nutrients and living habitats and microbes impact rock and mineral weathering and diagenesis rates through their effect on mineral solubility and speciation (Edwards et al., 2000a; Bennett et al., 2001; Rogers and Bennett, 2004). The recognition of the importance of mineral-microbe interactions has revived the classical discipline of mineralogy (Hochella, 2002), where modern mineralogists study minerals in the broadly defined field of "environmental mineralogy." The unique and diverse microbes discovered in various earth habitats have also provided microbiologists with unique opportunities to study them.

Silicates and oxides are ubiquitous earth materials, and these two groups of minerals are among those first and best studied in terms of mineral-microbe interactions. In earth surface environments where oxygen is abundant, aerobic microorganisms interact with oxide and silicate minerals to obtain essential nutrients and to use them as protection from lethal habitats. The production of surface polymers and siderophores help them attach and dissolve minerals as a way to extract nutrients (Liermann et al., 2000b; Maurice et al., 2000; Hersman et al., 2001a; Ams et al., 2002; Roberts et al., 2006; Maurice et al., 2009). In the subsurface conditions, where oxygen becomes limited, anaerobic microorganisms thrive by respiring oxidized forms of metals in place of oxygen (Lovley, 2000; Newman, 2001; Lloyd, 2002) with a consequence of either dissolving or precipitating minerals. In either process, it is the microbes that gain energy and grow.

2 Overview of mineral-microbe interactions

Many rocks and minerals contain nutrients essential to microbial growth, and microbes actively extract nutrients from solid materials (Uroz et al., 2009). Due to low solubility of phosphorous-containing mineral, such as apatite, phosphorous is often limited in natural environments. Thus, microbes preferentially colonize those mineral and rock surfaces that contain phosphorus, mostly apatite, olivine, feldspars, glass, and basalt to support growth (Bennett et al., 2001; Roberts, 2004; Rogers and Bennett, 2004; Roberts et al., 2006; Mauck and Roberts, 2007; Mailloux et al., 2009) (Fig. 1). Iron is another essential nutrient that is often limited because of formation of insoluble iron oxides under oxic conditions. Microbes can recognize Fe-containing minerals and accelerate the release of Fe from silicate mineral, such as hornblende (Kalinowski et al., 2000; Liermann et al., 2000a) and feldspars (Mauck and Roberts, 2007). In order to attach to mineral surfaces and use Fe as an nutrient, certain bacteria (such as *Shewanella oneidensis* MR-1) seem to be able to modify the molecular arrangement at its outer cell membrane and react to molecular configurations present at the crystal surface of goethite (Lower et al., 2001). Using vertical scanning interferometry and phase shifting interferometry, Lüttge and Conrad (Lüttge and Conrad, 2004) demonstrated that Shewanella oneidensis MR-1 can recognize not only mineral surfaces (such as calcite) but also specific high-energy sites to form trenches on the calcite surfaces. This observation is consistent with another study in showing that the dissolution features of hematite by Shewanella putrefaciens display crystallographic control and alignment with structural defects associated with screw and step dislocations (Rosso et al., 2003). The implication is that the electron transfer need not be local and microorganisms have a strategy to access specific sites on mineral surfaces.

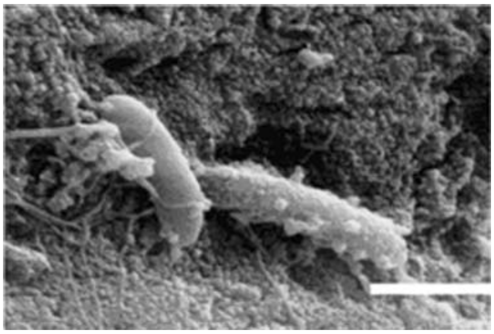

Fig. 1 Scanning electron microscope (SEM) photomicrograph of rod-shaped cells on basalt surface with precipitation of ferroan dolomite on cell surfaces after three months in anaerobic groundwater. Scale bar is 0.5 μm. Image courtesy of Jennifer A. Roberts (Roberts et al., 2004) with permission from the Geological Society of America

In the process of microbial attachment to mineral surfaces, extracellular polymeric substances (EPS) and other surface appendages may play important roles as they serve as anchors to solid surfaces and subsequent mineral dissolution (Barker et al., 1998; Welch et al., 1999) (Fig. 1). Some surface appendages could conduct electricity and may represent a common bacterial strategy for efficient electron transfer under anaerobic conditions (Gorby et al., 2006). As individual microbes discover advantages of living on mineral and rock surfaces because of sufficient supplies of nutrients and protection from lethal environmental stress and predation, they tend to produce signal molecules to attract other organisms to gradually build a community called biofilm (Harrison et al., 2005). In such a community, it is generally accepted that lichens (symbiotic associations between fungi and photosynthetic algae or cyanobacteria) are the first weathering pioneer organisms (Banfield et al., 1999) and complex microbial communities have been identified in lichens, and they work together to access atmospheric nitrogen and inorganic nutrients trapped in minerals and rocks. In natural environments, organisms living in biofilm have specific assignments of duties in a syntrophic relationship. Once a biofilm community is established and a function identified, minerals and rocks undergo weathering, i.e., some minerals and rocks dissolve, some precipitate, and some undergo transformation. There are various mechanisms of microbial weathering of minerals, i.e., via release of organic acids (Barker et al., 1998; Welch and Ullman, 1993) and other ligands (such as siderophiles) (Ullman and Welch, 2002; Kulczycki et al., 2007; Maurice et al., 2009), oxidation of reduced minerals and reduction of oxidized minerals (Santelli et al., 2001; Uroz et al., 2009). Each of these mechanisms will be reviewed in the following sections in the context of microbial effects on mineral reactions.

As a result of microbial activity, minerals and rocks are weathered at a significantly faster rate than in abiotic systems (Barker et al., 1997), often by orders of magnitudes (Barker et al., 1998). In the presence of microbial activity, the mineral weathering sequence is altered relative to abiotic systems (Bennett et al., 2001). In its absence, the most unstable silicate mineral weathers first, followed by more stable silicates. The order of weathering roughly follows the Bowen series (crystallization temperature), i.e., olivine → pyroxene → amphibole → biotite → orthoclase → muscovite → quartz, and Ca-rich plagioclase → Ca/Na plagioclase → Na-rich plagioclase → orthoclase → muscovite → quartz. However, the observed weathering sequence of minerals in an anaerobic, microbially controlled system, however, is almost opposite, with olivine stable with respect to microcline, and the relationship between microbial colonization and weathering rate is almost perfectly correlated. This opposite sequence is ascribed to the fact that olivine usually does not contain any phosphorous, whereas feldspars and quartz can contain certain amounts of phosphorous (Bennett et al., 2001).

In addition to microbial dissolution of minerals (Dong et al., 2003), microbial activity also contributes to the formation of different minerals, a process termed as biomineralization (Lüttge et al., 2005; Konhauser, 2007). Oxides, sulfides, and carbonates (Lian et al., 2006) are typical examples of biogenic minerals (Konhauser, 2007).

Microbial weathering of minerals and rocks has important implications for mobility and the ultimate fate of nutrients and contaminants. Those nutrients released from minerals and rocks not only support microbial growth but also contribute to soil fertility (Wu et al., 2007; Lian et al., 2008; Wu et al., 2008). For example, the release of K during the degradation of silicate minerals by bacteria has been reported in numerous studies (Lian et al., 2008 and references therein), and it may account for a significant fraction of K taken up by plants. Some elements released from minerals and rocks are toxic and constitute a significant environmental problem. For example, one recent study has shown that arsenic is released when *Burkholderia fungorum* dissolves apatite (Mailloux et al., 2009). The released arsenic may account for a significant fraction of arsenic in drinking groundwater in Southeast Asia.

3 Microbial dissolution of minerals

3.1 Role of siderophores and other organic compounds in mineral dissolution

Siderophores are low-molecular-weight organic ligands that form strong complexes with metals and radionuclides mostly in aerobic environments. Many recent researches have focused on siderophore sorption and dissolution of many minerals including Fe (hydr)oxides, Fe-rich aluminosilicates, Mn oxides, and Pb phosphate (Duckworth et al., 2009b; Maurice et al., 2009). Many aerobic microbes can produce siderophores as a means to extract essential nutrients from minerals. For example, *Pseudomonas mendocina* can produce siderophores to extract iron from goethite, hematite, ferrihydrite, and kaolinite (Hersman, 2000; Maurice et al., 2000; Hersman et al., 2001a; Hersman et al., 2001b; Maurice et al., 2001) by dissolving these minerals. The produced siderophores can dissolve these Fe minerals and support bacterial growth. The stability of siderophore-Fe(III) complexes is extremely high (Kraemer, 2004; Kraemer et al., 2005), suggesting a high efficiency of free siderophores in decreasing the Gibbs energy of iron oxide dissolution reactions. As a result, the bacterial growth rates may not be a simple function of iron oxide surface area or crystallinity, and it is probably the abundance of reactive sites in the structure of the iron (hydr)oxides that is available for effective binding of siderophores with bacteria (Hersman et al., 2001a). Because of the prevalence of aerobic bacteria and (hydr) oxides, siderophore-induced dissolution and precipitation of iron oxides and silicates likely play an important role in mineral reactions.

Siderophores and other ligands have been shown to form stable complexes with many other metals including Mo (Liermann et al., 2005), Cu (Kim et al., 2001), Co (Duckworth et al., 2009a), Mn (Duckworth and Sposito, 2005), Al (Desroches et al., 1999), and others, and the formation of certain siderophore-Mn(III) complexes is of particular importance. Mn(III) is an intermediate product of Mn(II) oxidation and Mn(IV) reduction. Because Mn (III) is unstable as a free ion and rapidly disproportionates to Mn(II) and Mn(IV) (Morgan, 2000), its presence in high concentrations in natural environments is ascribed to the formation of siderophore-Mn(III) complexes with exceptionally high stability constants. Siderophores can also dissolve a number of Mn oxides via reduction and nonreduction pathways (Duckworth and Sposito, 2007; Pena et al., 2007), forming siderophore-Mn(III) complexes in a number of aquatic environments.

3.2 Microbial oxidation of reduced minerals

3.2.1 Microbial oxidation of sulfides

Past studies have focused on the microbial oxidation of metal sulfides in coal mines and metal sulfide deposits. The ability of bacteria to oxidize metal sulfides causes significant environmental problems (e.g., acid mine drainage) (Druschel et al., 2004) as well as economic advantage (e.g., recovery of Au and other trace metals from sulfides and mine spoils) (Hao et al., 2010 and references therein). Microbial oxidation of reduced minerals occurs in a number of environments at both neutral and acidic pH.

Bacterial oxidation of sulfide minerals is the major factor in the formation of acid mine drainage (AMD). AMD forms because of the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

In the initial step, pyrite reacts with oxygen and water to produce ferrous iron, sulfate, and acidity. The second step involves the conversion of ferrous iron to ferric iron. This second reaction is the “rate determining” step for the overall sequence (Singer and Stumm, 1970), but its rate can be greatly accelerated by Fe(II)-oxidizing microorganisms. The third step involves the oxidation of additional pyrite by ferric iron. The ferric iron is generated by the initial oxidation reactions in steps one and two.

As AMD flows across the land, its high acidity and metal content can kill vegetation and other biota (Nordstrom and Alpers, 1999). AMD flow paths become “dead zones” that remain barren indefinitely (Fig. 2). The Fe(II) concentration decreases as AMD flows out to nearby streams and soils, and pH and Eh change in different ways depending on specific geochemical reactions involved (Fig. 2). In well-drained uplands, AMD dead zones often consist of bright orange mounds capped with tough crusts of oxidized iron (oxy)hydroxides (Fig. 2). In streams and wet lowlands, AMD pollution often results in the formation of “slime streamers” composed of algae and filamentous, acidophilic Fe(II), and sulfur-oxidizing microorganisms (Baker and Banfield, 2003).

Both autotrophic and heterotrophic archaea and bacteria catalyze iron and sulfur oxidation in AMD and may ultimately determine the rate of release of metals and sulfur to the environment. Due to the harsh chemical conditions overall, AMD communities contain fewer prokaryotic lineages than many other environments. The most extensively studied and common autotrophic groups are *Acidithiobacillus ferrooxidans* (up to 100,000 culturable cells per milliliter of AMD) and *Leptospirillum ferrooxidans* (Baker and Banfield, 2003; Nicormat et al., 2006). Because they are chemolithoautotrophic (i.e., they derive cellular carbon from CO_2 fixation and ATP from the oxidation of Fe(II) to Fe(III)); these Fe(II)-oxidizing bacteria can thrive in AMD and associated precipitates, both of which contain very little organic carbon. The activity of these bacteria is pH dependent with optimal conditions in the range of pH 2 to 3. Thus, once pyrite oxidation and acid production have begun, conditions are favorable for bacteria to further accelerate the reaction rate. At pH values of about 6 and above, bacterial activity is thought to be insignificant when compared to abiotic reaction rates. The catalyzing effect of the bacteria effectively removes constraints on pyrite weathering and allows the reactions to proceed rapidly. These microbial streamers and associated sediments also harbor aerobic organoheterotrophic bacteria, which may compete with Fe (II) oxidizing bacteria for O_2. Alternatively, these heterotrophic bacteria could enhance Fe(II) oxidation by

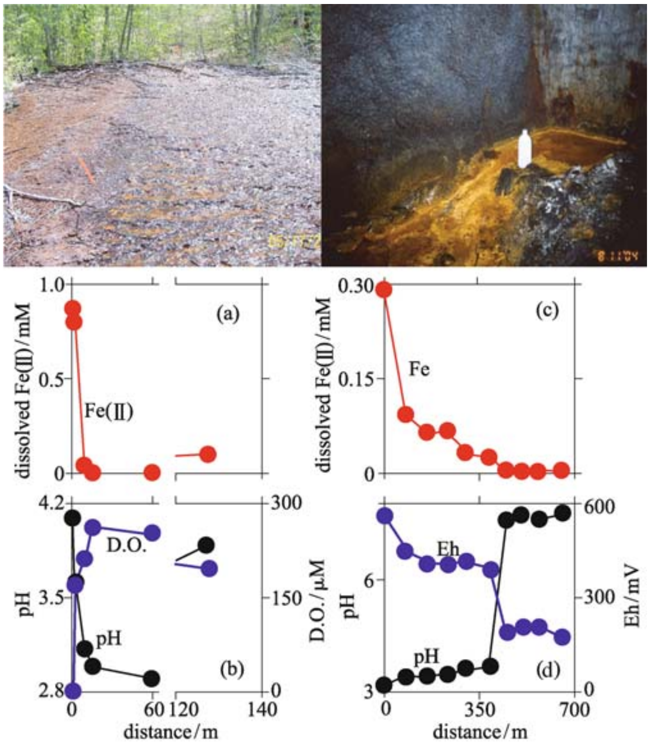

Fig. 2 Acid mine drainage in the Appalachian region of the United States and Shanxi Province, China, caused by extensive coal mining activities. Top left – Gum Boot Run, McKean County, Pennsylvania, US, photo taken by William Burgos. Top right – Sitai mine, Shanxi Province, photo taken by Fenghua Zhao. Bottom graphs (a) and (b): Lateral geochemical gradients measured in these AMD-impacted systems as acidic fluids pass over the iron mound in the Gum Boot Run system. (c) and (d): Lateral gradients downstream of Sitai mine into the Shili River watershed. The images and the data are provided by William Burgos and Fenghua Zhao

consuming dissolved organic carbon (which may be toxic to autotrophic bacteria) and produce CO_2 (as a C source for autotrophic Fe(II) oxidizers) (Johnson and McGinness, 1991; Marchand and Silverstein, 2003).

As a result of microbial iron and sulfur oxidation, many Fe(III) minerals precipitate, and they play important roles in water quality and trace metal biogeochemistry in AMD sites. Fe(III) minerals usually formed in AMD include jarosite at $pH < 3$ and high sulfate concentration, whereas ferrihydrite and goethite precipitate at pH 6.5 or higher (Bigham et al., 1996; Schwertmann and Carlson, 2005). Schwertmannite is a common precipitate at intermediate pH (3–4) and acts as an important sink for trace metals through adsorption or coprecipitation (Bigham and Nordstrom, 2000; Fukushi et al., 2003; Regenspurg and Peiffer, 2005; Espana et al., 2006). In time, this metastable phase transforms to more stable goethite (Bigham et al., 1996; Schwertmann and Carlson, 2005; Peretyazhko et al., 2009). A most recent laboratory study illustrated that the type of precipitates in AMD environments could be influenced by the concentrations of *A. ferrooxidans* and Fe^{2+}. When these concentrations are high, externally supplied ammonium is depleted, and K-jarosite may form. When these concentrations are low, high concentrations of externally supplied ammonium and Fe^{3+} results in the formation of K-NH_4-H_3O jarosite and schwertmannite (Wang et al., 2010b).

The AMD system most intensively studied is within the Richmond Mine at Iron Mountain in northern California (Nordstrom and Alpers, 1999; Nordstrom, 2000; Baker and Banfield, 2003) and Appalachian coal mines (Senko et al., 2008; Senko et al., 2009). The Richmond mine contains some of the most acidic mine waters in the world, with measured pH values as low as -3.6, dissolved metal concentrations as high as 200 g/L and sulfate 760 g/L (Nordstrom and Alpers, 1999). Many soluble metal sulfate minerals form from these mine waters. Extremely acidophilic prokaryotes with very low diversity make up microbial communities in these waters and precipitates, and their main ecological function is iron oxidation, but iron reduction can be present in underlying anoxic precipitates (Baker and Banfield, 2003). Because of their extremely high tolerance to low pH, these organisms can possibly be used as agents to remediate AMD as a better alternative than abiotic remediation.

Remediation strategies for AMD are divided into passive and active treatment systems. Active systems involve chemical addition, sludge production, and operator maintenance, and typically employ abiotic processes to neutralize acidity so that Fe, Al, and Mn (oxy)hydroxides precipitate (Johnson and Hallberg, 2005). Passive treatment systems are more cost-effective (Younger, 1997) and typically employ a combination of biotic and abiotic processes. In such systems, limestone beds and/or wetlands are used to neutralize acidity and precipitate the metals. In oxic limestone drains, AMD is passed through a limestone bed to neutralize the acidity and to promote the oxidation of Fe(II) and precipitation of Fe(III) oxides. As the AMD acidity is neutralized, the elevated pH in the bed enhances the rate of abiotic Fe(II) oxidation, subsequently resulting in the precipitation of Fe(III) (Cravotta and Trahan, 1999). Fe(III) (hydr)oxides typically accumulate on limestone surfaces (referred to as "armoring"), and this armoring limits further limestone dissolution and neutralization capacity. Armoring necessitates the replacement of limestone or flushing periodically during the life time of remediation in order to remove Fe(III) oxides from limestone surfaces. To overcome this armoring problem, biological low-pH Fe(II) oxidation can be exploited to spatially separate Fe oxidation and Fe(III) (hydr)oxide precipitation. The method involves two steps, i.e., the oxidative precipitation of Fe at low-pH, and the acid neutralization by a limestone bed. This method is expected to limit limestone armoring and clogging, decreases maintenance costs, and improves the overall system performance.

3.2.2 Biological recovery of precious metals from sulfides

The ability of acidophilic bacteria to oxidize metal sulfides not only causes significant environmental problems such as AMD but also brings economic advantage, such as microbial leaching and recovery of ores. If the concentration of metal in the ore is too low to economically mine it and it may be too expensive to concentrate it by conventional chemical means, microbial leaching and concentration may be a preferred choice. Microbial leaching and recovery is commonly used for metals, such as Au and Cu in sulfides. These metals can be released from refractory minerals by oxidation of the covalent metal-sulfide bond by strong oxidant, such as Fe^{3+}, and the process is catalyzed by acidophilic iron- and sulfur-oxidizing microorganisms (Ubaldini et al., 2000). After biooxidation, insoluble sulfide is totally or partially dissolved, and most of precious metals within sulfides can be extracted in the subsequent cyanidation process. Microorganisms in these biooxidation processes are added to the leaching solution, and some of them may be sorbed onto mineral particle surfaces (Ghauri et al., 2007). Compared with any conventional pretreatment processes, biooxidation has proven to be the most promising method for recovering refractory ores from both economic and environmental perspectives. The biooxidation process to recover gold from sulfides is commercially used in countries such as Australia, China, Ghana, Peru, and South Africa (Canales et al., 2002; Olson et al., 2003).

Microorganisms involved in the biooxidation process are usually mixed populations of acidophiles, and their diversity and mutual interactions are important considerations during the design of the bioleaching process. Therefore, understanding microbial community structure and its dynamic change during bioleaching of refractory gold from sulfide minerals is important to optimize environmental conditions so that the biooxidation rate can be optimized for commercial applications. It has now been shown that Leptospirillium ferriphilum and Acidithiobacillus caldus are widely distributed in bioleaching plants operating between 40°C and 55°C, as well as other species from other genera, including Acidiphilium, Acidocella, and Ferroplasma (Clark et al., 2006; Dhugues et al., 2008; Johnson and Hallberg, 2009b). These species, along with certain heterotrophic bacteria, may undergo succession in the bioleaching process in response to changes of pH, redox potential, ferrous iron concentration, and organic carbon availability (Hao et al., 2010).

3.2.3 Microbial oxidation of oceanic basalts and glass

Another important environment where microbes oxidatively dissolve minerals is oceanic crust. Microorganisms at and beneath the ocean floor play an important role in rock/glass alteration (Fisk et al., 1998; Furnes and Staudigel, 1999; Staudigel et al., 2006), chemical and isotopic exchange between the oceanic crust and the sea water (Furnes et al., 2001), and biogeochemical cycles of C, Fe, S, and other elements (Fisk et al., 1998; Edwards et al., 2005). The prominent role of microorganisms in the weathering of basalt and glass has been demonstrated in both laboratory culture study (Staudigel et al., 1995; Thorseth et al., 1995a; Staudigel et al., 1998; Bach and Edwards, 2003; Wu et al., 2007) and in-situ incubation experiments (Bach and Edwards, 2003). In these studies, Fe- and Mn-oxidizing lithoautotrophs obtained from deep-sea environments have been demonstrated to be capable of growth on basalt glass as the sole source of energy and they are found to enhance the rate of basalt dissolution by up to an order of magnitude (Edwards et al., 2004; Templeton et al., 2005). In these processes, they predominantly derive energy from the oxidation of sulfides, methane, ferrous iron and manganese, and H2, the reduction of certain ferric iron, sulfate, and CO_2, and the respiration and fermentation of organic matter.

Some unique textures result when microorganisms weather basaltic glass in the oceanic crust, such as tubular structures (Fig. 3) (Thorseth et al., 1995b; Fisk et al., 1998). These textures are typically accompanied by characteristic enrichments of certain elements and depletion of others as well as isotope variations (Thorseth et al., 1995b; Furnes et al., 2001; Fisk et al., 2003; Thorseth et al., 2003; Storrie-Lombardi and Fisk, 2004; Banerjee et al., 2006). Taken together, these features have been used as biosignatures to determine biogenicity of ancient rock records on early Earth and Mars (Furnes et al., 2004; Furnes et al., 2005; Fisk et al., 2006; McLoughlin et al., 2007). However, cautions have to be exercised not to overinterpret the importance of these lines of textural and geochemical evidence, unless other supporting evidence, such as nucleic acids and lipid biomarkers, is presented.

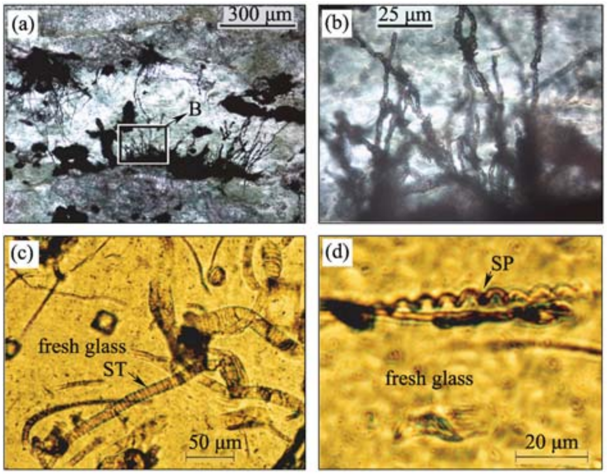

Fig. 3 Optical micrographs of tubular bioalteration textures in volcanic glass from pillow lavas and interpillow hyaloclastite. (a) Thin section from interpillow sample from the Euro Basalt of the Warrawoona Group, Pilbara Craton, Australia; (b) details of the bioalteration tubular textures. (c) & (d) bioalteration structures in Cretaceous fresh glass from pillow rims, Troodos ophiolite, Cyprus. Images courtesy of Hubert Staudigel (Staudigel et al., 2006) with permission from the Geological Society of America

3.2.4 Microbial reduction of oxidized minerals

In anaerobic environments, certain microorganisms are capable of utilizing Fe(III) as the electron acceptor in microbial respiration, a process called Fe(III) respiration (Lovley, 2000). Such microorganisms are called dissimilatory metal-reducing prokaryotes. Many other metals have been recently discovered to serve as the electron acceptor as well, and such studies are often conducted in the context of geochemical cycling and environmental remediation. Many metals are soluble in water in their high-valence states and become insoluble when reduced. For example, microbial reduction of Cr(VI) to Cr(III), U (VI) to U(IV), and Tc(VII) to Tc(IV) results in precipitation of these metals (Lovley, 2000; Lloyd, 2002; Wall and Krumholz, 2006).

A great number of minerals have been studied in the context of microbial reduction of metals including iron and manganese oxides (Lovley, 2000; Kappler and Straub, 2005; Roden, 2006), phyllosilicates (Dong et al., 2009; Stucki and Kostka, 2006), and other minerals containing oxidized forms of metals. Dissimilatory metal-reducing prokaryotes are also capable of reducing a number of other metals including Mn, Cr, U, Tc, As, and V, among others (Lovley, 2000), and many of them have been identified, isolated, and characterized (Lovley, 2000; Lovley et al., 2004). These organisms consist of both Bacteria and

Archaea with diverse physiological characteristics (from psychrophilic to thermophilic, facultative to obligate anaerobic, etc.). Two mostly intensively studied genera of bacteria are Geobacter and Shewanella (Pennisi, 2002).

How bacteria respire metals in solid minerals is still not well known, in part because we have not been able to observe the processes at the molecular level at the microbe-mineral interface under physiologically relevant conditions. The current understanding is that electron transfer process from bacteria to solid minerals is accomplished via six possible mechanisms, i.e., direct contact (Arnold et al., 1988; Nevin and Lovley, 2002), natural humic substances and related compounds as electron-shuttling compounds (Lovley and Blunt-Harris, 1999; Lovley et al., 1996; Nevin and Lovley, 2002), soluble shuttles produced by bacteria themselves (quinones and redox-active antibodies) (Marsili et al., 2008; Newman, 2008), nanowires (Reguera et al., 2005; Gorby et al., 2006; Reguera et al., 2006), EPS, such as polysaccharides (Marshall et al., 2006), and chemotaxis (Childers et al., 2002).

Oxides and phyllosilicates are the two most intensively studied categories of minerals to date. The rate and extent of microbial reduction of Fe(III) and Mn(IV) in oxides and phyllosilicates are generally correlated with crystallinity, surface area, and redox potential with amorphous Fe(III)- and Mn(IV)-containing minerals most bioreducible and more crystalline minerals least reducible (Roden and Zachara, 1996; Kostka et al., 1999; Dong et al., 2009; Jaisi et al., 2009). Microbial reduction of Fe(III) and Mn (IV) oxides often results in dissolution of the minerals and release of other adsorbed or structurally incorporated elements. Under favorable conditions, various biogenic minerals, such as siderite, vivianite, magnetite, and green rust precipitate depending on the solution chemistry and the saturation state of the precipitating minerals (Fredrickson et al., 1998; Fortin and Langley, 2005; Konhauser, 2007; Zhang et al., 2009a). These biogenic minerals may exhibit peculiar morphology, structure, and chemical and isotopic compositions that may be used as biosignatures (Beard et al., 1999; Vali et al., 2004; Benzerara and Menguy, 2009). In contrast, microbial reduction of Fe(III) in phyllosilicates only results in partial dissolution (Dong et al., 2003), and the extent of dissolution is influenced by a number of factors including the nature of the clay mineral, the extent of bioreduction, solution chemistry, and the nature of microorganisms involved (Dong et al., 2009). Although the phyllosilicates may be resistant to microbial dissolution, their physical and chemical properties may change substantially as a result of microbial activity (Stucki and Kostka, 2006) with profound consequences on soil fertility and contaminant mobility (Stucki, 2006). Some studies have taken an advantage of microbially promoted dissolution of iron oxides and phyllosilicates to purify kaolin (Shelobolina et al., 2005) and bauxite for industrial applications (Zhou et al., 2010). Recent research has focused on using bioreduced smectite clay mineral to reduce heavy metals (such as Tc and U) (Jaisi et al., 2008; Jaisi et al., 2009; Zhang et al., 2009b) and organic compounds (Hofstetter et al., 2003; Hofstetter et al., 2006; Neumann et al., 2008).

Given a growing body of research in this area in the last two decades, it is not possible to provide a comprehensive review on the topic. The interested readers are referred to some recent review chapters and papers, such as the following: Geomicrobiology: Interaction between microbes and minerals (Banfield and Nealson, 1997); Environmental microbe-metal interactions (Lovley, 2000) ; Biomineralization (Baeuerlein, 2000; Dove et al., 2003); Molecular Geomicrobiology (Banfield et al., 2005); Introduction to Geomicrobiology (Konhauser, 2007); Geomicrobiology (Elrlich and Newman, 2009); and Microbe-clay mineral interactions (Dong et al., 2009).

4 Microbial formation of minerals

4.1 Biologically controlled mineralization (BCM)

Biologically controlled mineralization refers to the process by which microorganisms exert a genetic and biochemical control over the nucleation and growth of certain minerals. The minerals produced by bacteria in BCM are usually well-ordered crystals with narrow size distributions, specific particle morphologies, and chemical purity (Bazylinski and Frankel, 2003). Magnetite in BCM represents a best studied example, and it possesses several unique characteristics, including high chemistry purity, crystallographic perfection, narrow size range, elongated hexaoctahedral prisms, and chains of crystals (Thomas-Keprta et al., 2000). These unique characteristics are distinct from those induced by microbial activity (see below) and have been used as biosignatures for life on Mars (Thomas-Keprta et al., 2000; Friedmann et al., 2001; Thomas-Keprta et al., 2002), although the subject has been hotly debated (Buseck et al., 2001; Golden et al., 2001; Golden et al., 2004), as discussed in a recent review paper (Benzerara and Menguy, 2009). It is argued that similar features may be found in abiotic magnetite as well (Golden et al., 2001; Golden et al., 2004).

Previous studies have focused on intracellular magnetite and gregite as typical examples of biologically controlled mineralization (Bazylinski and Frankel, 2000). The formation of these minerals, called magnetosomes, is genetically controlled by a group of bacteria called magnetotactic bacteria. These crystals are of single domain, have small size range (35–120 nm), and form chains of crystals. The arrangement of the magnetosomes in chains in a bacterium is supposed to maximize its magnetic dipole moment by overcoming its thermal forces. The magnetic dipole moment resulting from the presence of magnetosomes causes the cell to passively align along the geomagnetic field lines while it swims (magnetotaxis). Magnetotaxis is advantageous to motile microorganisms in vertical concentration gradients because it increases the efficiency of finding and maintaining an optimal position in vertical concentration gradients (such as oxygen gradient) (Bazylinski and Frankel, 2003). The formation of these magnetosomes involves iron uptake into the cell and some intracellular reduction/oxidation (Bazylinski and Frankel, 2004).

There are other intracellular precipitates, i.e., Fe-, As-, Mn-, Au-, Se-, and Cd-precipitates, but their biological and environmental functions remain unclear (Edwards and Bazylinski, 2008). Of particular note is the intracellular formation of iron and manganese granules by a dissimilatory metal-reducing bacteria *Shewanella putrefaciens* strain CN32 when this bacterium reduces Fe(III) in ferrihydrite and Mn(IV) in birnessite or pyrolusite (Glasauer et al., 2002; Glasauer et al., 2004; Glasauer et al., 2007). The iron granules consist of ferric hydroxide partially composed of small amounts of magnetite and/or maghemite, and the identity of the manganese granules is not determined. These intracellular granules have been proposed to be "reservoir of oxidant," a source of energy during the time periods of depletion of electron acceptors from natural environments (Glasauer et al., 2007). It is emphasized that it is not currently known if these granules are genetically controlled, because they have qualities of minerals produced by both MCM and BIM.

4.2 Biologically induced mineralization (BIM)

Biologically induced mineralization, BIM, is a much looser term than BCM and refers to mineral precipitation induced by microbial activity via alteration of local pH, removal of certain inhibitors, and mineral saturation state. Because of these diverse pathways and minerals formed, the presence of these biominerals cannot be used as biosignatures. Below, we review a few examples of BIM.

4.2.1 Microbial surfaces as nucleation sites for mineral precipitation

Living cells themselves can provide nucleation sites for mineral precipitation on their surfaces, and they induce the formation of biominerals (Dove et al., 2003). The cell surface has certain functional groups, mainly carboxyl, hydroxyl, amine, and phosphate groups. Most of these functional groups are negatively charged and thus attract positively charged metal cations from the natural environments (Beveridge and Murray, 1976; Beveridge and Murray, 1980), the first step for authigenic mineral formation (Beveridge et al., 1983; Ferris et al., 1986; Ferris et al., 1987). Cell surfaces often contain many appendages, including lipopolysaccharide (LPS) and extracellular polymeric substances (EPS). These appendages further help bind metal ions and serve as nucleation sites. Because metal binding to cell surfaces not only triggers mineral precipitation but also affects metal mobility in natural environments, a great deal of research has been devoted to quantitatively assess and predict the kinetics and capacity of metal binding to cell surfaces (Fein et al., 1997; Daughney et al., 2001; Borrok et al., 2005). Mineral precipitation around cell surface eventually encrusts the cell and results in preservation of bacterial cells in sedimentary records (Beveridge et al., 1983).

The newly formed precipitates are usually amorphous, but with time, they undergo transformation to more crystalline minerals. Many types of minerals have been observed on cell surfaces, including (hydr)oxides, silicates, amorphous silica, carbonates, phosphates, sulfates, and sulfides (Rickard and Morse, 2005; Pósfai and Dunin-Borkowski, 2006; Konhauser, 2007). These minerals are usually fine-grained and lack particular morphology. Because of large surface areas, these precipitates are important sorbents for a number of metals, organic compounds, and other agents in natural environments.

4.2.2 Microbial formation of carbonates

The study on microbial formation of carbonates has had a long history, beginning in the late nineteenth century (Ehrlich and Newman, 2009) when extensive evidence was presented for biogenic precipitation of $CaCO_3$. The early studies demonstrated that $CaCO_3$ precipitation was not specific to any group of bacteria and depended on environmental conditions. Subsequent work focused on the origin of massive carbonates in the Bahamas, and to date, it is clear that carbonates of the Bahamas are of both biogenic and chemical origins. Biogenic $CaCO_3$ is usually in the form of aragonite. It is also clear that phototrophic bacteria, such as cyanobacteria, play an important role in carbonate precipitation from diverse environments (Ehrlich and Newman, 2009). The precipitated carbonates are extracellular via diverse mechanisms, such as aerobic or anaerobic oxidation of carbon and nitrogen compounds, reduction of sulfate to sulfide by sulfate-reducing bacteria, hydrolysis, and removal of CO_2 from bicarbonate-containing solution (Ehrlich and Newman, 2009). More recent studies have expanded depositional environment of carbonates from marine environments (the Bahamas and the Gulf of Mexico) to caves (Barton and Northup, 2007) and saline lakes/lagoons (Wright, 1997; Wright and Wacey, 2005). In cave environments, the role of microorganisms has been demonstrated in the formation of speleothem and moonmilk (Barton and Northup, 2007). Despite the oligotrophic nature of caves, heterotrophic bacteria can be active in mediating calcium carbonate precipitation by increasing pH and providing nucleation sites (Wang et al., 2010a). In addition to biogenic formation of $CaCO_3$, other biogenic carbonates include dolomite, siderite, and rhodochrosite are also commonly present in these environments.

Biogenic precipitation of dolomite has recently received much attention and this biogenic mechanism may provide a partial solution to the well-known "dolomite problem." The problem can be simply stated as follows: dolomite rock is one of the most common sedimentary materials, yet efforts to chemically synthesize dolomite in the laboratory under simulated conditions (i.e., low temperature and pressure) have largely failed (Land, 1998). Dolomite formation is thermodynamically favorable but kinetically slow, i.e., there exists a kinetic energy barrier in its formation (Krauskopf and Bird, 1995).

Dolomite can be formed via the following pathways, as shown in Table 1.

Geological observations (i.e., poor preservation of fossils, the coarseness of grains, cavities, and pore spaces) indicate that many dolomite rocks are formed via the replacement of preexisting calcite (Reaction 1 and 2) over a long time under conditions of high salinity and pH, a low Ca/Mg ratio, and an elevated temperature (Krauskopf and Bird, 1995). Dolomite can also be formed via primary precipitation from aqueous solution (Reaction 3), especially for those dolomites that are associated with saline evaporite deposits (Vasconcelos and McKenzie, 1997; Wright, 1999; Wright and Oren, 2005; Wright and Wacey, 2005) and methane-bearing sediments and gas hydrates on ocean floor (Baker and Burns, 1985; Cavagna et al., 1999; Rodriguez et al., 2000; Pierre and Rouchy, 2004; Sassen et al., 2004). However, neither the replacement nor the direct precipitation mechanism has been rigorously demonstrated in the laboratory at low temperatures in the absence of microbial activity.

The recent discovery of microbially mediated dolomite formation in culture experiments with sulfate reducing bacteria (SRB) suggests that bacteria can overcome the kinetic energy barrier to dolomite formation by increasing pH and carbonate alkalinity (Vasconcelos et al., 1995; Warthmann et al., 2000) and by removing sulfate, a known inhibitor to homogeneous nucleation of dolomite in solution (Baker and Kastner, 1981). SRB may be important in mediating dolomite precipitation in nature, such as modern saline lakes and lagoons (Vasconcelos and McKenzie, 1997; Wright, 1999; Wright and Oren, 2005; Wright and Wacey, 2005). Among these, dolomites in the distal ephemeral lakes of the Coorong Region of South Australia are probably the best studied example. The role of SRB in dolomite precipitation in these lakes has been demonstrated with a combination of mineralogical, geochemical, isotopic, and microbial studies in both laboratory and in the field (Wright, 1999; Wright and Wacey, 2005; Wacey et al., 2007). One halophilic SRB that can promote dolomite precipitation has been isolated from a hypersaline coastal lagoon, Lagoa Vermelha, Rio de Janeiro, and Brazil (Warthmann et al., 2005). Some halophilic bacteria can precipitate dolomite even in the presence of sulfate (Sánchez-Román et al., 2008), and they may account for primary precipitation of dolomite in modern hypersaline environments. Methanogens may also be important in mediating dolomite precipitation (Roberts et al., 2004; Kenward et al., 2009). These results collectively suggest that SRB, halophiles, and methanogens all play an important role in dolomite formation, especially in saline environments and that removal of sulfate may not be a necessary prerequisite for dolomite precipitation (Sánchez-Román et al., 2009).

Gas hydrate and methane-seep deposits in deep oceans are the largest potential fossil fuel reservoir on Earth, and they play an important role in regulating global carbon cycle. Formation of dolomite in these environments is globally significant, both in modern (Kulm and Suess, 1990; Roberts and Aharon, 1994; vonRad et al., 1996; Sample and Reid, 1998; Stakes et al., 1999; Aloisi et al., 2000; Rodriguez et al., 2000; Greinert et al., 2001; Sassen et al., 2004; Formolo et al., 2004) and ancient (Jorgensen, 1992; Terzi et al., 1994; Cavagna et al., 1999; Peckmann et al., 1999; Peckmann et al., 2001; Peckmann and Thiel, 2004; Pierre and Rouchy, 2004) methane seeps and gas hydrate deposits. Multiple studies have published negative 13C values of authigenic dolomite associated with these deposits (Roberts and Aharon, 1994; Sample and Reid, 1998; Stakes et al., 1999; Aloisi et al., 2000; Greinert et al., 2001; Peckmann et al., 2001; Campbell et al., 2002; Pierre and Rouchy, 2004; Sassen et al., 2004), implying that dolomite may be formed by microbial oxidation of methane or organic matter coupled with sulfate reduction (Mazzullo, 2000). A recent study shows that dolomite formation in organic-rich marine sediments is controlled in part by competition between anaerobic methane oxidation and methanogenesis, which controls the speciation of dissolved CO_2. Anaerobic methane oxidation (AMO)

Table 1 Possible pathways for dolomite formation

mechanism	reaction	Ca	Mg	Sr	Mg/Ca	Sr/Ca	case study
replacive	$CaCO_3 + Mg^{2+} + 2HCO^{3-} \rightarrow CaMg(CO_3)_2 + CO_2 + H_2O$	—	↓	↑	↓	↑	(Baker and Burns, 1985)
replacive	$2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+}$	↑	↓	↑	↓	↑	(Kastner et al., 1990)
primary	$Ca^{2+} + Mg^{2+} + 4HCO^{3-} \rightarrow CaMg(CO_3)_2 + 2CO_2 + 2H_2O$	↓	↓	↓	↑	↑	(Wright and Wacey, 2005)

↑ = increases in aqueous concentration. ↓ = decreases in concentration. — = no change in concentration (Rodriguez et al., 2000). The relative decrease or increase in Ca and Mg is obvious from the reactions. Sr substitutes for Ca more easily than Mg. Thus, Sr is released to solution when calcite is replaced by dolomite (reaction 1 & 2) increases the concentration of CO_2 through sulfate reduction, favoring dolomite formation, while methanogenesis increases the pCO_2 of the pore waters, inhibiting dolomite formation (Moore et al., 2004). However, a direct link between a microbial function and dolomite formation pathways has not been established for important carbon reservoirs, such as gas hydrate and methane seep deposits. Moreover, dolomite formation under the in-situ conditions of gas hydrate deposits (i.e., in-situ pressure, temperature, and water chemistry) has not been attempted.

5 Techniques for studying mineral-microbe interactions

5.1 Transmission electron microscopy (TEM) and environmental cell TEM

TEM has been a primary tool to study mineral-microbe interactions at high spatial resolutions (Fredrickson et al., 1998; Dong et al., 2000; McLean et al., 2000; Dohnalkova et al., 2001; McLean and Beveridge, 2001; Glasauer et al., 2001; Liu et al., 2002; Glasauer et al., 2002; Glasauer et al., 2007; Geesey et al., 2008), but the spatial relationship of mineral-microbe interface for such studies may not be preserved intact, partly due to sample preparation necessary for conventional TEM observations. In conventional TEM, high vacuum is required not only to reduce scattering of the electron beam by gas molecules but also to minimize corrosion of the electron source. In such a high vacuum, biological materials and hydrous minerals (such as clays) dehydrate, resulting in bacterial cell rupture and mineral structure collapse. Thus, these materials have to be processed via fixation, dehydration, and embedding and sectioning prior to TEM observations (Kim et al., 1995; Fredrickson et al., 1998; Dong et al., 2000; McLean et al., 2000; Glasauer et al., 2001; Dohnalkova et al., 2001; McLean and Beveridge, 2001; Glasauer et al., 2002; Liu et al., 2002; Dong et al., 2003; Kim et al., 2004), assuming that the structure and the composition of these materials are not altered during sample preparation. However, these assumptions are never verified. Even with these assumptions, the standard procedures may not be adequate for observations of hydrous and expandable clay mineral structure, such as those of nontronite and smectite, because water-bearing nontronite and smectite tend to dehydrate under the TEM vacuum. For example, despite the effort to keep layer spacing of nontronite noncollapsed by impregnation with the Nanoplast resin, Kim et al. (2003) still observed collapse of (001) layers of nontronite in the conventional TEM electron column, making d(001) of microbially reduced nontronite indistinguishable from that of unreduced material. Stucki and Tessier (Stucki and Tessier, 1991) also observed homogenous layer spacing for both reduced and nonreduced smectite, illustrating the limitations of conventional TEM.

Alteration of oxidation states of metals introduced during the dehydration and embedding procedure for TEM observations is another issue, yet the preservation of oxidation states is essential to quantitatively evaluate the capabilities of bacteria to respire metals in mineral structures. Bulk chemical extractions (Stookey, 1970; Stucki, 1981; Stucki and Anderson, 1981; Amonette and Templeton, 1998) and Mössbauer spectroscopy (Dong et al., 2000; Kukkadapu et al., 2001; Kukkadapu et al., 2004) have been used to measure the extent of microbial reduction of iron, where oxidation states are generally preserved, but these techniques give no information on the spatial distribution of oxidized and reduced metals, relative to cell surface. Dohnalkova et al. (2001) attempted to preserve anaerobic states of various minerals by dehydrating, embedding, and sectioning samples in an anaerobic glove box and by excluding most fixatives and all heavy metal stains. The authors successfully observed crystalline biogenic minerals outside the outer membrane and amorphous or nanocrystalline material in cell periplasm. This is consistent with the current understanding of electron transfer mechanisms in dissimilatory metal reducing bacteria, where the mineral reductase activity is associated with the cell membrane, periplasm, and outer membrane.

Conventional TEM has not been used to probe time-course change of oxidation state of metals during microbial reduction, but this information is critical to reveal mechanisms of biooxidation and bioreduction of redox-sensitive metals. Lower et al. (2001) was probably the first to quantify the attachment of Shewanella oneidensis to goethite and diaspore surfaces by modified atomic force microscopy and demonstrated that the affinity of *S. oneidensis* for goethite was strongest under anaerobic conditions. The authors presented compelling evidence that a 150-kD protein in the outer membrane of the cell specifically interacted with the goethite surface to facilitate electron transfer. To truly understand the two-way interactions between microbes and minerals, it is equally important to simultaneously detect structural and compositional change of mineral surfaces as bacteria approach them. In other words, it is critical to observe how microbe and mineral respond when these two entities approach and interact with each other at the nanometer scale.

To overcome the sample dehydration problem associated with high vacuum required in the TEM electron column, material scientists have modified conventional TEM to study gas-solid interactions (Sharma and Weiss, 1998; Sharma, 2001). Several modifications, either to the specimen holder or to the microscope vacuum system, have been developed in order to restrict the gas path length to the sample area only. In the first design, the sample is sandwiched between two thin windows. This type of cell is ideally suited to the study of wet samples (biological materials) and is referred to as environmental cell (EC). In the second design, small differentially pumped apertures are located just above and below the sample to restrict gas flow into the rest of the microscope column and are generally referred to as differentially pumped environmental TEM.

Daulton et al. (2002) performed an elegant study in which they combined environmental cell transmission electron microscopy (EC-TEM) and electron energy loss spectroscopy (EELS) to study microbial reduction of chromium. To our knowledge, that is the first time to study bacteria and reduction products in their hydrated "native" states with comparable resolution and chemical capability with conventional TEM. Without any sample preparation, bacteria were observed intact inside EC-TEM, and in many cases, they were encrusted within mineral precipitates. The authors even determined the oxidation state of chromium in bioproduced mineral precipitates.

The EC-TEM system is described previously (Daulton et al., 2002; Kim et al., 2003). It is equipped with two interchangeable JEOL EC specimen holders (a two-line gas EC and a four-line gas/liquid EC) that are connected to the EC-TEM system by flexible and stainless steel lines. Both in-situ EC-TEM specimen holders are capable of circulating gas through the specimen chamber using two lines. The gas can be saturated with water vapor, enabling hydrated specimens to be examined in their "natural" wet state. The four-line holder has two additional service lines that can be used to independently inject several microliters of liquids from different reservoirs. Each EC holder consists of a small cylindrical cell sealed by two electron transparent windows on the top and the bottom. Each window is made of a 15–20 nm thick amorphous carbon (a-C) film covering seven hexagonally arrayed 0.15 mm apertures on a 3.5 mm diameter Cu disk. Prior to use, the windowed grids are tested to withstand a pressure differential of 250 Torr for 60 seconds. The EC-TEM system is fully computer controlled, facilitating the insertion and retraction of EC holders from the microscope column without breaching the delicate windows.

Kim et al. (2003) investigated microbially reduced nontronite using EC-TEM and observed that intact bacteria can be routinely imaged with EC-TEM with no evidence for rupture by partial decompression in the TEM column (Fig. 4). Multiple snapshots throughout the entire reduction process would make it possible to make a nearly real-time "video" of the attachment process. When EC-TEM imaging is coupled with EELS, interaction dynamics can be revealed. For example, it may be possible to determine at what locations on the cell surface mineral attachment occurs first, and at what location on the cell surface, the extent of Fe(III) reduction is the largest.

In addition to the real-time observation of the attachment process, the same authors (Kim et al., 2003) unequivocally demonstrated that layer contraction of expandable clay minerals associated with the high vacuum electron column of conventional TEM was avoided. Without any sample treatment, they observed the reduction of d(001) layer spacing from 1.50 nm to 1.26 nm as a result of microbial reduction of nontronite, whereas the conventional TEM could not distinguish the difference in layer spacing between unreduced and reduced nontronite. Recent development of TEM includes cryotechniques to freeze biological specimen so that they can be observed in their native and hydrated states (Beveridge, 2006). This is an alternative to EC-TEM and one of the best available means to eliminate or minimize deformation of biopolymer structure that is typically not possible to avoid using conventional TEM.

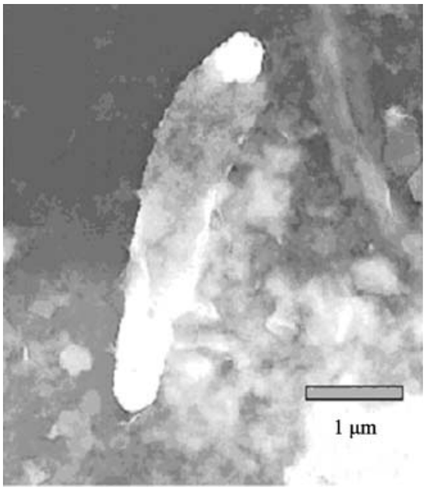

Fig. 4 Intact bacteria can be routinely imaged with EC-TEM with no evidence for rupture by partial decompression in the TEM column. The image shows dynamic attachment of nontronite onto *S. oneidensis* cells. Image courtesy of Jinwook Kim

5.2 Electron energy loss spectroscopy (EELS)

The EELS technique has been applied in mineralogy and materials research to determine the oxidation states of various metals including Fe (van Aken et al., 1998; van Aken et al., 1999; Golla and Putnis, 2001; van Aken and Liebscher, 2002), U (Xu and Wang, 1999), and Cr (Daulton et al., 2002). However, this technique has not been extensively applied in microbial reduction studies, with the exception of a few studies (Daulton et al., 2002). Compared to other techniques, such as electron microprobe analysis, Mössbauer spectroscopy, and X-ray absorption near edge structure (XANES) spectroscopy, the EELS technique possesses advantages of measuring oxidation states at high spatial resolution with adequate accuracy. In TEM's equipped with energy filters, the Fe^{3+} and Fe^{2+} distribution maps can be created at nanometer scale with adequate contrast (Golla and Putnis, 2001). This feature is especially attractive to study microbe-mineral systems, where microbial reduction of metals may be heterogeneous not only over the cell membrane but also across it, from the outer membrane, periplasm, into cytoplasm (Fig. 5).

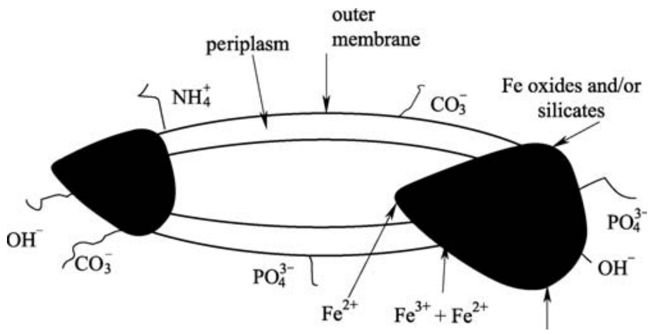

Fig. 5 A schematic diagram showing heterogeneous distributions of microbial functional groups on cell surface. This heterogeneity may result in heterogeneous mineral attachment and metal reduction over and across the cell surface

It has been well documented that minerals heterogeneously attach to cell surface (Grantham et al., 1997; Glasauer et al., 2001), and this may be due to heterogeneous distribution of negative functional groups on cell surface (Sonnenfeld et al., 1985; Sokolov et al., 2001). Heterogeneous mineral attachment may result in the extent of reduction and distribution of resulting biogenic solids being heterogeneous. In conventional TEM observations, artifacts associated with sample preparation (such as by centrifugation) cannot be completely eliminated. It is common to observe features of mineral detachment from cell surface, apparently associated with the centrifugation force. A recent sample preparation technique developed in our laboratory, embedding cell suspensions in agar prior to the dehydration step, appears to alleviate this problem. However, a better method is to observe cell-mineral association in-situ without any sample treatment. For example, heterogeneity in the extent of reduction over cell surface has never been studied before (Fig. 5), but these data can provide important information revealing mechanisms of microbial reduction of metals. With the advent of EELS coupled with EC-TEM, it is now possible to determine this heterogeneity at the nanometer scale. For example, the higher ratio of Fe^{2+}/Fe^{3+} should reflect the higher extent of bioreduction at a particular location on cell surface, and this variability can be mapped at a nanometer scale.

Minerals have also been found inside cells. In the magnetotactic bacteria, the chains of magnetosomes have been found aligned parallel to the cell axis, and they are believed to play a role in cell navigation (Bazylinski and Frankel, 2000; Bazylinski and Frankel, 2003). Glasauer et al. (Glasauer et al., 2002; Glasauer et al., 2004; Glasauer et al., 2007) reported intracellular iron and manganese minerals in *Shewanella putrefaciens* CN32, and Dohnalkova et al. (personal communication) even found nanocrystalline uraninite formation inside CN-32 cells. Cerussite ($PbCO_3$) was even found inside yeast and bacterial cells (Seabaugh et al., 2003). The distribution of these intracellular minerals is heterogeneous. Except for the well-documented magnetosomes, the formation mechanisms of other intracellular minerals have not been understood. Real-time high-resolution TEM observations of the dynamics of both extra- and intracellular mineral formation process, when coupled with EELS, could provide critical information on the mineral-microbe interaction mechanisms and metal biogeochemistry.

The value of the EELS technique is illustrated in the following example. Figure 6 shows an Fe-$M_{2,3}$ electron loss near edge structure (ELNES). The one on the left is Fe-$M_{2,3}$ ELNES of Fe standards (pyroxene solid solution) from van Aken et al. (1999), and the one on the upper right is Fe-$M_{2,3}$ ELNES of our standards hematite (100% Fe^{3+}) and ilmennite (100% Fe^{2+}). The one on the lower right is Fe-$M_{2,3}$ ELNES of unreduced and microbially reduced nontronite. Van Aken (van Aken et al., 1999) demonstrated that differences in the Fe-$M_{2,3}$ ELNES are a result of changes in Fe oxidation state and that differences in the crystal structure of Fe standards are of secondary importance. The authors further concluded that quantitative determination of Fe oxidation state in an unknown mineral can be accomplished by the energy difference between main maximum and prepeak (also called pre-edge). Using this criterion, the Fe^{3+}/Fe ratio was determined to be 90% and 30% for unreduced and bioreduced nontronite, respectively. These data are in good agreement with bulk chemical results by HCl extraction, illustrating the reliability of the method. Using the same procedure, the change of Fe^{3+}/Fe with the distance from the cell-magnetite interface from an earlier study (Dong et al., 2000) was determined. The hypothesis was that magnetite was actively reduced at the cell-magnetite interface (Fig. 7(a)), eventually forming siderite in the core encrusted by magnetite particles (Fig. 7(b)) by the end of reduction experiment (14 days) (Dong et al., 2000). Indeed, EELS detected the change of the Fe(III)/Fe ratio from siderite to magnetite (Fig. 8).

5.3 Other techniques

There are a suite of other techniques that are available to examine mineral-microbe interactions, such as synchrotron-based X-ray spectroscopy and X-ray microscopy (Templeton and Knowles, 2009) and nanosecondary mass spectroscopy (Herrmann et al., 2007), among others. These techniques greatly enhance our capability to investigate microbial growth, mineral dissolution, redox transformation, and biomineralization processes owning to their high chemical sensitivity and spatial resolution. Interested readers are referred to these review articles for information.

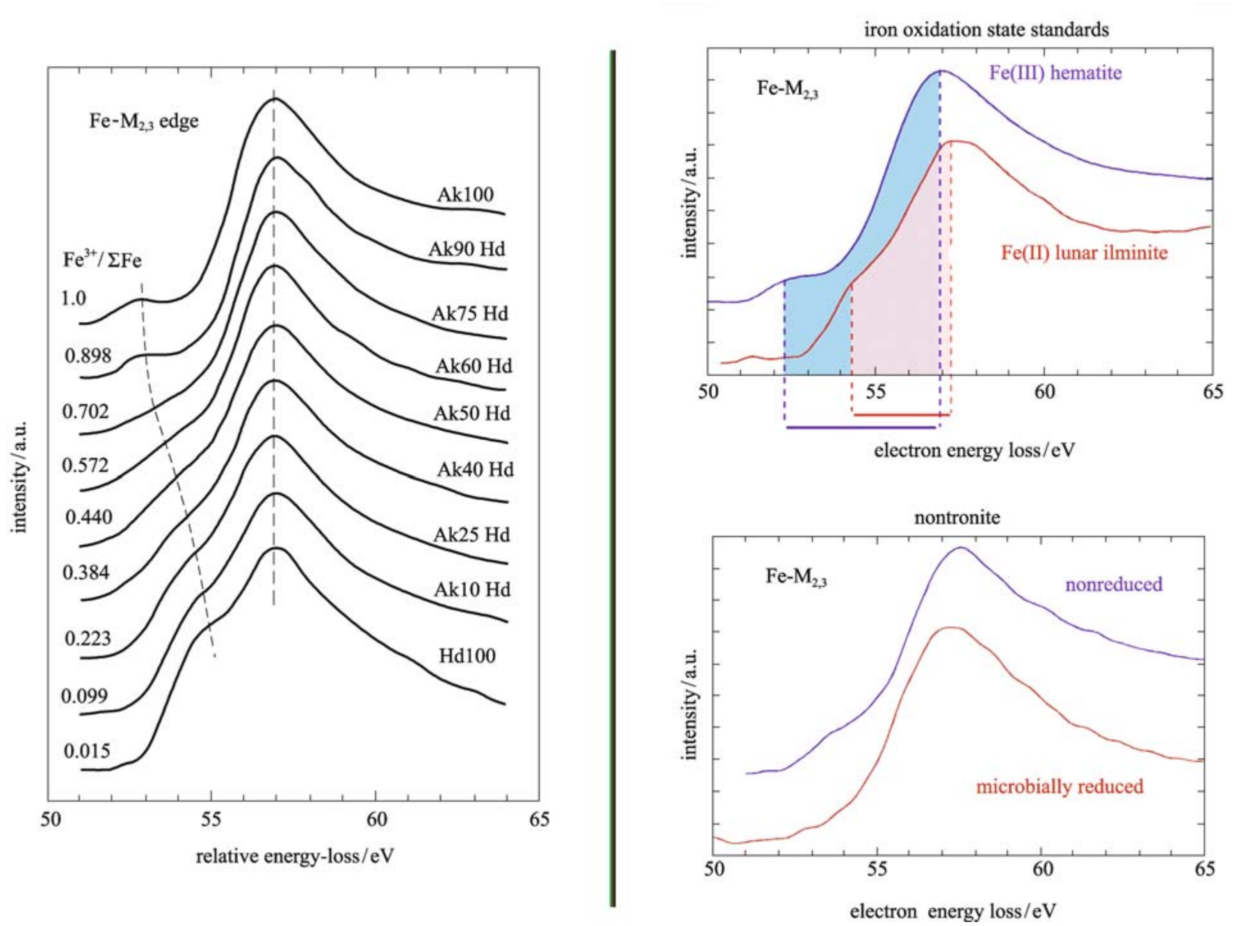

Fig. 6 Fe-M$_{2,3}$ electron loss near edge structure of Fe standards (pyroxene solid solution acmite-hedenbergite Ac-Hd) from van Aken et al. (van Aken et al., 1999) (left panel), Fe-M$_{2,3}$ ELNES of hematite (100% Fe^{3+}) and ilmennite (100% Fe^{2+}) standards (upper right), and Fe-M$_{2,3}$ ELNES of unreduced and microbially reduced nontronite (lower right), image courtesy of Jinwook Kim

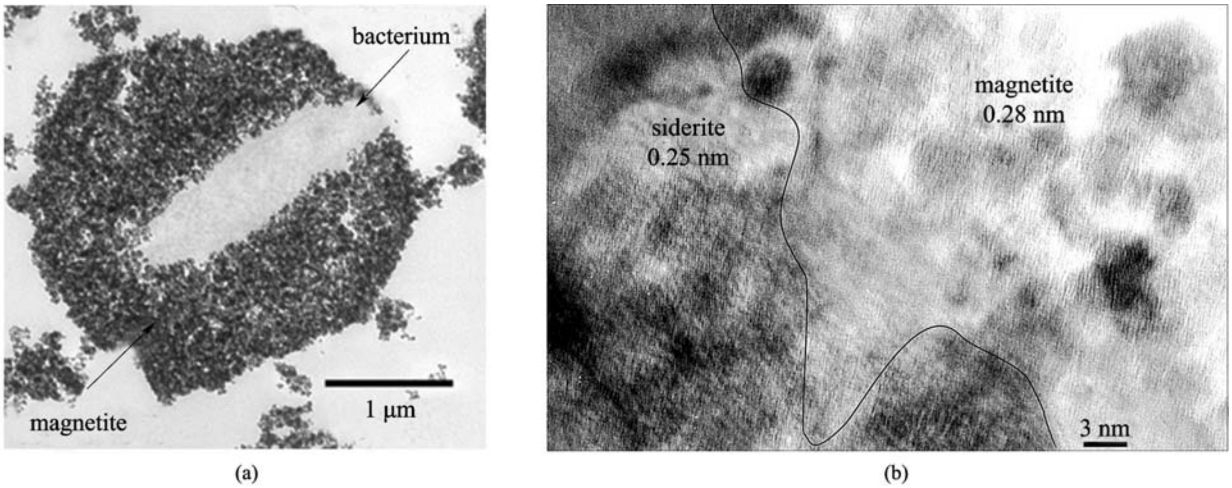

Fig. 7 (a) Magnetite coating Shewanella putrefaciens bacteria. The image was taken with conventional TEM. The sample was dehydrated, embedded, and sectioned following the standard procedure; (b) siderite formation from bioreduction of magnetite

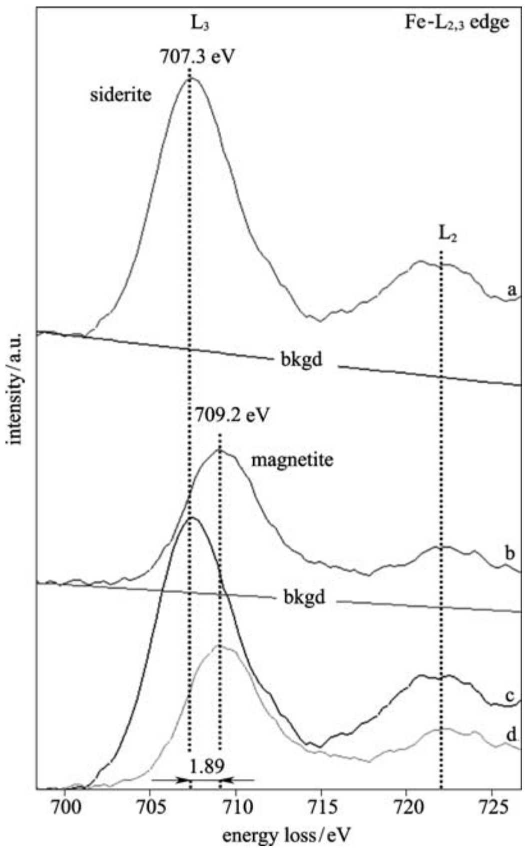

Fig. 8 The EELS spectra of magnetite and siderite (in Fig. 7 above) individually shown (top two) and superimposed to determine the Fe oxidation state in each mineral. The background was extracted by the standard inverse power law. An energy shift (~ 1.9 eV) of Fe-L_3 edges of magnetite and siderite was measured (dashed lines). The integral ratios of L_3 to L_2 for siderite (2.71) and the bulk magnetite (away from the siderite interface) (6.29), calculated by statistic analysis in the DigitalMicograph software, corresponded to ~ 24% and ~71% of Fe(III), respectively, based on the calibration curve (see Figure 1) of van Aken et al. (1998). These values of Fe(III) concentrations deviate from the stoichiometric Fe(III) content of siderite (0% Fe(III)) and magnetite (67% Fe(III)), illustrating the transient nature of these phases toward to their more stable structures, image courtesy of Jinwook Kim

Acknowledgements The author is grateful to Dr. Shucheng Xie for his invitation to write this review. This research was supported by grants from the U.S. Department of Energy (DE-FG02-07ER64369), the 111 project of China (No. B08030), the National Basic Research Program of China (2006CB701406), and the start-up funds of China University of Geosciences-Wuhan.

References

Aloisi G, Pierre C, Rouchy J M, Foucher J P, Woodside J, the MEDINAUT Scientific Party (2000). Methane-related authigenic carbonates of eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilisation. Earth Planet Sci Lett, 184 (1): 321–338

Amonette J E, Templeton J C (1998). Improvements to the quantitative assay of nonrefractory minerals for Fe(II) and total Fe using 1,10-phenanthroline. Clays Clay Miner, 46 (1): 51–62

Ams D A, Maurice P A, Hersman L E, Forsythe J H (2002). Siderophore production by an aerobic *Pseudomonas mendocina* bacterium in the presence of kaolinite. Chem Geol, 188 (3–4): 161–170

Arnold R G, DiChristina T J, Hoffmann M R (1988). Reductive dissolution of Fe(III) oxides by *Pseudomonas* sp. 200. Biotechnol Bioeng, 32 (9): 1081–1096

Bach W, Edwards K J (2003). Iron and sulfide oxidation within the basaltic ocean crust: implications for chemolithoautotrophic microbial biomass production. Geochim Cosmochim Acta, 67 (20): 3871–3887

Baeuerlein E (2000). Biomineralization: From Biology to Biotechnology and Medical Application. New York: Wiley-VCH, 294

Baker B J, Banfield J F (2003). Microbial communities in acid mine drainage. FEMS Microbiol Ecol, 44 (2): 139–152

Baker P A, Burns S J (1985). The occurrence and formation of dolomite in organic-rich continental margin sediments. AAPG Bull, 69: 1917–1930

Baker P A, Kastner M (1981). Constraints on the formation of sedimentary dolomite. Science, 213 (4504): 214–216

Banerjee N R, Furnes H, Muehlenbachs K, Staudigel H, de Wit M (2006). Preservation of ~3.4–3.5 Ga microbial biomarkers in pillow lavas and hyaloclastites from the Barberton Greenstone Belt, South Africa. Earth Planet Sci Lett, 241 (3–4): 707–722

Banfield J F, Barker W W, Welch S A, Taunton A (1999). Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. Proc Natl Acad Sci USA, 96 (7): 3404–3411

Banfield J F, Cervini-Silva J, Nealson K M (2005). Molecular Geomicrobiology. The Mineralogical Society of America, Chantilly VA, 294

Banfield J F, Nealson K H (1997). Geomicrobiology: Interaction Between Microbes and Minerals. Mineralogical Society of America, Atla Utah

Barker W W, Welch S A, Banfield J F (1997). Biogeochemical weathering of silicate minerals. In: Banfield J F, Nealson K M, eds. Geomicrobiology: Interaction Between Microbes and Minerals. Mineralogical Society of America, Washington D C, 35: 391–428

Barker W W, Welch S A, Chu S, Banfield J F (1998). Experimental observations of the effects of bacteria on aluminosilicate weathering. Am Mineral, 83: 1551–1563

Barton H A, Northup D E (2007). Geomicrobiology in cave environments: past, current and future perspectives. J Caves Karst Stud, 69 (1): 163–178

Bazylinski D A, Frankel R B (2000). Biologically controlled mineralization of magnetic iron minerals by magnetotactic bacteria. In: Lovley D R, ed. Environmental Microbe-Metal Interactions. Washington D C: ASM Press, 109–144

Bazylinski D A, Frankel R B (2003). Biologically controlled mineralization in prokaryotes. In: Dove P M, DeYoreo J J, Weiner S, eds. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America. Washington D C, 54: 217–247

Bazylinski D A, Frankel R B (2004). Magnetosome formation in prokaryotes. Nat Rev Microbiol, 2 (3): 217–230

Beard B L, Johnson C M, CoxL, SunH, Nealson K H, Aguilar C (1999). Iron isotope biosignatures. Science, 285 (5435): 1889–1892

Bennett P C, Rogers J R, Choi W J, Hiebert F K (2001). Silicates, silicate weathering, and microbial ecology. Geomicrobiological Journal, 18 (1): 3–19

Benzerara K, Menguy N (2009). Looking for traces of life in minerals. C R Geosci, 8 (7): 617–628

Beveridge T J (2006). Cryotransmission electron microscopy is enabling investigators to examine native, hydrated structures in bacteria and biofilms. Microbe, 1: 279–284

Beveridge T J, Meloche J D, Fyfe W S, Murray R G E (1983). Diagenesis of metals chemically complexed to bacteria: laboratory formation of metal phosphates, sulfides, and organic condensates in artificial sediments. Appl Environ Microbiol, 45 (3): 1094–1108

Beveridge T J, Murray R G E (1976). Uptake and retention of metals by cell walls of Bacillus subtilis. J Bacteriol, 127 (3): 1502–1518

Beveridge T J, Murray R G E (1980). Sites of metal deposition in the cell wall of Bacillus subtilis. J Bacteriol, 141 (2): 876–887

Bigham J M, Nordstrom D K (2000). Iron and aluminum hydroxysulfates from acid sulfate waters. In: Alpers C N, Jambor J L, Nordstrom D K, eds. Sulfate Minerals, Crystallography, Geochemistry and Environmental Significance: Reviews in Mineralogy and Geochemistry. Mineralogical Society of America, Washington D C, 40: 351–403

Bigham J M, Schwertmann U, Traina S J, Winland R L, Wolf M (1996). Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim Cosmochim Acta, 60 (12): 2111–2121.

Boone D R, Liu Y, Zhao Z J, Balkwill D L, Drake G R, Stevens T O, Aldrich H C (1995). *Bacillus infernus* sp. nov., an Fe(III)- and Mn (IV)-reducing anaerobe from the deep terrestrial subsurface. Int J Syst Bacteriol, 45 (3): 441–448

Borrok D, Turner B F, Fein J B (2005). A universal surface complexation framework for modeling proton binding onto bacterial surfaces in geologic settings. Am J Sci, 305 (6–8): 826–853

Buseck P R, Dunin-Borkowski R E, Devouard B, Frankel R B, McCartney M R, Midgley P A, Posfai M, Weyland M (2001). Magnetite morphology and life on Mars

Campbell K A, Farmer J D, Des Marais D (2002). Ancient hydrocarbon seeps from the Mesozoic convergent margin of California: carbonate geochemistry, fluids and palaeoenvironments. Geofluids, 2 (2): 63–94

Canales C, Acevedo F, Gentina J C (2002). Laboratory-scale continuous bio-oxidation of a gold concentrate of high pyrite and enargite content. Process Biochem, 37 (10): 1051–1055

Cavagna S, Clari P, Martire L (1999). The role of bacteria in the formation of cold seep carbonates: geological evidnece from Monferrato (Tertiary, NW Italy). Sediment Geol, 126 (1–4): 253–270

Chapelle F H, O'Neill K, Bradley P M, Methé B A, Ciufo S A, Knobel L L, Lovley D R (2002). A hydrogen-based subsurface microbial community dominated by methanogens. Nature, 415 (6869): 312–315

Childers S E, Ciufo S, Lovley D R (2002). Geobacter metallireducens accesses insoluble Fe(III) oxide by chemotaxis. Nature, 416 (6882): 767–769

Clark M E, Batty J D, van Buuren C B, Dew D W, Eamon M A (2006). Biotechnology in minerals processing: Technological breakthroughs creating value. Hydrometallurgy, 83 (1–4): 3–9

Costa K C, Navarro J B, Shock E L, Zhang C L, Soukup D, Hedlund B P (2009). Microbiology and geochemistry of great boiling and mud hot springs in the United States Great Basin. Extremophiles, 13 (3): 447–459

Cravotta C A I, Trahan M K (1999). Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. Appl Geochem, 14: 2922–2923

Daughney C J, Fowle D A, Fortin D E (2001). The effect of growth phase on proton and metal adsorption by Bacillus subtilis. Geochim Cosmochim Acta, 65 (7): 1025–1035

Daulton T L, Little B J, Lowe K, Jones-Meehan J (2002). Electron energy loss spectroscopy techniques for the study of microbial chromium(VI) reduction. J Microbiol Methods, 50 (1): 39–54

Desroches S, Biron F, Berthon G (1999). Aluminum speciation studies in biological fluids Part 5. A quantitative investigation of Al(III) complex equilibria with desferrioxamine, 2,3-dihydroxybenzoic acid, Tiron, CP20 (L1), and CP94 under physiological conditions, and computer-aided assessm. Journal of Inorganic Chemistry, 75 (1): 27–35

Dhugues P, Joulian C, Spolaore P, Michel C, Garrido F, Morin D (2008). Continuous bioleaching of a pyrite concentrate in stirred reactors: population dynamics and exopolysaccharide production vs. bioleaching performance. Hydrometallurgy, 94 (1–4): 34–41

Dohnalkova A C, Gorby YA, McLean J, Fredrickson J K, Kennedy D W (2001). Biogenic mineral formation by iron reducing bacteria. Microsc Microanal, 7 (Suppl 2): 756–757

Dong H L, Fredrickson J K, Kennedy D W, Zachara J M, Kukkadapu R K, Onstott T C (2000). Mineral transformation associated with the microbial reduction of magnetite. Chem Geol, 169 (3–4): 299–318

Dong H L, Jaisi D P, Kim J W, Zhang G (2009). Microbe-clay mineral interactions. Am Mineral, 94 (11–12): 1505–1519

Dong H L, Kostka J E, Kim J W (2003). Microscopic evidence for microbial dissolution of smectite. Clays Clay Miner, 51 (5): 502–512

Dong H L, Yu B (2007). Geomicrobiological processes in extreme environments: a review. Episodes, 30 (3): 202–216

Dove P M, De Yoreo J J, Weiner S (2003) Biomineralization. Mineralogical Society of America, Washington D C, 381

Druschel G K, Baker B J, Gihring T M, Banfield J F (2004). Acid mine drainage biogeochemistry at Iron Mountain, California. Geochem Trans, 5 (2): 13–32

Duckworth O W, Bargar J R, Jarzecki A A, Oyerinde O, Spiro T G, Sposito G (2009a). The exceptionally stable cobalt(III) –desferrioxamine B complex. Mar Chem, 113 (1–2): 114–122

Duckworth O W, Bargar J R, Sposito G (2009b). Coupled biogeochemical cycling of iron and manganese as mediated by microbial siderophores. Biometals, 22 (4): 605–613

Duckworth O W, Sposito G (2005). Siderophore-manganese(III) interactions. I. Air-oxidation of manganese(II) promoted by desferrioxamine B. Environ Sci Technol, 39 (16): 6037–6044

Duckworth O W, Sposito G (2007). Siderophore-promoted dissolution of synthetic and biogenic layer-type Mn oxides. Chem Geol, 242 (3–4): 497–508

Edwards H G M, Villar S E J, Parnell J, Cockell C S, Lee P (2005). Raman spectroscopic analysis of cyanobacterial gypsum halotrophs and relevance for sulfate deposits on Mars. Analyst, 130 (6): 917–923

Edwards K, Bach W, McCollom T, Rogers D (2004). Neutrophilic iron-oxidizing bacteria in the ocean: their habitats, diversity, and roles in mineral deposition, rock alteration, and biomass production in the deep-sea. Geomicrobiol J, 21 (6): 393–404

Edwards K J, Bazylinski D A (2008). Intracellular minerals and metal deposits in prokaryotes. Geobiology, 6 (3): 309–317

Edwards K J, Bond P L, Druschel G K, McGuire M M, Hamers R J, Banfield J F (2000a). Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. Chem Geol, 169 (3–4): 383–397

Edwards K J, Bond P L, Gihring T M, Banfield J F (2000b). An archaeal iron-oxidizing extreme acidophile important in acid mine drainage. Science, 287 (5459): 1796–1799

Ehrlich H L, Newman D K (2009) Geomicrobiology. Boca Raton F L: CRC Press, 606

Espana J S, Pamo E L, Pastor E S, Andres J R, Rubi J A M (2006). The removal of dissolved metals by hydroxysulphate precipitates during oxidation and neutralization of acid minewaters, Iberian Pyrite Belt. Appl Geochem, 12 (3): 269–298

Fein J B, Daughney C J, Yee N, Davis T A (1997). A chemical equilibrium model for metal adsorption onto bacterial surfaces. Geochim Cosmochim Acta, 61 (16): 3319–3328

Ferris F G, Beveridge T J, Fyfe W S (1986). Iron-silica crystallite nucleation by bacteria in a geothermal sediment. Nature, 320 (6063): 609–611

Ferris F G, Fyfe W S, Beveridge T J (1987). Bacteria as nucleation sites for authigenic minerals in a metal-contaminated lake sediment. Chem Geol, 63 (3–4): 225–232

Fisk M R, Giovannoni S J, Thorseth I H (1998). Alteration of oceanic volcanic glass: textural evidence of microbial activity. Science, 281 (5379): 978–980

Fisk M R, Popa R, Mason O U, Storrie-Lombardi M C, Vicenzi E P (2006). Iron-magnesium silicate bioweathering on Earth (and Mars?). Astrobiology, 6 (1): 48–68

Fisk M R, Storrie-Lombardi M C, Douglas S, Popa R, McDonald G, Di Meo-Savoie C (2003). Evidence of biological activity in Hawaiian subsurface basalts. Geochem Geophys Geosyst, 4 (12): 1103

Formolo M J, Lyons T W, Zhang C L, Kelley C, Sassen R, Horita J, Cole D R (2004). Quantifying carbon sources in the formation of authigenic carbonates at gas hydrate sites in the Gulf of Mexico. Chem Geol, 205 (3–4): 253–264

Fortin D, Langley S (2005). Formation and occurrence of biogenic iron-rich minerals. Earth Sci Rev, 72 (1–2): 1–19

Fredrickson J K, Balkwill D L (2006). Geomicrobial processes and biodiversity in the deep terrestrial subsurface. Geomicrobiol J, 23 (6): 345–356

Fredrickson J K, McKinley J P, Bjornstad B N, Long P E, Ringelberg D B, White D C, Krumholz L R, Suflita J M, Colwell F S, Lehman R M, Phelps T J, Onstott T C (1997). Pore-size constraints on the activity and survival of subsurface bacteria in a late Cretaceous shale-sandstone sequence, Northwestern New Mexico. Geomicrobiol J, 14 (3): 183–202

Fredrickson J K, Onstott T C (1996). Microbes deep inside the earth. Sci Am, 275 (4): 68–73

Fredrickson J K, Zachara J M, Kennedy D W, Dong H, Onstott T C, Hinman N W, Li S M (1998). Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacterium. Geochim Cosmochim Acta, 62 (19–20): 3239–3257

Friedmann E I, Wierzchos J, Ascaso C, Winklhofer M (2001). Chains of magnetite crystals in the meteorite ALH84001: evidence of biological origin. Proc Natl Acad Sci USA, 98 (5): 2176–2181

Fukushi K, Sasaki M, Sato T, Yanase N, Amano H, Ikeda H (2003). A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. Appl Geochem, 18 (8): 1267–1278

Furnes H, Banerjee N R, Muehlenbachs K, Kontinen A (2005). Preservation of biosignatures in metaglassy volcanic rocks from the Jormua ophiolite complex, Finland. Precambrian Research, 136 (2): 125–137

Furnes H, Banerjee N R, Muehlenbachs K, Staudigel H, de Wit M (2004). Early life recorded in archean pillow lavas. Science, 304 (5670): 578–581

Furnes H, Muehlenbachs K, Torsvik T, Thorseth I H, Tumyr O (2001). Microbial fractionation of carbon isotopes in altered basaltic glass from the Atlantic Ocean, Lau Basin and Costa Rica Rift. Chemical Geology, 173 (4): 313–330

Furnes H, Staudigel H (1999). Biological mediation in ocean crust alteration: how deep is the deep biosphere? Earth Planet Sci Lett, 166 (3–4): 97–103

Geesey G G, Borch T, Reardon C L (2008). Resolving biogeochemical phenomena at high spatial resolution through electron microscopy. Geobiology, 6 (3): 263–269

Ghauri M A, Okibe N, Johnson D B (2007). Attachment of acidophilic bacteria to solid surfaces: The significance of species and strain variations. Hydrometallurgy, 85 (2–4): 72–80

Glasauer S, Langley S, Beveridge T J (2001). Sorption of Fe (hydr) oxides to the surface of Shewanella putrefaciens: cell-bound fine-grained minerals are not always formed de novo. Appl Environ Microbiol, 67 (12): 5544–5550

Glasauer S, Langley S, Beveridge T J (2002). Intracellular iron minerals in a dissimilatory iron-reducing bacterium. Science, 295 (5552): 117–119

Glasauer S, Langley S, Beveridge T J (2004). Intracellular manganese granules formed by a subsurface bacterium. Environ Microbiol, 6 (10): 1042–1048

Glasauer S, Langley S, Boyanov M I, Lai B, Kemner K, Beveridge T J (2007). Mixed-valence cytoplasmic iron granules are linked to anaerobic respiration. Appl Environ Microbiol, 73 (3): 993–996

Golden D C, Ming D W, Morris R V, Brearley A, Lauer H V, Treiman A H, Zolensky M E, Schwandt C S, Lofgren G E, McKay G A (2004). Evidence for exclusively inorganic formation of magnetite in Martian meteorite ALH84001. Am Mineral, 89: 681–695

Golden D C, Ming D W, Schwandt C S, Lauer H V, Socki R A, Morris R V, Lofgren G E, McKay G A (2001). A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteroite ALH84001. Am Mineral, 86 (3): 370–375

Golla U, Putnis A (2001). Valence state mapping and quantitative electron spectroscopic imaging of exsolution in titanohematite by energy-filtered TEM. Phys Chem Miner, 28 (2): 119–129

Gorby Y A, Yanina S, McLean J S, Rosso K M, Moyles D, Dohnalkova A, Beveridge T J, Chang I S, Kim B H, Kim K S, Culley D E, Reed S B, Romine M F, Saffarini D A, Hill E A, Shi L, Elias D A, Kennedy

D W, Pinchuk G, Watanabe K, Ishii S, Logan B, Nealson K H, Fredrickson J K (2006). Electrically conductive bacterial nanowires produced by Shewanella oneidensis strain MR-1 and other microorganisms. Proc Natl Acad Sci USA, 103 (30): 11358–11363

Grantham M C, Dove P M, Dichristina T J (1997). Microbially catalyzed dissolution of iron and aluminum oxyhydroxide mineral surface coatings. Geochim Cosmochim Acta, 61 (21): 4467–4477

Greinert J, Bohrmann G, Suess E (2001) Gas hydrate associated carbonates and methane venting at Hydrate Ridge: classification, distribution, and origin of authigenic carbonates. In: Paull C K, Dillon W P, eds. Natural Gas Hydrates: Occurrence, Distribution and Detection. Geophysical Monograph, American Geophysical Union. Washington D C, 124: 99–113

Hao C B, Dong H L, Zhang H (2010). Succession of acidophilic bacterial community during biooxidation of refractory gold-containing sulfides. Geomicrobiol J (In press)

Harrison J, Turner R J, Marques L, Ceri H (2005). A new understanding of these mcirobial communities is driving a revolution that may transform the science of microbiology. Am Sci, 93 (6): 508–515

Herrmann A M, Ritz K, Nunan N, Clode P L, Pett-Ridge J, Kilburn M R, Murphy D V, O'Donnell A G, Stockdale E A (2007). Nano-scale secondary ion mass spectrometry–A new analytical tool in biogeochemistry and soil ecology: a review article. Soil Biol Biochem, 39 (8): 1835–1850

Hersman L E (2000) The role of siderophores in iron oxide dissolution. In: Lovley D R, ed. Environmental microbe-metal interactions. Washington D C: ASM Press, 145–157

Hersman L E, Forsythe J H, Ticknor L O, Maurice P A (2001a). Growth of *Pseudomonas mendocina* on Fe(III) (hydr)oxides. Appl Environ Microbiol, 67 (10): 4448–4453

Hersman L E, Huang A, Maurice P A, Forsythe J H (2001b). Siderophore and reductant production by *Pseudomonas mendocina* in response to Fe deprivation. Geomicrobiological Journal, 18 (1): 1–13

Hochella MF Jr (2002). There's plenty of room at the bottom: Nanoscience in geochemistry. Geochim Cosmochim Acta, 66 (5): 735–743

Hofstetter T B, Neumann A, Schwarzenbach R P (2006). Reduction of nitroaromatic compounds by Fe(II) species associated with iron-rich smectites. Environ Sci Technol, 40 (1): 235–242

Hofstetter T B, Schwarzenbach R P, Haderlein S B (2003). Reactivity of Fe(II) species associated with clay minerals. Environ Sci Technol, 37 (3): 519–528

Jaisi D P, Dong H, Morton J P (2008). Partitioning of Fe(II) in reduced nontronite (NAu-2) to reactive sites: Reactivity in terms of Tc(VII) Reduction. Clays Clay Miner, 56 (2): 175–189

Jaisi D P, Dong H, Plymale A E, Fredrickson J K, Zachara J M, Heald S M, Liu C (2009). Reduction and long-term immobilization of technetium by Fe(II) associated with clay mineral nontronite. Chem Geol, 264 (1–4): 127–138

Johnson D B, Hallberg K B (2005). Acid mine drainage remediation options: a review. Sci Total Environ, 338 (1–2): 3–14

Johnson D B, Hallberg K B (2009a) Carbon, iron, and sulfur metabolism in acidophilic microorganisms. In: Poole R K, ed. Advances in Microbial Physiology. Amsterdam: Academic Press, 54: 201–255

Johnson D B, Hallberg K B (2009b) Carbon, iron, and sulfur metabolism in acidophilic microorganisms. In: Poole R K, ed. Advances in Microbial Physiology. Amsterdam: Academic Press, 201–255

Johnson D B, McGinness S (1991). Ferric iron reduction by acidophilic heterotrophic bacteria. Appl Environ Microbiol, 57 (1): 207–211

Jorgensen NO (1992). Methane-derived carbonate cementation of Holocene marine sediments from Kattegat, Denmark. Cont Shelf Res, 12 (10): 1209–1218

Kalinowski B E, Liermann L J, Brantley S L, Barnes A, Pantano C G (2000). X-ray photoelectron evidence for bacteriaenhanced dissolution of hornblende. Geochim Cosmochim Acta, 64 (8): 1331–1343

Kappler A, Straub K L (2005) Geomicrobiological cycling of iron. In: Banfield J F, Cervini-Silva J, Nealson K H, eds. Molecular Geomicrobiology. Chantilly VA: The Mineralogical Society of America, 59: 85–108

Kashefi K, Holmes D E, Reysenbach A L, Lovley D R (2002). Use of Fe (III) as an electron acceptor to recover previously uncultured hyperthermophiles: isolation and characterization of Geothermobacterium ferrireducens gen. nov., sp. nov. Appl Environ Microbiol, 68 (4): 1735–1742

Kastner M, Elderfield H, Martin J B, Suess E, Kvenvolden K A, Garrison R E (1990) Diagenesis and interstitial-water chemistry at the Peruvian continental margin-major constituents and strontium isotopes. In: Suess E, von Huene R E A, eds. Proceedings of Ocean Drilling Program, Scientific Results. Ocean Drilling Program. College Station TX, 112: 413–440

Kenward P A, Goldstein R H, González L A, Roberts J A (2009). Precipitation of low-temperature dolomite from an anaerobic microbial consortium: the role of methanogenic Archaea. Geobiology, 7 (5): 556–565

Kim C, Lorenz W W, Hoopes J T, Dean J F D (2001). Oxidation of phenolate siderophores by the multicopper oxidase encoded by the Escherichia coli yacK gene. J Bacteriol, 183 (16): 4866–4875

Kim J W, Dong H, Seabaugh J, Newell S W, Eberl D D (2004). Role of microbes in the smectite-to-illite reaction. Science, 303 (5659): 830–832

Kim J W, Furukawa Y, Daulton T, Lavoie D, Newell S (2003). Characterization of microbially Fe(III)–reduced nontronite: environmental cell transmission electron microscopy study. Clays Clay Miner, 51(4): 382–389

Kim J W, Peacor D R, Tessier D, Elsass F (1995). A technique for maintaining texture and permanent expansion of smectite interlayers for TEM observations. Clays Clay Miner, 43 (1): 51–57

Konhauser K (2007) Introduction to Geomicrobiology. Oxford: Blackwell Publishing

Kostka J E, Wu J, Nealson K H, Stucki J W (1999). The impact of structural Fe(III) reduction by bacteria on the surface chemistry of smectite clay minerals. Geochim Cosmochim Acta, 63 (22): 3705–3713

Kraemer S (2004). Iron oxide dissolution and solubility in the presence of siderophores. Aquat Sci, 66 (1): 3–18

Kraemer S M, Butler A, Borer P, Cervini-Silva J (2005). Siderophores and the dissolution of iron-bearing minerals in marine systems. Rev Mineral Geochem, 59 (1): 53–84

Krauskopf K B, Bird D K (1995) Introduction to geochemistry. New York: McGraw-Hill

Krumholz L R, McKinley J P, Ulrich F A, Suflita J M (1997). Confined subsurface microbial communities in Cretaceous rock. Nature, 386 (6620): 64–66

Kukkadapu R K, Zachara J M, Fredrickson J K, Kennedy D W (2004). Biotransformation of two-line silica-ferrihydrite by a dissimilatory Fe (III)-reducing bacterium: Formation of carbonate green rust in the presence of phosphate. Geochim Cosmochim Acta, 68 (13): 2799–2814

Kukkadapu R K, Zachara J M, Smith S C, Fredrickson J K, Liu C X (2001). Dissimilatory bacterial reduction of Al-substituted goethite in subsurface sediments. Geochim Cosmochim Acta, 65 (17): 2913–2924

Kulczycki E, Fowle D A, Knapp C, Graham D W, Roberts J A (2007). Methanobactin-promoted dissolution of Cu-substituted borosilicate glass. Geobiology, 5 (3): 251–263

Kulm L D, Suess E (1990). Relationship between carbonate deposits and fluid venting: Oregon accretionary prism. J Geophys Res, 95 (B6): 8899–8915

Land L S (1998). Failure to precipitate dolomite at 25°C from dilute solutions despite 1000-fold oversaturation after 32 years. Aquat Geochem, 4 (3/4): 361–368

Lian B, Hu Q N, Chen J, Ji J F, Teng H H (2006). Carbonate biomineralization induced by soil bacterium Bacillus megaterium. Geochim Cosmochim Acta, 70 (22): 5522–5535

Lian B, Wang B, Pan M, Liu C Q, Teng H H (2008). Microbial release of potassium from K-bearing minerals by thermophilic fungus Aspergillusfumigatus. Geochim Cosmochim Acta, 72 (1): 87–98

Liermann L J, Guynn R L, Anbar A, Brantley S L (2005). Production of a molybdophore during metal-targeted dissolution of silicates by soil bacteria. Chem Geol, 220 (3–4): 285–302

Liermann L J, Kalinowski B E, Brantley S L, Ferry J G (2000a). Role of bacterial siderophores in dissolution of hornblende. Geochim Cosmochim Acta, 64 (4): 587–602

Liermann L J, Kalinowski B E, Brantley S L, Ferry J G (2000b) Role of bacterial siderophores in dissolution of hornblende

Liu C, Zachara J M, Fredrickson J K, Kennedy D W, Dohnalkova A (2002). Modeling the inhibition of the bacteral reduction of U(VI) by beta-MnO2(s). Environ Sci Technol, 36 (7): 1452–1459

Lloyd J R (2002). Bioremediation of metals; the application of microorganisms that make and break minerals. Microbiology Today, 29: 67–69

Lovley D R (2000) Environmental Microbe-Metal Interactions. Washington D C: ASM press, 408

Lovley D R, Blunt-Harris E L (1999). Role of humic-bound iron as an electron transfer agent in dissimilatory Fe(III) reduction. Appl Environ Microbiol, 65 (9): 4252–4254

Lovley D R, Coates J D, Bluent-Harris E L, Philips E J P, Woodward J C (1996). Humic substances as electron acceptors for microbial respiration. Nature, 382 (6590): 445–448

Lovley D R, Holmes D E, Nevin K P (2004). Dissimilatory Fe(III) and Mn(IV) reduction. Adv Microb Physiol, 49: 219–286

Lower S K, Hochella M F Jr, Beveridge T J (2001). Bacterial recognition of mineral surfaces: nanoscale interactions between Shewanella and alpha-FeOOH. Science, 292 (5520): 1360–1363

Lüttge A, Conrad P G (2004). Bacterial control of calcite dissolution kinetics. Appl Environ Microbiol, 70: 1627–1637

Lüttge A, Zhang L, Nealson K H (2005). Mineral surfaces and their implications for microbial attachment: results from Monte Carlo simulations and direct surface observations. Am J Sci, 305 (6–8): 766–790

Mailloux B J, Alexandrova E, Keimowitz A R, Wovkulich K, Freyer G A, Herron M, Stolz J F, Kenna T C, Pichler T, Polizzotto M L, Dong H L, Bishop M, Knappett P S K (2009). Microbial mineral weathering for nutrient acquisition releases arsenic. Appl Environ Microbiol, 75 (8): 2558–2565

Marchand E A, Silverstein J (2003). The role of enhanced heterotrophic bacterial growth on iron oxidation by Acidithiobacillus ferrooxidans. Geomicrobiol J, 20 (3): 231–244

Marshall M, Beliaev J A S, Dohnalkova A C, Kennedy D W, Shi L, Wang Z, Boyanov M I, Lai B, Kemner K M, Mclean J S, Reed S B, Culley D E, Bailey V L, Simonson C J, Saffarini D A, Romine M F, Zachara J M, Fredrickson J K (2006). *c*-type cytochrome-dependent formation of U(IV) nanoparticles by Shewanella oneidensis. PLoS Biol, 4 (8): e268

Marsili E, Baron D B, Shikhare I D, Coursolle D J, Gralnick J A, Bond D R (2008). Shewanella secretes flavins that mediate extracellular electron transfer. Proc Natl Acad Sci USA, 105 (10): 3968–3973

Mauck B S, Roberts J A (2007). Mineralogic control on abundance and diversity of surface-adherent microbial communities. Geomicrobiol J, 24 (3): 167–177

Maurice P A, Haack E A, Mishra B (2009). Siderophore sorption to clays. Biometals, 22 (4): 649–658

Maurice P A, Lee Y-J, Hersman L E (2000). Dissolution of Al-substituted goethites by an aerobic *Pseudomonas mendocina* var. bacteria. Geochim Cosmochim Acta, 64 (8): 1363–1374

Maurice P A, Vierkorn M A, Hersman L E, Fulghum J E, Ferryman A (2001). Enhancement of kaolinite dissolution by an aerobic *Pseudomonas mendocina* bacteria. Geomicrobiological Journal, 18 (1): 21–35

Mazzullo S J (2000). Organogenic Dolomitization in peritidal to deep-sea sediments. J Sediment Res, 70 (1): 10–23

McLean J, Beveridge T J (2001). Chromate reduction by a pseudomonad isolated from a site contaminated with chromated copper arsenate. Appl Environ Microbiol, 67 (3): 1076–1084

McLean J S, Beveridge T J, Phipps D (2000). Isolation and characterization of a chromium-reducing bacterium from a chromated copper arsenate-contaminated site. Environ Microbiol, 2 (6): 611–619

McLoughlin N, Brasier M D, Wacey D, Green O R, Perry R S (2007). On biogenicity criteria for endolithic microborings on early Earth and beyond. Astrobiology, 7 (1): 10–26

Meyer-Dombard D R, Shock E L, Amend J P (2005). Archaeal and bacterial communities in geochemically diverse hot springs of Yellowstone National Park, USA. Geobiology, 3 (3): 211–227

Moore T S, Murray R W, Kurtz A C, Schrag D P (2004). Anaerobic methane oxidation and the formation of dolomite. Earth Planet Sci Lett, 229 (1–2): 141–154

Morgan J J (2000). Manganese in natural waters and earth's crust: its availability to organisms. Met Ions Biol Syst, 37: 1–34

Neumann A, Hofstetter T B, Lüssi M, Cirpka O A, Petit S, Schwarzenbach R P (2008). Assessing the redox reactivity of structural iron in smectites using nitroaromatic compounds as kinetic probes. Environ Sci Technol, 42 (22): 8381–8387

Nevin K P, Lovley D R (2002). Mechanisms for Fe(III) oxide reduction in sedimentary environments. Geomicrobiological Journal, 19 (2): 141–159

Newman D K (2001). Microbiology. How bacteria respire minerals. Science, 292 (5520): 1312–1313

Newman D K (2008). From iron oxides to infections. Geobiology, 6 (3): 196–200

Nicormat D, Dick W A, Tuovinen O H (2006). Assessment of the microbial community in a constructed wetland that receives acid coal mine drainage. microbial. Ecology, 51: 83–89

Nordstrom D K (2000). Advances in the hydrochemistry and microbiology of acid mine waters. Int Geol Rev, 42 (6): 499–515

Nordstrom D K, Alpers C N (1999). Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc Natl Acad Sci USA, 96 (7): 3455–3462

Olson G J, Brierley J A, Brierley C L (2003). Bioleaching review part B: progress in bioleaching: applications of microbial processes by the minerals industries. Appl Microbiol Biotechnol, 63 (3): 249–257

Peckmann J, Gischler E, Oschmann W, Reitner J (2001). An early carboniferous seep community and hydrocarbon-derived carbonates from the Harz Mountains, Germany. Geology, 29 (3): 271–274

Peckmann J, Thiel V (2004). Carbon cycling at ancient methane-seeps. Chem Geol, 205 (3–4): 443–467

Peckmann J, Thiel V, Michaelis W, Clari P, Gaillard C, Martire L, Reitner J (1999). Cold seep deposits of Beauvoisin (Oxfordian; southeastern France) and Marmorito (Miocene; norther Itlay): microbially induced authigenic carbonates. Int J Earth Sci, 88 (1): 60–75

Pedersen K (1997). Microbial life in deep granitic rock. FEMS Microbiol Rev, 20(3–4): 399–414

Pena J, Duckworth O W, Bargar J R, Sposito G (2007). Dissolution of hausmannite (Mn3O4) in the presence of the trihydroxamate siderophore desferrioxamine B. Geochim Cosmochim Acta, 71 (23): 5661–5671

Pennisi E (2002). Geobiologists: as diverse as the bugs they study. Science, 296(5570): 1058–1060

Peretyazhko T, Zachara J M, Boily J F, Xia Y, Gassman P L, Arey B W, Burgos W D (2009). Mineralogical transformations controlling acid mine drainage chemistry. Chem Geol, 262 (3–4): 169–178

Pierre C, Rouchy J M (2004). Isotopic compositions of diagenetic dolomites in the Tortonian marls of the western Mediterranean margins: evidence of the past gas hydrate formation and dissociation. Chem Geol, 205 (3–4): 469–484

Pósfai M, Dunin-Borkowski R E (2006). Sulfides in biosystems. Rev Mineral Geochem, 61 (1): 679–714

Priscu J C, Christner B C (2004) Earth's icy biosphere. In: Bull A T, ed. Microbial diversity and bioprospecting. Washington D C: ASM press

Regenspurg S, Peiffer S (2005). Arsenate and chromate incorporation in schwertmannite. Appl Geochem, 20 (6): 1226–1239

Reguera G, McCarthy K D, Mehta T, Nicoll J S, Tuominen M T, Lovley D R (2005). Extracellular electron transfer via microbial nanowires. Nature, 435 (7045): 1098–1101

Reguera G, Nevin K P, Nicoll J S, Covalla S F, Woodard T L, Lovley D R (2006). Biofilm and nanowire production leads to increased current in Geobacter sulfurreducens fuel cells. Appl Environ Microbiol, 72 (11): 7345–7348

Reysenbach A L, Ehringer M, Hershberger K L (2000a). Microbial diversity at 83°C in calcite spring, Yellowstone Nationla Park: another environment where the Aquificales and “Korarchaeota” coexist. Extremephiles, 4: 61–67

Reysenbach A L, Longnecker K, Kirshtein J (2000b). Novel bacterial and archaeal lineages from an in situ growth chamber deployed at a Mid-Atlantic Ridge hydrothermal vent. Appl Environ Microbiol, 66 (9): 3798–3806

Reysenbach A L, Shock E (2002). Merging genomes with geochemistry in hydrothermal ecosystems. Science, 296 (5570): 1077–1082

Rickard D, Morse J W (2005). Acid volatile sulfide (AVS). Mar Chem, 97 (3–4): 141–197

Roberts H H, Aharon P (1994). Hydrocarbon-derived carbonate buildups of the northern Gulf-of-Mexico continental slope- a review of submersible investigations. Geo-Mar Lett, 14 (2–3): 135–148

Roberts J A (2004). Inhibition and enhancement of microbial surface colonization: the role of silicate composition. Chem Geol, 212 (3–4): 313–327

Roberts J A, Bennett P C, Gonzalez L A, Macpherson G L, Milliken K L (2004). Microbial precipitation of dolomite in methanogenic groundwater. Geology, 32 (4): 277–280

Roberts J A, Fowle D A, Hughes B T, Kulczycki E (2006). Attachment behavior of Shewanella putrefaciens onto magnetite under aerobic and anaerobic conditions. Geomicrobiol J, 23 (8): 631–640

Roden E E (2006). Geochemical and microbiological controls on dissimilatory iron reduction. C R Geosci, 338 (6–7): 456–467

Roden E E, Zachara J M (1996). Microbial reduction of crystalline Fe (III) oxides: influence of oxide surface area and potential for cell growth. Environ Sci Technol, 30 (5): 1618–1628

Rodriguez N M, Paull C K, Borowski W S (2000) Zonation of authigenic carbonates within gas-hydrate bearing sedimentary sections on the Blake Ridge: offshore southeastern North America. In: Paull C K, Matsumoto R, Wallace P J, Dillon W P, eds. Proceedings of Ocean Drilling Program, Scientific Research, 164: 301–312

Rogers J R, Bennett P C (2004). Mineral stimulation of subsurface microorganisms: release of limiting nutrients from silicates. Chem Geol, 203 (1–2): 91–108

Rosso K M, Zachara J M, Fredrickson J K, Gorby Y A, Smith S C (2003). Nonlocal bacterial electron transfer to hematite surfaces. Geochim Cosmochim Acta, 67 (5): 1081–1087

Sample J C, Reid M R (1998). Contrasting hydrogeologic regimes along strike-slip and thrust faults in the Oregon convergent margin: Evidence from the chemistry of syntectonic carbonate cements and veins. Geol Soc Am Bull, 110 (1): 48–59

Sánchez-Román M, McKenzie J A, Wagener A D R, Rivadeneyra M A, Vasconcelos C (2009). Presence of sulfate does not inhibit low-temperature dolomite precipitation. Earth Planet Sci Lett, 285 (1–2): 131–139

Sánchez-Román M, Vasconcelos C, Schmid T, Dittrich M, McKenzie J A, Zenobi R, Rivadeneyra M A (2008). Aerobic microbial dolomite at the nanometer scale: Implications for the geologic record. Geology, 36 (11): 879–882

Santelli C M, Welch S A, Westrich H R, Banfield J F (2001). The effect of Fe-oxidizing bacteria on Fe-silicate mineral dissolution rates. Chem Geol, 180 (1–4): 99–115

Sassen R, Roberts H H, Carney R, Milkov A V, DeFreitas D A, Lanoil B, Zhang C L (2004). Free hydrocarbon gas, gas hydrate, and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial processes. Chem Geol, 205 (3–4): 195–217

Schwertmann U, Carlson L (2005). The pH-dependent transformation of schwertmannite to goethite at 25°C. Clay Miner, 40 (1): 63–66

Seabaugh J L, Palmieri M, Crawford P A, Dong H, Champine J E (2003) Interaction of lead and calcium with lead-resistant microorganisms from soil contaminated with Chat. The American Society for Microbiology 103nd General Meeting, Washington D C

Senko J M, Wanjugi P, Lucas M, Bruns M A, Burgos W D (2008). Characterization of Fe(II) oxidizing bacterial activities and communities at two acidic Appalachian coalmine drainage-impacted sites. ISME J, 2 (11): 1134–1145

Senko J M, Zhang G X, McDonough J T, Bruns M A, Burgos W D (2009). Metal reduction at low pH by a Desulfosporosinus species: implications for the biological treatment of acidic mine drainage. Geomicrobiol J, 26 (2): 71–82

Sharma R (2001). Design and applications of environmental cell transmission electron microscopy for in situ observations of gas-solid reactions. Microsc Microanal, 7 (6): 494–506

Sharma R, Weiss K (1998). Development of a TEM to study in situ structural and chemical changes at an atomic level during gas-solid interactions at elevated temperatures. Microsc Res Tech, 42 (4): 270–280

Shelobolina E S, Pickering S M, Lovely D R (2005). Fe-Cycle bacteria from industrial clays mined in Georgia, USA. Clays Clay Miner, 53 (6): 580–587

Singer P C, Stumm W (1970). Acidic mine drainage: the rate-determining step. Science, 167 (3921): 1121–1123

Sokolov I, Smith D S, Henderson G S, Gorby Y A, Ferris F G (2001). Cell surface electrochemical heterogeneity of the Fe(III)-reducing bacteria *Shewanella putrefaciens*. Environ Sci Technol, 35 (2): 341–347

Sonnenfeld E M, Beveridge T J, Koch A L, Doyle R J (1985). Asymmetric distribution of charge on the cell wall of *Bacillus subtilis*. J Bacteriol, 163 (3): 1167–1171

Stakes D S, Orange D, Paduan J B, Salamy K A, Maher N (1999). Cold-seeps and authigenic carbonate formation in Monterey Bay, California. Mar Geol, 159 (1–4): 93–109

Staudigel H, Chastain R A, Yayanos A, Bourcier W (1995). Biologically mediated dissolution of glass. Chem Geol, 126 (2): 147–154

Staudigel H, Furnes H, Banerjee N R, Dilek Y, Muehlenbachs K (2006). Microbes and volcanoes: a tale of the oceans, ophiolites, and greenstone belts. GSA Today, 16 (10): 4–10

Staudigel H, Yayanos A, Chastain R A, Davies G, Verdurmen E A, Schiffman P, Bourcier R, De Baar H (1998). Biologically mediated dissolution of volcanic glass in seawater. Earth Planet Sci Lett, 164 (1–2): 233–244

Stevens TO, McKinley JP (1995). Lithoautotrophic microbial ecosystems in deep basalt aquifers. Science, 270 (5235): 450–455

Stookey L L (1970). Ferrozine-a new spectrophotometric reagent for iron. Anal Chem, 42 (7): 779–781

Storrie-Lombardi M C, Fisk M R (2004). Elemental abundance distributions in suboceanic basalt glass: evidence of biogenic alteration. Geochem Geophys Geosyst, 5 (10): Q10005

Stucki J W (1981). The quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1,10-phenanthroline: II. A photochemical method. Soil Sci Soc Am J, 45: 638–641

Stucki J W (2006) Properties and behavior of iron in clay minerals. In: Bergaya F, Lagaly G, Theng B G K, eds. Handbook of Clay Science, Elsevier: Amsterdam, 423–476

Stucki J W, Anderson W L (1981). The quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1,10-phenanthroline: I. SOurces of variability. Soil Sci Soc Am J, 45: 633–637

Stucki J W, Kostka J E (2006). Microbial reduction of iron in smectite. C R Geosci, 338 (6–7): 468–475

Stucki J W, Tessier D (1991). Effects of iron oxidation state on the texture and structural order of Na-nontronite gels. Clays Clay Miner, 39 (2): 137–143

Templeton A, Knowles E (2009). Microbial Transformations of Minerals and Metals: Recent Advances in Geomicrobiology Derived from Synchrotron-Based X-Ray Spectroscopy and X-Ray Microscopy. Annu Rev Earth Planet Sci, 37 (1): 367–391

Templeton A S, Staudigel H, Tebo B M (2005) Diverse Mn(II)-oxidizing bacteria isolated from submarine basalts at Loihi Seamount Geomicrobiology Journal, 22 (3–4), 127–139

Terzi C, Lucchi F R, Vai G B, Aharon P (1994). Petrography and stable-isotope aspects of cold vent activity imprinted on Miocene age calcari-a-lucina from Tuscan and Romagna Apennines, Italy. Geo-Mar Lett, 14 (2–3): 177–184

Thomas-Keprta K L, Bazylinski D A, Kirschvink J L, Clemett S J, McKay D S, Wentworth S J, Vali H, Gibson E K Jr, Romanek C S (2000). Elongated prismatic magnetite crystals in ALH84001 carbonate globules: potential Martian magnetofossils. Geochim Cosmochim Acta, 64 (23): 4049–4081

Thomas-Keprta K L, Clemett S J, Bazylinski D A, Kirschvink J L, McKay D S, Wentworth S J, Vali H, Gibson E K, Romanek C S (2002). Magnetofossils from ancient Mars: a robust biosignature in the martian meteorite ALH84001. Appl Environ Microbiol, 68 (8): 3663–3672

Thorseth I H, Furnes H, Tumyr O (1995a). Textural and chemical effects of bacterial activity on basaltic glass: an experimental approach. Chem Geol, 119 (1–4): 139–160

Thorseth I H, Pedersen R B, Christie D M (2003) Microbial alteration of 0–30-Ma seafloor and sub-seafloor basaltic glasses from the Australian Antarctic Discordance Earth and Planetary Science Letters, 215 (1–2), 237–247

Thorseth I H, Torsvik T, Furnes H, Muehlenbachs K (1995b). Microbes play an important role in the alteration of oceanic crust. Chem Geol, 126 (2): 137–146

Ubaldini S, Veglio F, Beolchini F, Toro L, Abbruzzese C (2000). Gold recovery from a refractory pyrrhotite ore by biooxidation. Int J Miner Process, 60 (3–4): 247–262

Ullman W J, Welch S A (2002) Organic ligands and feldspar dissolution. In: Hellman R, Wood S A, eds. Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar. The Geochemical Society, St. Louis, MO. 7: 3–35

Uroz S, Calvaruso C, Turpault M P, Frey-Klett P (2009). Mineral weathering by bacteria: ecology, actors and mechanisms. Trends Microbiol, 17 (8): 378–387

Vali H, Weiss B, Li Y L, Sears S K, Kim S S, Kirschvink J L, Zhang C L (2004). Formation of tabular single-domain magnetite induced by Geobacter metallireducens GS-15. Proc Natl Acad Sci USA, 101 (46): 16121–16126

van Aken P A, Liebscher B (2002). Quantification of ferrous/ferric ratios in minerals: new evaluation schemes of Fe L-23 electron energy-loss near-edge spectra. Phys Chem Miner, 29 (3): 188–200

van Aken P A, Liebscher B, Styrsa V J (1998). Quantitative determination of iron oxidation states in minerals using Fe L-2,L-3-edge electron energy-loss near-edge structure spectroscopy. Phys Chem Miner, 25 (5): 323–327

van Aken P A, Styrsa V J, Liebscher B, Woodland A B, Redhammer G J (1999). Microanalysis of Fe^{3+}/Sigma Fe in oxide and silicate minerals by investigation of electron energy-loss near-edge structures (ELNES) at the Fe M-2,M-3 edge. Phys Chem Miner, 26 (7): 584–590

Vasconcelos C, McKenzie J A (1997). Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil). J Sediment Res, 67: 378–390

Vasconcelos C, McKenzie J A, Bernasconi S, Grujic D, Tiens A J (1995). Microbial mediation as a possible mechanism for natural dolomite formation at low temperature. Nature, 377 (6546): 220–222

VonRad U, Rosch H, Berner U, Geyh M, Marchig V, Schulz H (1996). Authigenic carbonates derived from oxidized methane vented from the Makran accretionary prism off Pakistan. Mar Geol, 136 (1–2): 55–77

Wacey D, Wright D T, Boyce A J (2007). A stable isotope study of microbial dolomite formation in the Coorong Region, South Australia. Chem Geol, 244 (1–2): 155–174

Wall J D, Krumholz L R (2006). Uranium reduction. Annu Rev Microbiol, 60 (1): 149–166

Wang H M, Zeng C P, Liu Q Y, Liu D, Qiu X, Gong L F (2010a). Calcium Carbonate Precipitation Induced by a Bacterium Strain Isolated from an Oligotrophic Cave in Central China. Front Earth Sci China (In press)

Wang X, Li Y, Lu A H, Wang C Q (2010b). Features of precipitates formed by different cultivations of Acidithiobacillus ferrooxidans. Front Earth Sci China (In press)

Warthmann R, van Lith Y, Vasconcelos C, McKenzie J A, Karpoff A M (2000). Bacterially induced dolomite precipitation in anoxic culture experiments. Geology, 28 (12): 1091–1094

Warthmann R, Vasconcelos C, Sass H, McKenzie J A (2005). *Desulfovibrio brasiliensis* sp. nov., a moderate halophilic sulfate-reducing bacterium from Lagoa Vermelha (Brazil) mediating dolomite formation. Extremephiles, 9 (3): 255–261

Welch S A, Barker W W, Banfield J F (1999). Microbial extracellular polysaccharides and plagioclase dissolution. Geochim Cosmochim Acta, 63 (9): 1405–1419

Welch S A, Ullman W J (1993). The effect of organic acids on plagioclase dissolution rates and stoichiometry. Geochim Cosmochim Acta, 57 (12): 2725–2736

Wright D (1999). The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. Sediment Geol, 126 (1–4): 147–157

Wright D T (1997). An organogenic origin for widespread dolomite in the Cambrian Eilean Dubh Formation, Northwestern Scotland. J Sediment Res, 67: 54–64

Wright D T, Oren A (2005). Nonphotosynthetic bacteria and the formation of carbonates and evaporites through time. Geomicrobiol J, 22 (1–2): 27–53

Wright D T, Wacey D (2005). Precipitation of dolomite using sulphate-reducing bacteria from the Coorong Region, South Australia: significance and implications. Sedimentology, 52 (5): 987–1008

Wu L L, Jacobson A D, Chen H C, Hausner M (2007). Characterization of elemental release during microbe-basalt interactions at $T = 28°C$. Geochim Cosmochim Acta, 71 (9): 2224–2239

Wu L L, Jacobson A D, Hausner M (2008). Characterization of elemental release during microbe–granite interactions at $T = 28°C$. Geochim Cosmochim Acta, 72 (4): 1076–1095

Xu H F, Wang Y F (1999). Electron energy-loss spectroscopy (EELS) study of oxidation states of Ce and U in pyrochlore and uraninite-natural analogues for Pu- and U-bearing waste forms. J Nucl Mater, 265 (1–2): 117–123

Younger P L (1997). The longevity of minewater pollution: a basis for decision-making. Sci Total Environ, 194–195: 457–466

Zhang G, Dong H, Jiang H, Kukkadapu R K, Kim J W, Eberl D, Xu Z (2009a). Biomineralization associated with microbial reduction of Fe^{3+} and oxidation of Fe^{2+} in solid minerals. Am Mineral, 94 (7): 1049–1058

Zhang G X, Senko J M, Kelly S D, Tan H, Kemner K M, Burgos W D (2009b). Microbial reduction of iron(III)-rich nontronite and uranium (VI). Geochim Cosmochim Acta, 73 (12): 3523–3538

Zhou Y F, Wang R C, Lu X C, Chen T H (2010). Role of Adhered Paenibacillus polymyxa in the Dissolution and Flotation of Bauxite: A Dialytic Investigation. Front Earth Sci China (In press)

Zierenberg RA, Adams M W W, Arp A J (2000). Life in extreme environments: hydrothermal vents. Proc Natl Acad Sci USA, 97 (24): 12961–12962