The Role of Microorganisms in the Formation, Dissolution and Transformation of Secondary Minerals in Mine Rock and Drainage: A Review

Jose Eric Ortiz-Castillo[1], Mohamad Mirazimi[1], Maryam Mohammadi[1], Eben Dy[2] and Wenying Liu[1,*]

[1] Department of Materials Engineering, University of British Columbia, 309-6350 Stores Road, Vancouver, BC V6T 1Z4, Canada

[2] Energy, Mining and Environment Research Center, National Research Council Canada, 4250 Wesbrook Mall, Vancouver, BC V6T 1W5, Canada;

*Correspondence: wenying.liu@ubc.ca

Abstract

Mine waste rock and drainage pose lasting environmental, social, and economic threats to the mining industry, regulatory agencies, and society as a whole. Mine drainage can be alkaline, neutral, moderately or extremely acidic and contains significant levels of sulfate, dissolved iron, and frequently a variety of heavy metals and metalloids, such as cadmium, lead, arsenic, and selenium. In acid neutralization by carbonate and silicate minerals, a range of secondary minerals can form and possibly scavenge these potentially harmful elements. Apart from the extensively-studied microbial-facilitated sulfide oxidation, the diverse microbial communities present in mine rock and drainage may also participate in the formation, dissolution, and transformation of secondary minerals influencing the mobilization of these metals and metalloids. This article reviews major microbial-mediated geochemical processes occurring in mine rock piles that affect drainage chemistry, with a focus on the role of microorganisms in the formation, dissolution and transformation of secondary minerals. Understanding this is crucial for developing biologically-based measures to deal with contaminant release at the source, *i.e.*, source control.

Keywords: mine rock drainage; sulfide oxidation; neutralization by silicates; secondary iron minerals; toxic element scavenging.

1. Introduction

The challenge of managing large volumes of mine rock and drainage is expected to persist for a long period of time, which warrants continued efforts in research to understand the problem and strategic planning in the development of strategies for prevention, control, and remediation [1,2]. The quality of mine drainage depends on the intertwined processes of geology, mineralogy, geochemistry, hydrology, and microbiology [3–6]. Ferguson and Erickson [7] categorized the factors that affect acid generation and contaminant release into primary, secondary and tertiary. This categorization provides a structured approach for organizing the discussion of acid formation and metal leaching at mine sites. Primary factors are those directly involved in the acid generation and metal leaching, such as sulfide oxidation. Secondary factors refer to those that control the consumption or alteration of products from acid generation reactions, such as neutralization of acid by carbonate minerals and the formation of secondary minerals. Tertiary factors are the physical aspects of the solid materials that influence acid and metal generation and mobilization, such as particle size.

The complex geochemical reactions responsible for mine drainage generation have been studied by many researchers, as reviewed by Nordstrom *et al.* [6]. Much of the mine drainage problem originates from oxidation of sulfide minerals, such as pyrite (FeS_2). Sulfide oxidation and subsequent acid neutralization by carbonate and silicate minerals result in hydrolysis of iron and aluminum and concomitant formation of a range of iron and aluminum secondary minerals. Microorganisms significantly influence the kinetics of acid generation, neutralization, and formation and dissolution of secondary minerals [8]. Understanding these influences is essential for drainage quality prediction and subsequent design and implementation of control and remediation measures [9]. The interest in understanding the interactions between microorganisms and minerals has significantly increased in the past two decades, as shown by the number of journal publications by different scientific and engineering disciplines between 2000 and 2020 (Figure 1).

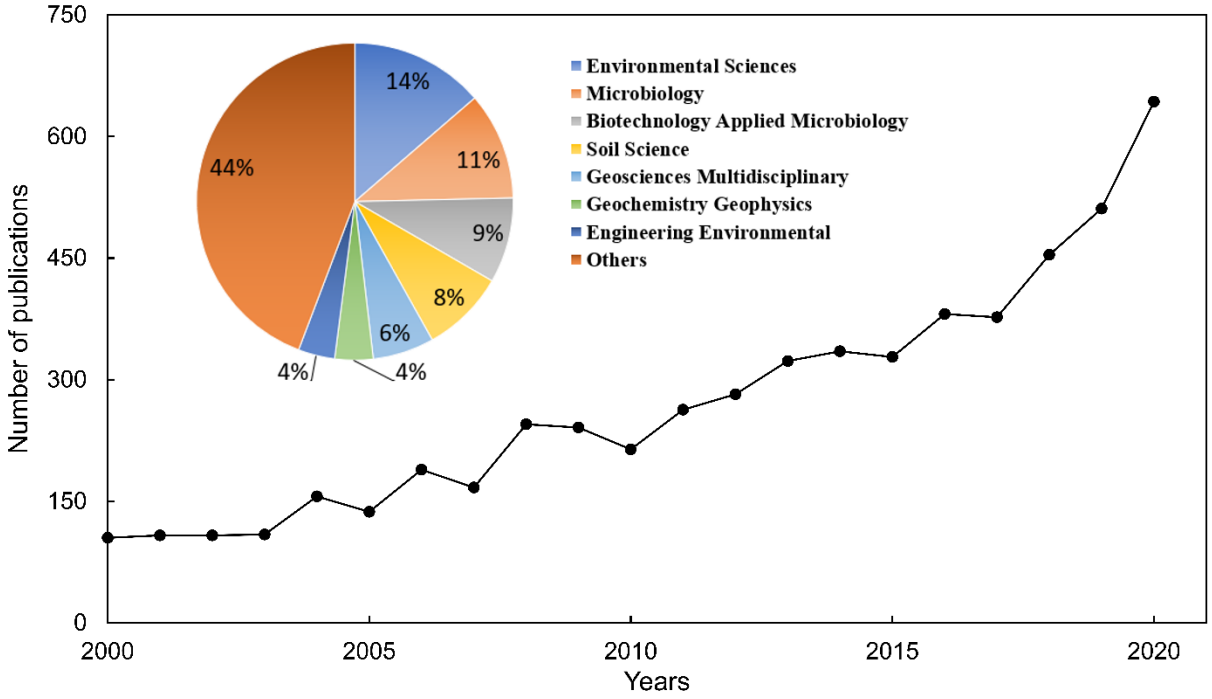

Figure 1. The number of journal publications in the past two decades (2000–2020) obtained by searching ISI Web of Science using keywords "minerals" and "microorganisms". "Others" include research areas contributing to ≤ 3% of the total publications: Mineralogy, Chemical Engineering, Metallurgy Metallurgical Engineering, Mining Mineral Processing, Plant Sciences, Ecology, Agronomy, Food Science Technology, Materials Science Multidisciplinary, Multidisciplinary Sciences, Water Resources, Chemistry Multidisciplinary, Biochemistry Molecular Biology, Biology, Energy Fuels, Chemistry Physical, Multidisciplinary Agriculture, Astronomy and Astrophysics.

This review article focuses on the roles of microorganisms in important biogeochemical processes that control mine drainage quality, with a focus on the formation, dissolution, and transformation of secondary minerals. Secondary mineralization controls acidity and mobilization of various toxic elements, posing long-term issues to management of mine drainages [10]. In the case of acid mine drainage, Fe and Al are usually the major dissolved metals, possibly with elevated concentrations of trace metals, such as Cu, Pb, Zn, Cd, Mn, Co, and Ni. In mine discharges of a more circumneutral nature, trace metal concentrations tend to be lower due to the formation of secondary mineral phases and increased adsorption of trace metals to these secondary minerals

[11–13]. Certain elements may remain in solution in the form of oxyanions as pH increases, in particular, the metalloids As, Se, and Sb [11–13]. Secondary mineral formation, dissolution, and transformation are intimately linked with the mobility of metals and metalloids that may eventually become contaminants [14]. Understanding the important roles of microorganisms in these geochemical processes is crucial to the design of biologically-based remediation techniques [15], and particularly, the development of biologically-based source control measures.

2. Microbial communities in mine waste rock piles

A large diversity of microorganisms with unique functions exists in mine rock piles. Minerals and rocks provide habitats and nutrients for microorganisms and they in turn impact mineral dissolution, solubility, and speciation [16,17]. Microorganisms use minerals and dissolved chemical species in different enzymatic and non-enzymatic processes as: (1) electron acceptors, *e.g.*, the use of sulfate and Fe(III) to replace oxygen in the respiration process [18]; (2) energy sources, such as the oxidation of dissolved ferrous ions and sulfide-sulfur to provide energy [19]; (3) nutrient sources, *e.g.*, the preferential colonization of microorganisms on phosphorous-bearing mineral and rock surfaces [20]; and (4) a detoxification pathway, such as the reduction of toxic Cr(VI) to much less toxic Cr(III) [21].

In general, any sulfidic rock and acid mine drainage system comprises several microbial niches, but compared with many other environments, it contains fewer prokaryotic lineages, possibly because of the limited number of energy-deriving reactions available in such acidic environments [22]. Often less than five groups distinct at the genera level of the prokaryotic taxa make up the communities in any specific microenvironment, among which at least two archaeal and eight bacterial divisions have representatives able to thrive under the extreme conditions typical of acid mine drainage [23]. The metabolic functions that underpin these communities include autotrophic and heterotrophic iron and sulfur oxidation, anaerobic sulfur oxidation, and ferric iron reduction, which control flows of iron, sulfur, and carbon in the system (Figure 2) [24].

Schippers *et al.* [15] surveyed more than 70 sulfidic mine dumps and heaps around the world and identified various bacteria, archaea, and eukarya including algae, fungi, yeasts and protozoa. The maximum number of total microbial cells found in these sites ranges from 10^6 to 10^8 cells per

gram of solid. The major groups identified were iron- and sulfur-oxidizing bacteria and archaea, Fe(III) and Mn (IV) reducing microorganisms, and nitrate and sulfate reducing microorganisms [15,25]. The most dominant bacteria were iron-oxidizers belonging to four genera: the Gram-positive strains related to *Acidimicrobium* or *Ferrimicrobium* and the Gram-negative genera *Acidithiobacillus* and *Leptospirillum* [15]. In the more acidic (pH 0) and higher temperature environment at the Richmond Mine, iron-oxidizing archaea, *i.e.*, *Ferroplasma acidarmanus* (strain fer1), were found to comprise 85% of the microbial communities [26]. Baumler *et al.* demonstrated that the growth of this acidophilic archaeon was chemolithotrophic in the presence of Fe(II) and heterotrophic in the absence of Fe(II) and that the heterotrophic growth required the presence of sulfate [27]. Later, Druschel *et al.* concluded that Fe(III) oxidized the majority of the sulfur intermediate species on pyrite surfaces at the Richmond Mine, which explains much lower abundance of the sulfur-oxidizing microorganisms compared with the iron-oxidizers [23].

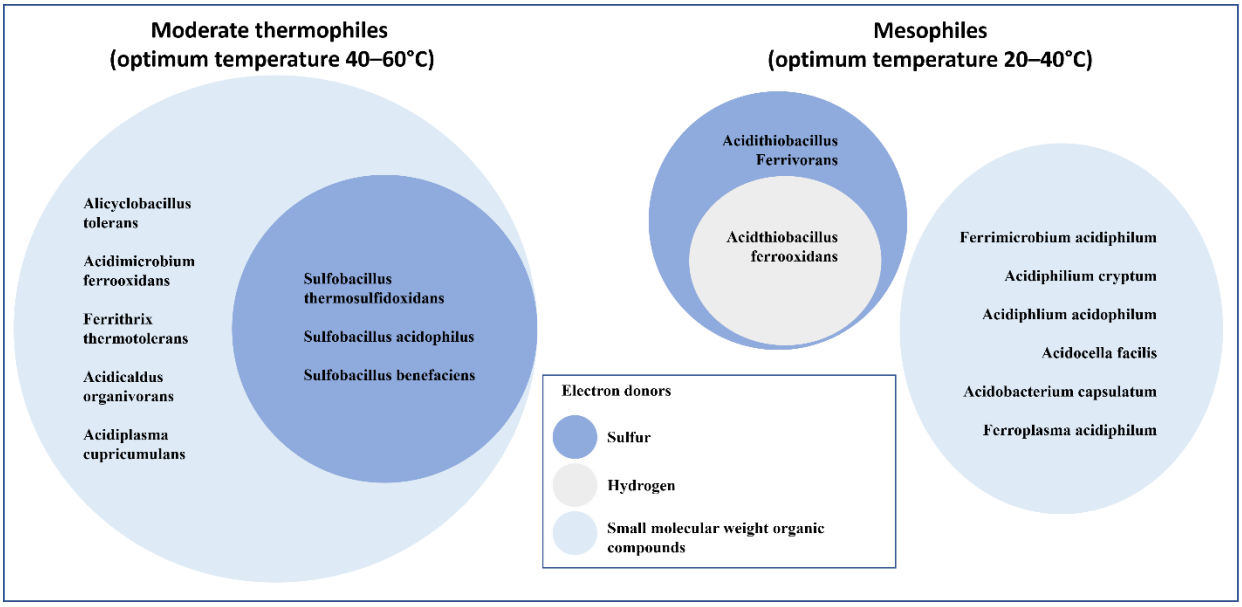

Figure 2. Acidophilic bacteria and archaea that catalyze the ferric - ferrous iron cycling. Adapted from Johnson [28]

Major factors influencing the size, composition, and activities of microbial communities include mineralogy as well as environmental factors, such as pH, oxygen content, temperature, carbon source, and energy source. Mineralogy plays a fundamental role in the diversity and function of

microbial communities. Mineral surface composition, such as carbonate, silicate, and aluminosilicate, influences microbial community structure and growth of biofilms [29]. Using high-throughput pyrosequencing, Jones *et al.* [29] reported that approximately 70 – 90% of the variance in phylogenetic diversity was controlled by the type of mineral surface regardless of the environmental pressures. Furthermore, the mineral surface could be significantly different from the bulk mineral due to factors such as adsorption of secondary minerals and incongruent dissolution from previous episodes of leaching [30]. Dissolution may be focused in microenvironments such as those at or near bacterial attachment sites on the mineral surfaces [30]. Microorganisms affects the rate of mineral weathering by using a variety of organic metabolic products excreting from the cells, such as siderophore and alginate [31–33].

The diversity and function of the microbial communities are also controlled by environmental factors, which may in turn be influenced by mineral compositions of the mine rock heaps and dumps [34]. The richness and size of microbial communities typically decrease when the pH and oxygen of the environment decrease. Using phylogenetic analyses of 16S rRNA genes, Mendez *et al.* [35] compared the phylotype richness in highly disturbed, extremely (pH 2.7) and moderately (pH 5.7) acidic lead-zinc mine tailing samples with those from a vegetated off-site control sample (pH 8). The authors showed that phylotype richness in these communities decreased from 42 in the control to 24 in the moderately acidic samples and 8 in the extremely acidic tailing samples. Schippers *et al.* [25] reported that cell counts for all microorganisms reduced at reduced oxygen concentrations in two different uranium mine wastes. The microorganisms participate in important geochemical processes, such as sulfide oxidation, acid neutralization, and concomitant secondary mineralization.

3. Microbial-facilitated iron and sulfur cycling

Metal sulfide oxidation is a biogeochemical process that generates acid mine drainage [36]. Common sulfide minerals in mine waste include pyrite, pyrrhotite, and marcasite, with other sulfides that could be important on some sites, such as chalcopyrite, chalcocite, arsenopyrite, sphalerite, galena, and enargite. Oxidation of sulfides by Fe(III) and dissolved oxygen has been

comprehensively studied and reviewed [6,37]. In general, the major oxidant is oxygen at circumneutral pH, whereas Fe(III) becomes the principal oxidant under acidic conditions [38].

Using pyrite as an example, its oxidation occurs via a sequence of reactions [38–40]. A simplified oxidation reaction is initiated by oxygen, as shown by Eq. 1. The Fe(II) ions released are then oxidized by oxygen to Fe(III) via Eq. 2. Ferric (III), under acidic conditions, is an important oxidant for most sulfide minerals. Pyrite oxidation by Fe(III) is shown in Eq. 3. Another example is the oxidation of an iron-rich sphalerite by Fe(III) (Eq. 4), which is the main reason for elevated zinc concentrations in some mine drainage [41].

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \text{Eq. 1}$$

$$14Fe^{2+} + 3.5O_2 + 14H^+ = 14Fe^{3+} + 7H_2O \quad \text{Eq. 2}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \text{Eq. 3}$$

$$4Zn_{0.75}Fe_{0.25}S + 32Fe^{3+} + 16H_2O = 3Zn^{2+} + 33Fe^{2+} + 4SO_4^{2-} + 32H^+ \quad \text{Eq. 4}$$

The rate of sulfide oxidation is influenced by the type of sulfides, its crystal structure, and the type of oxidant. Pyrrhotite is oxidized much faster than pyrite. Nicholson and Scharer [42] found that the rate of pyrrhotite oxidation by oxygen ranged from 6 to 14 x 10^{-9} mol·m^{-2}s^{-1} at 22°C, which is 100 times those measured for pyrite. The different morphological forms of Fe sulfide have the following relative oxidation rate: marcasite > framboidal pyrite > massive pyrite [43]. Oxidation of pyrrhotite and pyrite by Fe(III) occurs faster than by oxygen. Janzen *et al.* [44] found that the average oxidation rate of pyrrhotite by Fe(III) was 3.5 x 10^{-8} mol·m^{-2}s^{-1} at pH 2.75, around one order of magnitude faster than that by oxygen. The faster kinetics was attributed to a mechanism that Fe(III) can bind chemically to the mineral surface readily, but oxygen cannot [45]. Williamson and Rimstidt [40] compiled data on oxidation of pyrite by oxygen and ferric ions and formulated empirical rate laws applicable over a wide range of solution compositions. The authors found that the rate of pyrite oxidation was in the range of 7.8 x 10^{-10} to 6.3 x 10^{-7} mol·m^{-2}s^{-1} by ferric and in the range of 2.9 x 10^{-11} to 3.3 x 10^{-9} mol·m^{-2}s^{-1} by oxygen. In other words, the former could be one or two orders of magnitude greater than the latter.

Given much faster sulfide oxidation by ferric ions, the generation of ferric ions from ferrous oxidation (Eq. 2) is considered as the rate-limiting step for sulfide oxidation under acidic conditions [38]. The presence of iron-oxidizing microorganisms could significantly influence the reaction kinetics of oxidation of Fe(II) to Fe(III) [6]. Meruane and Vargas [46] reported that chemical oxidation of ferrous predominated over bacterial oxidation at pH values over 5, with a constant oxidation rate of about 1.6 x 10^{-9} mol·L^{-1}·s^{-1} between pH 5.5 and 7, whereas chemical oxidation proceeded very slowly under acidic solutions. However, the presence of acidophilic microorganisms at acidic conditions significantly accelerates ferrous oxidation. Singer and Stumm [38] reported that the rate increased by a factor larger than 10^6. Nordstrom [47] measured the biotic iron oxidation rate in a mountain stream containing acid mine effluent to be in the range of 2 to 8 x 10^{-7} mol·L^{-1}·s^{-1}, five to eight orders of magnitude faster than the abiotic rate.

The degree to which microorganisms enhance ferrous oxidation is found to depend on the number of iron-oxidizing microbial cells present, the level of microbial activities of the cells, and pH [48]. Stoner *et al.* [49] studied multi-parametric effects on iron oxidation by enrichment cultures of moderately thermophilic (50 °C) acidophilic mining bacteria and concluded that the Fe(II) oxidation rate was around 2 x 10^{-13} g Fe(II) per min per bacterial cell. Edwards *et al.* [50] measured the iron oxidation rate of both planktonic (free floating) and sessile (attached) *ferrooxidans* (pH <1.0, 42 °C) and concluded that the oxidation rate was approximately equivalent in both enrichments, the value being 2 x 10^{-14} g Fe(II) per min per bacterial cell. It has been found that pH inhibits the ferrous iron-oxidizing system of *T. ferrooxidans* at values below 1.3 [51]. This bacterial-catalyzed Fe(II) oxidation process may provide ferric ions at a rate of the same order of magnitude as that of pyrite oxidation by ferric ions [52].

Sulfide bioleaching is thought to occur via "indirect" and "direct" mechanisms, which were first explained by Silverman and Erlich [53]. Sand *et al.* [54] used the terms "non-contact" and "contact" to describe the role of planktonic and sessile organisms. The “indirect” or “non-contact” mechanism, which has been widely accepted, involves microbial-catalyzed oxidation of ferrous to ferric and then direct chemical oxidation of sulfide minerals by ferric ions [36,55–60]. The “direct” or “contact” mechanism means an attack on the crystal lattice of a sulfide mineral through enzymatic oxidation by attached microbial cells [61]. This mechanism has not been

completely confirmed because it is difficult to exclude the effect of non-contact mechanism. Dong *et al.* [62] found that to study the "contact mechanism", surface passivation by elemental sulfur needed to be eliminated because the attachment of sulfur-oxidizing microorganisms limited the contact oxidation of iron.

Figure 3 is a schematic showing the iron and sulfur cycling in sulfidic mine rock and drainage systems. While autotrophic iron-oxidizers use Fe(II) as a main source of energy, different heterotrophic microorganisms (*e.g. Acidiphilium spp*., *Sulfobacillus spp*., and *Acidobacterium spp*.) can reduce Fe(III) with organic matter as the electron donor [63–65]. Under anoxic conditions, some iron-oxidizing microorganisms, such as *At. ferrooxidans* and *Sulfobacillus spp*., can participate in the reduction of Fe(III) [66]. Iron cycling between ferric and ferrous could be achieved by moderately thermophilic iron-oxidizing bacteria, which have been shown to be capable of reducing ferric to ferrous under anaerobic conditions with organic carbon as the carbon and energy source [67–69].

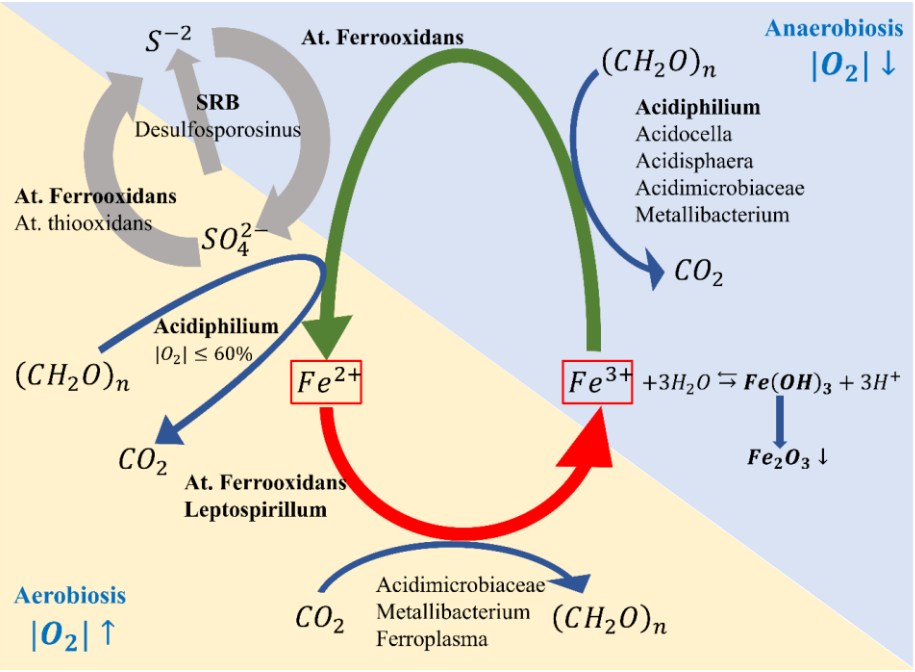

Figure 3. Geomicrobiological model of the role of microorganisms in iron and sulfur cycling in sulfidic mine rock and drainage systems. Image adapted from: [70]

Another important group of chemical species present in sulfidic mine rock and drainage systems is sulfur compounds. Chemolithotrophic sulfur-oxidizing microorganisms can oxidize sulfide to sulfate under both aerobic and anaerobic conditions [66]. Borilova *et al.* [71] found that under high redox potential conditions, sulfate was the first dissolved sulfur species generated by iron-oxidizing bacteria. Reduction of Fe(III) is reported to be coupled with sulfide oxidation in anaerobic conditions [72]. As part of the sulfur cycle, sulfate-reducing microorganisms, *e.g. Desulfosporosinus spp*., participate in sulfate reduction under anoxic conditions [73]. Microbial fermentation and respiration contribute to the carbon cycling in sulfidic mine rock and drainage systems. Different microorganisms, such as *Veillonella*, *Staphylococcus*, *Paludibacter*, and *Clostridium spp*., produce organic intermediates via fermentation that are used by syntropic microorganisms (*e.g. Syntrophobacter spp*.) to generate hydrogen and acetate [63]. These organic compounds are used as substrates by different sulfate-reducing microorganisms and methanogens [74].

4. Influence of microorganisms on acid neutralization by carbonate and silicate minerals

4.1 Neutralization by carbonate minerals

Sulfide occurrences are accompanied by large amounts of gangue minerals of diverse mineralogy. The dissolution of these minerals may neutralize acid generated by sulfide oxidation, thus controlling the environment pH [75]. Even though sulfide reactions have been extensively studied, less focus has been put on acid-neutralizing minerals, including: (1) Ca and Mg-bearing carbonates; (2) oxides and hydroxides of Ca, Mg, and Al; (3) silicate minerals; and (4) phosphates (primarily apatite) [76]. Laboratory and field studies have provided plenty of knowledge of sulfide oxidation and weathering of acid-consuming carbonate and silicate minerals [77]. However, current static and kinetic methods, based on which mine permitting, acid mine drainage control, and mine closure plans are evaluated, do not give sufficient consideration of rock mineralogy and the kinetics of various acid generating and neutralizing reactions [76,78,79]. Uncertainties in interpretation of these test results may lead to situations where acid generation was not expected, but later developed, such as Newmont Rain facility in Nevada and Cyprus Thompson Creek in Idaho [80].

The most important minerals offering neutralization are carbonate minerals, including calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], ankerite [$Ca(Fe,Mg)(CO_3)_2$], siderite [$FeCO_3$] or mixtures thereof [37]. Based on their acid neutralization capacity, Ca-Mg carbonate minerals are categorized as "dissolving" with the highest level of reactivity [81]. In contrast, siderite dissolution releases iron, whose hydrolysis produces protons, making the overall dissolution of siderite neutral or even net acid producing [37,82]. Hence, it is important to highlight that alkalinity of different carbonate minerals is not conserved [76]. Nevertheless, the current ABA test procedure does not distinguish between different types of carbonate minerals and the application calculation factor of 31.25 may overestimate the carbonate neutralization potential [37,82]. Microorganisms may participate and alter neutralization processes by carbonate materials. Certain microorganisms were found to inhibit calcite dissolution by attaching to the high-energy sites of the calcite surfaces and thereby preventing etch pits from dissolution [83,84].

4.2 Neutralization by silicate minerals

In contrast with carbonate minerals, the neutralizing potential of silicate minerals has not been fully characterized [85]. It is known that the rate of dissolution of silicate minerals is much lower than that of carbonate minerals and that they contribute to neutralization in the long term [81,86–88]. Silicate minerals are classified into anhydrous (orthosilicates, metasilicates, dissilicates, and subsilicates), and hydrous silicates (zeolites, mica, serpentine, and clay), based on chemical composition and optical and physical properties [89]. Based on their reactivity, they are grouped into fast weathering (*e.g.*, anorthite and olivine), intermediate weathering (*e.g.*, hornblende, serpentine, and chlorite), slow weathering (*e.g.*, albite, gibbsite, and kaolinite), very slow weathering (*e.g.*, feldspar), and inert (*e.g.*, quartz) [81]. Weathering of silicate minerals introduces ions into solution, mainly Na, K, Ca, Mg and Al, and may be associated with mineral alteration to other minerals [76,90,91]. An example is the dissolution of intermediate weathering chlorite, as shown in Eq. 5, which provides neutralization potential [88].

$$(Mg, Fe, Al)_6[AlSi_3O_{10}](OH)_8 + 16H^+ = [6(Mg, Fe, Al)]^{13+} + Al^{3+} + 3H_4SiO_4 + 6H_2O \quad \text{Eq. 5}$$

Silicates are ubiquitous on earth and microorganisms use them to obtain nutrition and as habitats [92]. Apart from the chemical and hydrological factors, the presence of diverse microbial

communities plays important catalytic roles, as shown in Figure 4, in biogeochemical processes affecting silicate weathering rates [93,94]. Microorganisms selectively destroy certain beneficial minerals for meeting nutritional requirements [95]. For example, the transformation of silicate minerals, such as vermiculite, causes the release of K, Mg, Al as mineral nutrients for microbial communities [96]. Several strains of bacteria were found to produce organic and inorganic acids and extracellular polymers, which help increase the release of cations from biotite (Si, Fe, Al) and plagioclase feldspar (Si, Al) by up to two orders of magnitude compared to abiotic controls [20].

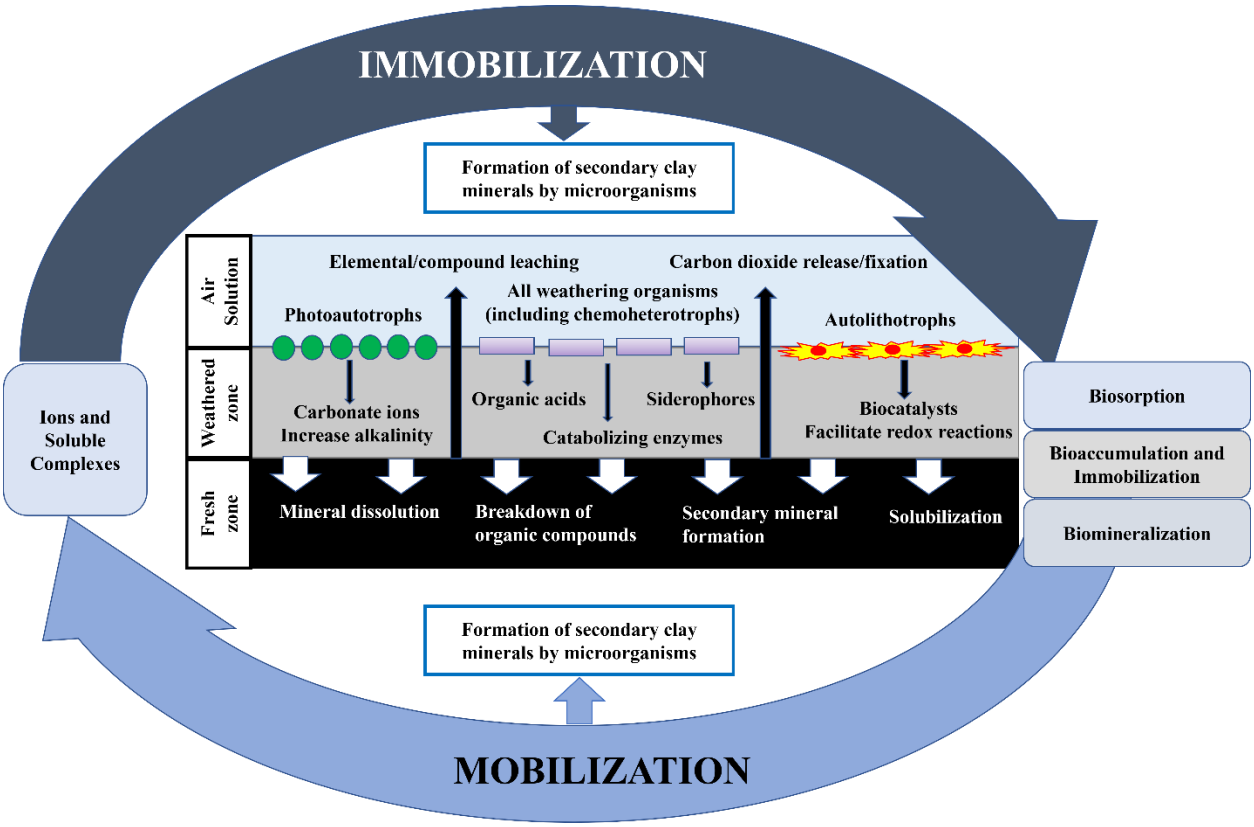

Figure 4. Diagram of biogeochemical processes involved in the transformation of clay minerals and weathering mechanisms on geological substrates. Images adapted from: [97,98]

The efficiency of microbial mobilization of elements from silicate dissolution depends on the type of microbial species and the biochemical mechanisms involved [30,99,100]. The presence of carbon, nitrogen, and nutrient sources can strongly influence microbial mineral weathering [101]. Phosphorous is an essential nutrient for microorganisms. Hence, in carbon rich and phosphorous scarce environments silicate minerals are weathered rapidly, even feldspars, which are typically

resistant to weathering [95]. Iron is another essential nutrient that is often limited because of formation of insoluble iron oxides. Stranghoener *et al.* [102] found that certain microbial species can accelerate the release of structurally bound Fe from basaltic rocks and use it as a nutrient once the environment becomes nutrient depleted. Kalinowski *et al.* [103] concluded that decreasing the carbon content of the growth media was associated with a reduction in Fe and Si release rate from hornblende.

Microorganisms could exert their effects either by directly colonizing the mineral surfaces [104], or without direct contact with the dissolving mineral [105]. The surface-attached microorganisms were found to be more efficient than the unattached ones in siderophore production and selective dissolution of Fe, Al, and Si from biotite [99]. The direct microbial attachment onto mineral surfaces can occur by electrostatic attraction between negatively charged microbial cells and positively charged mineral surfaces (*e.g.* Fe- and Al- oxides). The microbial attachment onto negatively charged silicate surfaces depends on the mineral surface composition and the microbial cell walls [104,106]. The direct attachment initially increases the mineral surface area due to the presence of microbial hyphae, which facilitates later weathering [107,108]. The attached microbial cells produce extracellular polymeric substances (EPS) and other complex biogenic molecules that help create highly reactive microenvironments [106,109–111]. Some bacteria or fungi were found to produce citric and oxalic acids, which are very effective in proton-promoted dissolution of silicates [8]. *Bacillus mucilaginosus* was found to dissolve soil minerals and mica by producing organic acids and polysaccharides [112]. Some microorganisms enhance silicate dissolution by excreting siderophores, which form complexes with metals, particularly Fe, and also Al and to a lesser extent Si [111]. Different studies have shown that complexation tends to predominate initially when the pH is near-neutral, whereas proton-promoted acidification predominates later as pH becomes increasingly acidic [100,113,114].

5. Formation of secondary minerals

The oxidation of pyrite and other sulfides releases proton, sulfate, and a diversity of metal cations into solution. Neutralization of acidity by carbonate minerals and silicates leads to hydrolysis of Fe and Al and concomitant formation of a series of soluble and insoluble Fe and Al secondary

minerals. Three major types of secondary minerals can form: relatively soluble metal sulfate [10], poorly crystalline, relatively insoluble iron and aluminum hydroxysulfates [115], and well-crystalline minerals of the alunite supergroup, including alunite, jarosite and related phases [116]. The formation and dissolution of these secondary minerals play an important role in controlling the fate of acids and metals released upon weathering of mineralized rocks, coal deposits, metallic ore deposits, and mine wastes. Secondary mineralization, on the one hand, may generate acid and in turn accelerate sulfide oxidation [117]. On the other hand, secondary minerals, such as scorodite, may form coatings on sulfide surfaces, limiting their further oxidation [118]. Formation and dissolution of secondary minerals are highly influenced by microbial activities.

5.1 Soluble metal sulfate salts

Metal sulfate salts crystallize during the dry season when water is evaporated and the liquor is concentrated, a phenomenon termed "efflorescence". These efflorescent minerals typically occur close to their respective parent sulfides [119]. Different soluble ferrous and ferric iron sulfate hydrates form on the surfaces of oxidizing pyrite, including melanterite ($Fe^{II}SO_4{\cdot}7H_2O$) (Eq. 6), melanterite group minerals containing various proportions Cu and Zn in solid solution, römerite ($Fe^{II}Fe^{III}_2(SO_4)_4{\cdot}14H_2O$), copiapite ($Fe^{II}Fe^{III}_4(SO_4)_6{\cdot}(OH)_2{\cdot}20H_2O$), and coquimbite ($Fe^{III}_2(SO_4)_3{\cdot}9H_2O$) [120]. Anglesite ($PbSO_4$) occurs on galena-rich mine wastes and chalcanthite ($CuSO_4{\cdot}5H_2O$) occurs on chalcopyrite-rich rocks [121].

During dry periods, melanterite is commonly one of the first minerals to crystallize and precipitate from water, forming emerald green crystal aggregates. Upon exposure to air, these aggregates alter to a fine white powder composed mainly of melanterite (Eq. 6), and minor amounts of rozenite ($FeSO_4{\cdot}4H_2O$) and szomolnokite ($FeSO_4{\cdot}H_2O$) [41]. Melanterite often appears as a precursor to other secondary minerals, such as the formation of copiapite from melanterite exposed to air (Eq. 7). The formation of these secondary minerals is associated with the transient storage of Fe^{2+}, SO_4^{2-} and acidity. The longer the dry period, the more severe the environmental impact during the wet period [41].

$$FeS_2 + 3.5O_2 + 8H_2O = FeSO_4{\cdot}7H_2O + H_2SO_4 \quad \text{Eq. 6}$$

$$5FeSO_4{\cdot}7H_2O + O_2 + H_2SO_4 = Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2{\cdot}20H_2O + 15H_2O \quad \text{Eq. 7}$$

During wet periods, the dissolution of melanterite produces acid and releases high concentrations of Fe^{2+}, Zn^{2+}, SO_4^{2-} and a diverse range of potentially toxic elements [10,13]. In the case of iron(III) and Al(III) sulfates, they undergo considerable hydrolysis, which releases acid into water, resulting in the first-flush acids (pH 2.6 – 3.8) [121]. Sainz *et al.* [122] characterized the time sequence of leachate discharges from 57 waste rock dumps before and after rainfall in southwest Spain. They observed that metal loadings after rainfalls generally experienced the initial rapid release over a period of 1 to 7 days, followed by a deceleration period of variable duration.

The simple dissolution of melanterite does not affect water pH, as shown by Eq. 8. However, pH has been found to decrease as a result of melanterite dissolution [41]. The decrease in pH was attributed to the stronger hydrolysis of acidic Fe(II) than that of SO_4^{2-} [120]. The hydrolysis of Fe(II) (Eq. 9) generates acid and the hydrolysis of SO_4^{2-} (Eq. 10) provides the buffering capacity. The equilibrium constants for Eq. 9 and 10 are $K = 10^{-9.5}$ and $K = 10^{-12.1}$, respectively, at 25 °C and 1 atm. The larger equilibrium constant for the former indicates that the net outcome of melanterite dissolution is generation of acidity [41].

$$FeSO_4{\cdot}7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O \quad \text{Eq. 8}$$

$$Fe(H_2O)_6^{2+} + H_2O = Fe(OH)(H_2O)_5^{+} + H_3O^{+} \quad \text{Eq. 9}$$

$$SO_4^{2-} + H_2O = HSO_4^{-} + OH^{-} \quad \text{Eq. 10}$$

The dissolution of melanterite is considered as the initiator of the so-called “propagation cycle” that causes accelerated pyrite oxidation by ferric ions [41]. In an unsaturated zone and increasing water turbidity, the oxidation of ferrous to ferric by O_2 (Eq. 11) is accelerated by the hydrolysis of ferric and the flocculation of colloidal ferric. This oxidative dissolution reaction generates acid, which may decrease pH to a level where soluble ferric ions are available for pyrite oxidation. Pyrite oxidation generates acid resulting in further decrease in pH of the system. The creation of an acidic environment provides essential conditions for the growth of different acidophiles [15].

The presence of these microorganisms will further accelerate pyrite oxidation and may serve as nucleation sites for the formation of secondary minerals [123].

$$FeSO_4 \cdot 7H_2O + 0.25O_2 = Fe(OH)_3 + H_2SO_4 + 4.5H_2O \quad \text{Eq. 11}$$

5.2 Relatively insoluble, amorphous hydroxysulfates and oxyhydroxides

A range of insoluble iron and aluminum hydroxysulfates and oxyhydroxides, typically of poor crystallinity and difficult to characterize, form from acidic sulfate waters [115]. pH is among the key parameters controlling the formation and the nature of the precipitates. Based on the analyses of 28 mine drainage sites, Bigham *et al.* [124] concluded that ferrihydrite (typically $Fe_5HO_8 \cdot 4H_2O$) or a mixture of ferrihydrite and goethite (α-FeOOH) formed at pH 6.5 or higher; In the intermediate pH range of 6.5 to 4.5, the precipitates were mixtures of ferrihydrite and schwertmannite (ideally $Fe_8O_8(OH)_6SO_4$); When pH was in the range of 4.5 to 2.8, the predominant form of precipitates was schwertmannite, with trace to minor amounts of goethite and/or jarosite [$(H, K, Na)Fe_3(OH)_6(SO_4)_2$]; In the pH range of 2.5 to 1.5, the formation of jarosite probably dominated. Scorodite and amorphous hydrous ferric arsenate may be produced from arsenic mineral weathering, with other major amorphous arsenic phases identified as hydrous ferric oxyhydroxides, kaňkite ($FeAsO_4 \cdot 3.5H_2O$), pharmacosiderite ($KFe_4(AsO_4)_3(OH)_4 \cdot 6–7H_2O$), yukonite ($Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20} \cdot 15H_2O$), and Ca–Fe arsenates [125].

The stability field of a secondary iron mineral changes as the value of the solubility product is changed [126,127]. Due to the variability in the actual composition of the mineral, a meaningful solubility product is expressed as a solubility window [128]. Schwertmannite, as the dominant solid phase, controls the activities of both major and minor elements in acid sulfate waters. The general formula is $Fe_8O_8(OH)_x(SO_4)_y$, where $4.5 \le x \le 6$, $1.0 \le y \le 1.75$, and $8 - x = 2y$. The dissolution reaction and the solubility product K are shown as Eq. 12 and Eq. 13. According to Bigham *et al.* [124], the solubility window of schwertmannite is 18.0 ± 2.5; the dissolution of goethite and the associated solubility product are shown as Eq. 14 and Eq. 15.

$$Fe_8O_8(OH)_x(SO_4)_y + (24 - 2y)H^+ = 8Fe^{3+} + ySO_4^{2-} + 0.5(24 - 2y + x)H_2O \quad \text{Eq. 12}$$

$$\log K = 8\log a_{Fe}^{3+} + y\log a_{SO4}^{2-} + (24 - 2y)pH \quad \text{Eq. 13}$$

$$FeOOH + 3H^+ = Fe^{3+} + 2H_2O \quad \text{Eq. 14}$$

$$\log K = \log a_{Fe}^{3+} + 3pH \quad \text{Eq. 15}$$

By comparing solubility product of schwertmannite (18), goethite (1.4), K-jarosite (-12.51) and ferrihydrite (5.0) [124], one can conclude that jarosite and goethite are the phases that ultimately control the solubility of iron in mine drainage waters. Above pH 2, all are metastable with respect to goethite. The jarosite stability field would be changed by the selection of a different log K, the reported value of which varies from -7.12 to -14.8 [129]. Experimental results showed that schwertmannite gradually hydrolyzed and transformed to goethite and jarosite [130]. As shown in Eq. 16, the solution pH decreases and the SO_4^{2-} concentration increases during transformation [115,131]. At higher pH values, ferrihydrite is formed but is also unstable with respect to goethite [132]. The field of metastability for schwertmannite is markedly influenced by a change in logK of either jarosite or ferrihydrite [115].

$$Fe_8O_8(OH)_{5.5}(SO_4)_{1.25} + 2.5H_2O = 8FeOOH + 2.5H^+ + 1.25SO_4^{2-} \quad \text{Eq. 16}$$

Microorganisms influence secondary mineral behavior as a result of direct metabolic activities and passive Fe sorption and nucleation reaction [133]. The rate of Fe(II) oxidation to Fe(III), which is greatly accelerated by iron-oxidizing microorganisms, affects formation and phase of secondary iron hydroxysulfate minerals. Rapid oxidation is more likely to be associated with schwertmannite formation and slow oxidation tends to be associated with jarosite formation [134,135]. Iron-oxidizing bacteria *Ferrovum sp*. and relatives of *Gallionella* were found in schwertmannite samples collected in acidic iron-sulfate rich mine waters [136,137]. Feng *et al.* [138] proposed a three-stage mechanism for the formation of schwertmannite in the presence of an iron-oxidizing bacteria, *A. ferrooxidans*: (1) a nucleation stage; (2) ferrihydrite and schwertmannite formation; and (3) formation of a "hedgehog" morphology by the transformation of ferrihydrite or schwertmannite to lepidocrocite and goethite. Some microorganisms decrease iron concentration in solution through siderophore production, which forms complexes with iron in solution [114]. The bioreduction of Fe(III) oxides or dissolved Fe(III) by iron-reducing bacteria may produce Fe(II)-containing secondary minerals, such as magnetite,

siderite, vivianite, green rusts, and chukanovite, and the actual Fe(II)-containing secondary mineral produced is influenced by the type of electron donors present [139,140].

5.3 Well-crystalline minerals of the alunite supergroup

The most common secondary sulfate minerals belong to the jarosite and the alunite families, with a typical formula of $AB_3(SO_4)_2(OH)_6$, where A is normally K^+, Na^+, H_3O^+, Pb^{2+}, NH^{4+} or Ag^+, and B is usually Fe^{3+} or Al^{3+}, *e.g.* jarosite $KFe_3(SO_4)_2(OH)_6$ and alunite $KAl_3(SO_4)_2(OH)_6$ [141]. They form in acidic and oxic aqueous environments rich in ferric, aluminum, and sulfate resulting from weathering in the oxidation zone of polymetallic sulfide deposits [116]. Alunite is the dominant secondary sulfate mineral formed from Al derived from weathering of clay minerals [9].

The formation of alunite and jarosite releases acid (Eq. 17 and 18). Their subsequent dissolution may further release latent acid depending on pH (Eq. 19 and 20). Qian *et al.* [142] found that the dissolution of both minerals shows a V-shaped behavior with respect to pH. The minimum jarosite dissolution occurred at pH 3.4, below which the dissolution was acid-consuming and above which the dissolution was acid-generating. Similarly, alunite dissolution occurred to a minimal extent at pH 5.5. From this perspective, jarosite may be of greater concern for managing aged mine waste rock, which may contain a significant amount of jarosite [142].

$$3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O = KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad \text{Eq. 17}$$

$$3Al^{3+} + K^+ + 2SO_4^{2-} + 6H_2O = KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad \text{Eq. 18}$$

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O = 3Fe(OH)_3 + K^+ + 2SO_4^{2-} + 3H^+ \quad \text{Eq. 19}$$

$$KAl_3(SO_4)_2(OH)_6 + 3H_2O = 3Al(OH)_3 + K^+ + 2SO_4^{2-} + 3H^+ \quad \text{Eq. 20}$$

Jones [143] analyzed the product stability during jarosite-alunite formation and showed that high concentrations of Al^{3+} were needed in solution to obtain Al-substituted jarosite. This was attributed to the difference in the hydration energies of Al (III) and Fe (III) ions. The former has a higher hydration energy, implying that an additional energy barrier must be overcome to replace Fe(III) with Al(III).

Microbial interactions in jarosite and alunite environments contribute to the evolution of the acidity of the environments [144]. Biochemical activities of microorganisms together with the ferrolysis of hydrous Fe(II)-oxides are found to be pathways to generate highly acidic conditions, favoring alunite formation [145]. The precipitation of jarosite promotes the acidic environment needed for the growth of different acidophilic microorganisms, such as *Acidithiobacillus ferrooxidans* [146]. The presence of schwertmannite and K-jarosite is indicative of the development of acidic microenvironments for bacteria colonization in these porous layers of iron precipitates [147]. These microorganisms were found to be coated by jarosite precipitates, which serve as nucleation sites for further mineralization on sulfide surfaces and this may eventually terminate sulfide oxidation [148]. The reduction of iron sulfate minerals, such as jarosite, by sulfate-reducing microorganisms present in jarosite can potentially contribute to the natural attenuation of toxic heavy metals via the formation of metal sulfides [149].

6. Influence of secondary minerals on the mobility of toxic elements

6.1 Uptake of toxic elements by secondary minerals

Sequestration of trace metals and oxyanions by secondary iron minerals occur through the following mechanisms: substitution for Fe in the atomic structures, co-precipitation with Fe, surface adsorption, and complexation via ion exchange between oxyanions and sulfate [150–152]. Melanterite, one of the first highly soluble sulfate minerals to crystallize in sulfide-rich part of mine rock piles, can incorporate different metals, such as copper, into its atomic structure by substituting Cu for Fe [153]. Cd, Cu, Pb, and Zn are incorporated into ferrihydrites via co-precipitation with ferrihydrites [154]. High concentrations of trace metals, such as Cu, Zn, Pb, Co, have been found in schwertmannite due to co-precipitation of these elements during schwertmannite formation [150,155].

In term of oxyanions, arsenic (III) has been found to be adsorbed onto schwertmannite surfaces through formation of As(III) – Fe(III) – SO_4^{2-} precipitates and ion exchange between schwertmannite SO_4^{2-} and As(III). At extremely high Fe(III) to As(III) ratio, the adsorbed As(III) may be oxidized by ferric to As(V) [156,157]. Schwertmannite is reported to have a higher adsorption capacity for arsenate than for molybdate and chromate [11]. The adsorption occurs via

complexation with iron hydroxyl surface groups and ion exchange between the oxyanions and SO_4^{2-} [11]. Adsorption of selenate is reported to occur through inner-sphere complexation with hematite and a mixture of outer- and inner- surface complexation with goethite and hydrous ferric oxide [158,159]. Jarosite and schwertmannite were found to facilitate the reduction of Cr(VI) to Cr(III) by sulfide, which was attributed to ferric on the iron mineral surfaces acting as the electron bridge in the reduction process [160,161].

Microorganisms have certain resistance to different heavy metals and other contaminants, such as arsenic [162]. Most microorganisms present in acidic mine environments have one or more plasmids that are related to metal-resistant genes (*i.e.* acidophilic heterotrophs of the genera *Acidiphilium* and *Acidocella*) [163]. Navarro *et al.* [164] studied the possible role of genomic islands present in some extreme acidophiles and found an apparent correlation between the number of metal resistance genes and the metal tolerance. However, tolerance of metals does not solely result from metal resistance genes. There are other metal tolerance mechanisms involved, such as complexation of free metals by sulfate ions and tolerance to metal influx via an internal positive cytoplasmic transmembrane potential [165].

6.2 Transformation of secondary minerals and the resulting release of toxic elements

Long-term transformation of secondary minerals may lead to the formation of new secondary phases and cause the release of trace metals and oxyanions that have already been sequestered [166]. Major factors that could influence secondary mineral transformation include chemical weathering, temperature, salt concentration around mineral grains, and microbial activities [167]. Microbial colonization on secondary mineral surfaces could lead to mineral solubilization and transformation, which may affect mobilization of acidity and previously held trace metals.

Fe(III)- or Mn(IV) (hydr)oxides with adsorbed metals are dissolved by anaerobic Fe(III)-and Mn(IV)-reducing microorganisms and the adsorbed metals are released [24,168,169]. Schwertmannite and jarosite are transformed to goethite by microorganisms in the presence of organic carbon, promoting the mobility of heavy metals [170,171]. During schwertmannite transformation, As(III) is released into solution, the concentration of which is controlled by exchange of As(III) for sulfate and As(III) re-adsorption to new phases formed [172,173]. Burton

et al. [174] found that Fe(II)-promoted transformation of schwertmannite to goethite may help stabilize solid-phase arsenic and postpone its subsequent release to solution. Adsorbed arsenate and chromate were found to inhibit Fe(II)-induced transformation of schwertmannite [175]. Arsenic adsorbed on goethite surfaces undergoes changes in speciation in the presence of both As(V)-reducing and As(III)-oxidizing bacteria via a detoxification pathway in aerobic environment, but the change is reported to have a negligible effect on As release [92,176]. Arsenate co-precipitated with jarosite may be mobilized when jarosite encounters sulfide ions and undergoes sulfidization process [177]. Metal-reducing microorganisms were found to participate in the reduction of Cr(VI) to Cr(III), most likely as a detoxification mechanism [21].

Vithana *et al.* [178] proposed that the transformation of secondary minerals was driven by dissimilatory microbial reduction and Fe(II)-catalysed conversion of schwertmannite and jarosite to goethite. The conditions that favor the transformation are anoxic, reducing, circumneutral, and rich in organic carbon [178]. Even in sulfidic mine rock and drainage environments often characterized by very low biodiversity [24], Bao *et al.* [170] found that Fe(III)- and sulfate-reducing bacteria significantly enhanced the conversion of schwertmannite and jarosite, with organic carbon being the major factor limiting the conversion rate. Organic matter is also found to affect the transformation of ferrihydrite to lepidocrocite and goethite [179]. These microorganisms utilize secondary minerals as the terminal electron acceptors via two mechanisms (Figure 5): direct electron transfer by attaching to the mineral surfaces using motility proteins and flagella; and indirect electron transfer by producing endogenous electron shuttles and Fe(III) complexing agents, *e.g.*, quinones or siderophores [180]. The crystallinity of iron minerals is reported to influence the rate of transformation, with more amorphous forms being more prone to be transformed than the less amorphous forms [170]. Some acidophilic heterotrophs can reduce Fe(III) from both amorphous and crystalline forms of insoluble ferric hydroxysulfate [69]. Under oxygen restricted conditions and in the presence of organic carbon, some iron-oxidizers (identified as a strain of *S. acidophilus*) were shown to be capable of reducing Fe(III) from iron-containing minerals, such as ferric hydroxide, jarosite, and goethite [67].

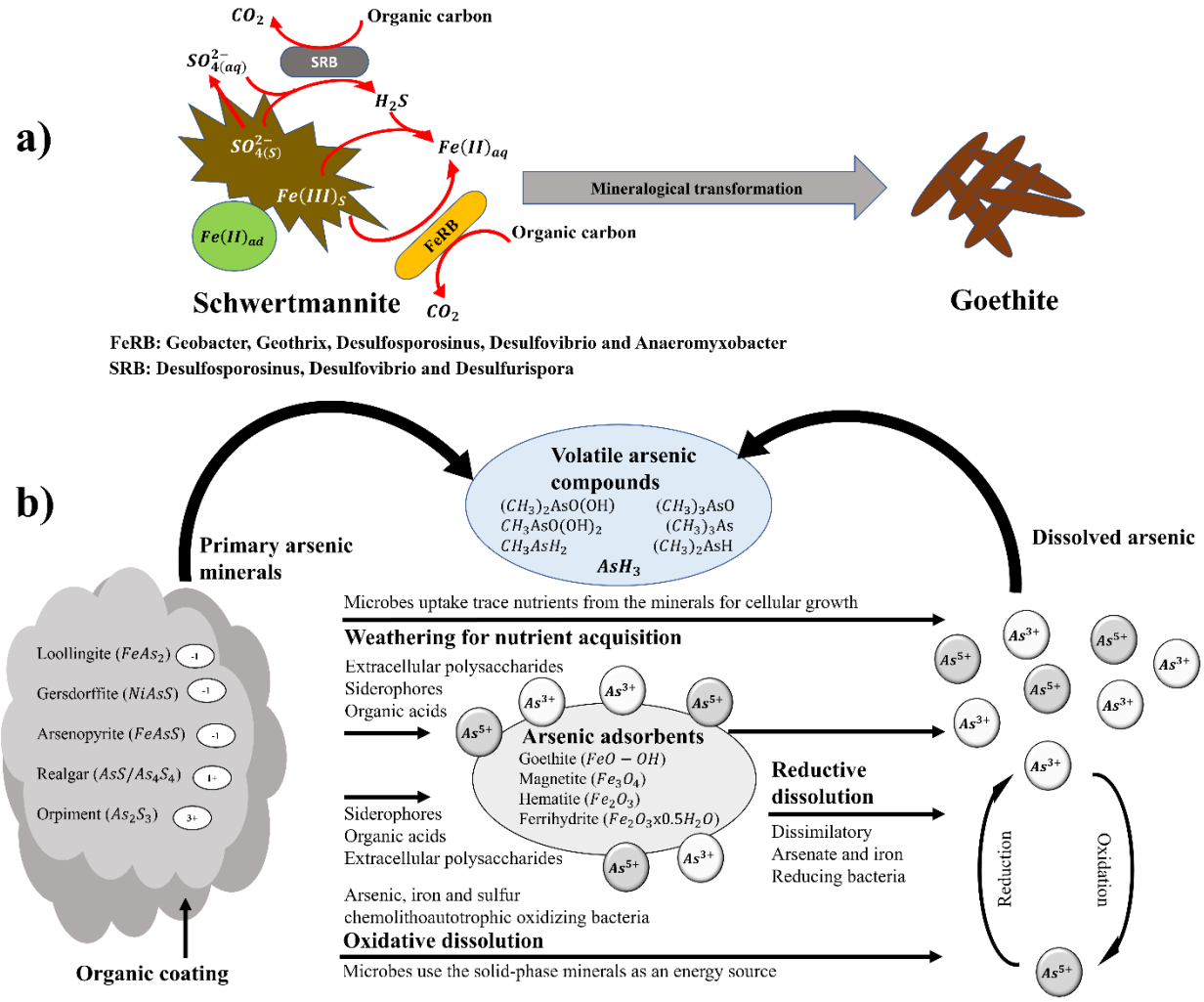

Figure 5. (a) Role of microorganisms in the transformation of schwertmannite to goethite (Adapted from: [170]); (b) Role of microorganisms in the mobilization of arsenic in mining environments (Adapted from: [181])

7. Future practical applications of microbial-mineral interactions for remediation

Microbial consortia in mine rock and drainage environments participate in different enzymatic and non-enzymatic processes that directly affect or are influenced by the formation, dissolution, and transformation of secondary minerals and mobilization of metals and metalloids. Microbial processes both respond to and modify the environment in which they are found. It is crucial to understand the spatial and temporal variations in the composition and activities of the microbial communities in mine rock and drainage systems. This understanding can be used as passive and

active tools to: (1) reveal mineral composition and level of weathering [182]. For example, the microbial populations were reported to be distinctively associated with the different oxidation stages of the tailings in the abandoned tailings impoundment of a Pb-Zn mine, with *Acidithiobacillus ferrooxidans* and *Leptospirillum spp*. being consistently present in the acidic tailings, and acidophilic archaea, mostly *Ferroplasma acidiphilum*, being predominant in the oxidized zones [183]; (2) act as a performance indicator of the remediation efforts. An example is that in phytoremediation the abundance of autotrophic iron- and sulfur oxidizing bacteria was used as an indicator of plant death and that increases in neutrophilic heterotrophic bacteria was indicative of the establishment of plants [184–186]; (3) develop novel microbiologically-based remediation strategies, especially measures for controlling contaminant release at the source, *i.e.*, source control.

Water treatment, though effective in most cases, can be prohibitively expensive. Given that the origin of the problem is the constituent release at its source, source control measures have been considered to be a preferred solution to acid mine drainage and metal leaching [187]. Microorganisms, on the one hand, catalyze geochemical processes leading to acid mine drainage and metal leaching, such as iron and sulfur-oxidizing microorganisms. On the other hand, they can potentially be used for metal immobilization, such as the use of sulfate-reducing bacteria to promote the conversion of sulfate to sulfide and the concomitant precipitation of metals as metal sulfides [188]. As an example, Figure 6 shows a schematic of the roles of these microorganisms in the bioremediation of pyritic mine rock. Understanding how the kinetics of certain microbial processes can be influenced is essential for developing biologically-based techniques for remediation [15].

Biologically-based source control measures that either inhibit the activities of certain microorganisms or stimulate the activities of other more beneficial microorganisms have been developed and tested in the past several decades. These measures are broadly divided into five main categories here: (1) application of bactericides to inhibit microbial activities involved in constituent release; (2) passivation of mineral oxidation with encapsulation to minimize microbial-mineral interactions; (3) stimulation of biofilm growth of beneficial microorganisms by adding inorganic nutrients; (4) application of dry covers; and (5) organic amendments. The

adoption of molecular tools by the mining industry, such as fluorescence in situ hybridisation (FISH), amplification of rRNA genes, separation by denaturing gradient gel electrophoresis (PCR-DOGE) and cloning has allowed the understanding of microorganisms in mine rock and drainage environments [189]. Recent advances in Next Generation Sequencing and associated metagenomics, proteomics, and metabolomics bring new opportunities to characterize and enhance the metabolic capacities of certain microorganisms, such as sulfate-reducing bacteria, for remediation [190].

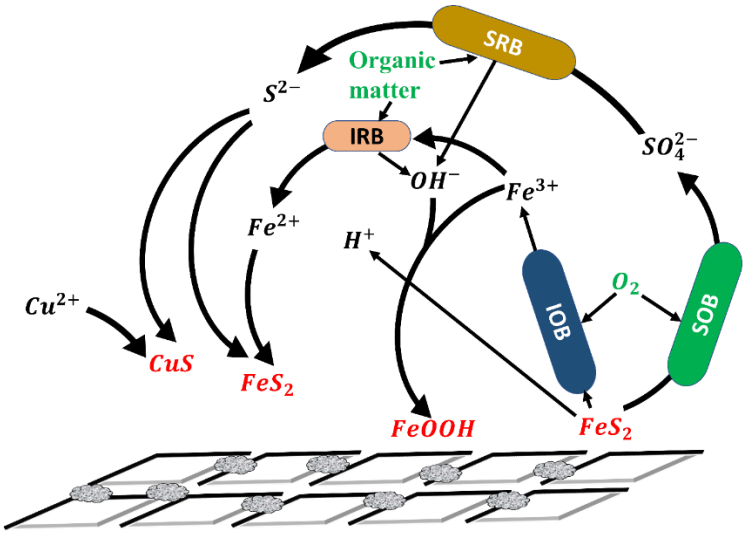

Figure 6. Schematic of the role of microorganisms in the bioremediation of pyritic mine rock. Adapted from: [191]. SOB: sulfur-oxidizing microorganisms; IOB: iron-oxidizing microorganisms; IRB: iron-reducing microorganisms; SRB: sulfur-reducing microorganisms.

Author Contributions: Conceptualization: W.L. and E.D.; investigation: J.E.O.C, M. Mirazimi, and M. Mohammadi; data curation: J.E.O.C, M. Mirazimi, and M. Mohammadi; writing—original draft preparation, J.E.O.C and W.L.; writing—review and editing, J.E.O.C, M. Mirazimi, M. Mohammadi E.D., and W.L.; investigation: J.E.O.C, M. Mirazimi, and M. Mohammadi; funding acquisition: W.L. and E.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from Energy, Mining and Environment Research Center, National Research Council Canada.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hudson-Edwards, K.A.; Jamieson, H.E.; Lottermoser, B.G. Mine wastes: past, present, future. *Elements* **2011**, *7*, 375–380, doi:10.2113/gselements.7.6.375.

2. Vriens, B.; Plante, B.; Seigneur, N.; Jamieson, H. Mine waste rock: insights for sustainable hydrogeochemical management. *Minerals* **2020**, *10*, 728, doi:10.3390/min10090728.

3. Jamieson, H.E. Geochemistry and mineralogy of solid mine waste: Essential knowledge for predicting environmental impact. *Elements* **2011**, *7*, 381–386, doi:10.2113/gselements.7.6.381.

4. Jamieson, H.E.; Walker, S.R.; Parsons, M.B. Mineralogical characterization of mine waste. *Appl. Geochemistry* **2015**, *57*, 85–105, doi:10.1016/j.apgeochem.2014.12.014.

5. Nordstrom, D.K. Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. *Appl. Geochemistry* **2011**, *26*, 1777–1791, doi:10.1016/j.apgeochem.2011.06.002.

6. Nordstrom, D.K.; Blowes, D.W.; Ptacek, C.J. *Hydrogeochemistry and microbiology of mine drainage: An update*; Elsevier Ltd, 2015; Vol. 57; ISBN 3035413037.

7. Ferguson, K.D.; Erickson, P.M. *Environmental management of solid waste: dredged material and mine tailings*; 1988; ISBN 978-3-642-61362-3.

8. Ehrlich, H.L. How microbes influence mineral growth and dissolution. *Chem. Geol.* **1996**, *132*, 5–9, doi:10.1016/s0009-2541(96)00035-6.

9. Amos, R.T.; Blowes, D.W.; Bailey, B.L.; Sego, D.C.; Smith, L.; Ritchie, A.I.M. Waste-rock hydrogeology and geochemistry. *Appl. Geochemistry* **2015**, *57*, 140–156, doi:10.1016/j.apgeochem.2014.06.020.

10. Jambor, J.L.; Nordstrom, D.K.; Alpers, C.N. Metal-sulfate salts from sulfide mineral oxidation. *Rev. Mineral. Geochemistry* **2000**, *40*, 303–350, doi:10.2138/rmg.2000.40.6.

11. Antelo, J.; Fiol, S.; Gondar, D.; López, R.; Arce, F. Comparison of arsenate, chromate and molybdate binding on schwertmannite: surface adsorption vs anion-exchange. *J. Colloid Interface Sci.* **2012**, *386*, 338–343, doi:10.1016/j.jcis.2012.07.008.

12. Baleeiro, A.; Fiol, S.; Otero-Fariña, A.; Antelo, J. Surface chemistry of iron oxides formed by neutralization of acidic mine waters: removal of trace metals. *Appl. Geochemistry* **2018**, *89*, 129–137, doi:10.1016/j.apgeochem.2017.12.003.

13. Smuda, J.; Dold, B.; Friese, K.; Morgenstern, P.; Glaesser, W. Mineralogical and geochemical study of element mobility at the sulfide-rich Excelsior waste rock dump from the polymetallic Zn-Pb-(Ag-Bi-Cu) deposit, Cerro de Pasco, Peru. *J. Geochemical Explor.* **2007**, *92*, 97–110, doi:10.1016/j.gexplo.2006.08.001.

14. Brown, G.E.; Foster, A.L.; Ostergren, J.D. Mineral surfaces and bioavailability of heavy metals: a molecular-scale perspective. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, *96*, 3388–3395,

doi:10.1073/pnas.96.7.3388.

15. Schippers, A.; Breuker, A.; Blazejak, A.; Bosecker, K.; Kock, D.; Wright, T.L. The biogeochemistry and microbiology of sulfidic mine waste and bioleaching dumps and heaps, and novel Fe(II)-oxidizing bacteria. *Hydrometallurgy* **2010**, *104*, 342–350, doi:10.1016/j.hydromet.2010.01.012.

16. Dong, H. Mineral-microbe interactions: a review. *Front. Earth Sci. China* **2010**, *4*, 127–147, doi:10.1007/s11707-010-0022-8.

17. Miot, J.; Benzerara, K.; Kappler, A. Investigating microbe-mineral interactions: recent advances in X-ray and electron microscopy and redox-sensitive methods. *Annu. Rev. Earth Planet. Sci.* **2014**, *42*, 271–289, doi:10.1146/annurev-earth-050212-124110.

18. Singleton, R. The sulfate-reducing bacteria: an overview. In *The sulfate-reducing bacteria: contemporary perspectives*; Odom, J., Singleton J-R, Eds.; Springer-Verlag: New York, 1993; pp. 1–20 ISBN 978-1-4613-9263-7.

19. Nemati, M.; Harrison, S.T.L.; Hansford, G.S.; Webb, C. Biological oxidation of ferrous sulphate by thiobacillus ferrooxidans: a review on the kinetic aspects. *Biochem. Eng. J.* **1998**, *1*, 171–190, doi:10.1016/S1369-703X(98)00006-0.

20. Barker, W.W.; Welch, S.A.; Chu, S.; Banfield, J.F. Experimental observations of the effects of bacteria on aluminosilicate weathering. *Am. Mineral.* **1998**, *83*, 1551–1563, doi:10.2138/am-1998-11-1243.

21. Cummings, D.E.; Fendorf, S.; Singh, N.; Sani, R.K.; Peyton, B.M.; Magnuson, T.S. Reduction of Cr(VI) under acidic conditions by the facultative Fe(III)-reducing bacterium acidiphilium cryptum. *Environ. Sci. Technol.* **2007**, *41*, 146–152, doi:10.1021/es061333k.

22. Mesa, V.; Gallego, J.L.R.; González-Gil, R.; Lauga, B.; Sánchez, J.; Méndez-García, C.; Peláez, A.I. Bacterial, archaeal, and eukaryotic diversity across distinct microhabitats in an acid mine drainage. *Front. Microbiol.* **2017**, *8*, 1756, doi:10.3389/fmicb.2017.01756.

23. Druschel, G.K.; Baker, B.J.; Gihring, T.M.; Banfield, J.F. Acid mine drainage biogeochemistry at Iron Mountain, California. *Geochem. Trans.* **2004**, *5*, 13–32, doi:10.1063/1.1769131.

24. Baker, B.J.; Banfield, J.F. Microbial communities in acid mine drainage. *FEMS Microbiol. Ecol.* **2003**, *44*, 139–152, doi:10.1016/S0168-6496(03)00028-X.

25. Schippers, A.; Hallmann, R.; Wentzien, S.; Sand, W. Microbial diversity in uranium mine waste heaps. *Appl. Environ. Microbiol.* **1995**, *61*, 2930–2935, doi:10.1128/aem.61.8.2930-2935.1995.

26. Edwards, K.J.; Bond, P.L.; Druschel, G.K.; McGuire, M.M.; Hamers, R.J.; Banfield, J.F. Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. *Chem. Geol.* **2000**, *169*, 383–397, doi:10.1016/S0009-2541(00)00216-3.

27. Baumler, D.J.; Jeong, K.C.; Fox, B.G.; Banfield, J.F.; Kaspar, C.W. Sulfate requirement for heterotrophic growth of “ferroplasma acidarmanus” strain fer1. *Res. Microbiol.* **2005**, *156*, 492–498, doi:10.1016/j.resmic.2004.12.007.

28. Johnson, D.B. The biogeochemistry of biomining. In *Geomicrobiology: molecular and environmental perspective*; Barton, L.L., Mandl, M., Loy, A., Eds.; Springer: Dordrecht, Germany, 2010; pp. 401–426 ISBN 9789048192038.

29. Jones, A.A.; Bennett, P.C. Mineral ecology: surface specific colonization and geochemical drivers of biofilm accumulation, composition, and phylogeny. *Front. Microbiol.* **2017**, *8*, 491, doi:10.3389/fmicb.2017.00491.

30. Ullman, W.J.; Kirchman, D.L.; Welch, S.A.; Vandevivere, P. Laboratory evidence for microbially mediated silicate mineral dissolution in nature. *Chem. Geol.* **1996**, *132*, 11–17, doi:10.1016/s0009-2541(96)00036-8.

31. Banfield, J.F.; Barker, W.W.; Welch, S.A.; Taunton, A. Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, *96*, 3404–3411, doi:10.1073/pnas.96.7.3404.

32. Hersman, L.; Lloyd, T.; Sposito, G. Siderophore-promoted dissolution of hematite. *Geochim. Cosmochim. Acta* **1995**, *59*, 3327–3330, doi:10.1016/0016-7037(95)00221-K.

33. Welch, S.A.; Vandevivere, P. Effect of microbial and other naturally occurring polymers on mineral dissolution. *Geomicrobiol. J.* **1994**, *12*, 227–238, doi:10.1080/01490459409377991.

34. Valentín-Vargas, A.; Root, R.A.; Neilson, J.W.; Chorover, J.; Maier, R.M. Environmental factors influencing the structural dynamics of soil microbial communities during assisted phytostabilization of acid-generating mine tailings: a mesocosm experiment. *Sci. Total Environ.* **2014**, *500–501*, 314–324, doi:10.1016/j.scitotenv.2014.08.107.

35. Mendez, M.O.; Neilson, J.W.; Maier, R.M. Characterization of a bacterial community in an abandoned semiarid lead-zinc mine tailing site. *Appl. Environ. Microbiol.* **2008**, *74*, 3899–3907, doi:10.1128/AEM.02883-07.

36. Schippers, A. Biogeochemistry of metal sulfide oxidation in mining environments, sediments, and soils. In *Sulfur biogeochemistry - past and present*; Geological Society of America, 2004; pp. 49–62 ISBN 9780813723792.

37. Blowes, D.W.; Ptacek, C.J.; Jambor, J.L.; Weisener, C.G. The geochemistry of acid mine drainage. In *Treatise on geochemistry*; 2003; pp. 149–204 ISBN 978-0-08-043751-4.

38. Singer, P.C.; Stumm, W. Acidic mine drainage: the rate-determining step. *Science* **1970**, *167*, 1121–1123, doi:10.1126/science.167.3921.1121.

39. Nicholson, R. V.; Gillham, R.W.; Reardon, E.J. Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. *Geochim. Cosmochim. Acta* **1988**, *52*, 1077–1085,

doi:10.1016/0016-7037(88)90262-1.

40. Williamson, M.A.; Rimstidt, J.D. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim. Cosmochim. Acta* **1994**, *58*, 5443–5454, doi:10.1016/0016-7037(94)90241-0.

41. Frau, F. The formation-dissolution-precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: environmental implications. *Mineral. Mag.* **2000**, *64*, 995–1006, doi:10.1180/002646100550001.

42. Nicholson, R. V.; Scharer, J.M. Chapter 2. Laboratory studies of pyrrhotite oxidation kinetics. In *Environmental geochemistry of sulfide oxidation*; Alpers, C.N., Blowes, D.W., Eds.; ACS Symposium series: Washington, DC, USA, 1994; pp. 14–30 ISBN 9780841227729.

43. Pugh, C.E.; Hossner, L.R.; Dixon, J.B. Oxidation rate of iron sulfides as affected by surface area, morphology, oxygen concentration, and autotrophic bacteria. *Science* **1984**, *137*, 309–314, doi:10.1097/00010694-198405000-00003.

44. Janzen, M.P.; Nicholson, R. V.; Scharer, J.M. Pyrrhotite reaction kinetics: reaction rates for oxidation by oxygen, ferric iron, and for nonoxidative dissolution. *Geochim. Cosmochim. Acta* **2000**, *64*, 1511–1522, doi:10.1016/S0016-7037(99)00421-4.

45. Luther, G.W. Pyrite oxidation and reduction: molecular orbital theory considerations. *Geochim. Cosmochim. Acta* **1987**, *51*, 3193–3199, doi:10.1016/0016-7037(87)90127-X.

46. Meruane, G.; Vargas, T. Bacterial oxidation of ferrous iron by acidithiobacillus ferrooxidans in the pH range 2.5–7.0. *Hydrometallurgy* **2003**, *71*, 149–158, doi:10.1016/S0304-386X(03)00151-8.

47. Nordstrom, D.K. The rate of ferrous iron oxidation in a stream receiving acid mine effluent. In *Selected papers in the hydrologic sciences*; Subitzky, S., Ed.; United States Geological Survey Water-Supply Paper, 1985; Vol. 2270, pp. 113–119.

48. Edwards, K.J.; Bond, P.L.; Banfield, J.F. Characteristics of attachment and growth of thiobacillus caldus on sulphide minerals: a chemotactic response to sulphur minerals? *Environ. Microbiol.* **2000**, *2*, 324–332, doi:10.1046/j.1462-2920.2000.00111.x.

49. Stoner, D.L.; Miller, K.S.; Fife, D.J.; Larsen, E.D.; Tolle, C.R.; Johnson, J.A. Use of an intelligent control system to evaluate multiparametric effects on iron oxidation by thermophilic bacteria. *Appl. Environ. Microbiol.* **1998**, *64*, 4555–4565, doi:10.1128/aem.64.11.4555-4565.1998.

50. Edwards, K.J.; Schrenk, M.O.; Hamers, R.; Banfield, J.F. Microbial oxidation of pyrite; experiments using microorganisms from an extreme acidic environment. *Am. Mineral.* **1998**, *83*, 1444–1453, doi:10.2138/am-1998-11-1233.

51. Sand, W. Ferric iron reduction by thiobacillus ferrooxidans at extremely low pH-values. *Biogeochemistry* **1989**, *7*, 195–201, doi:10.1007/BF00004217.

52. Nordstrom, D.K.; Southam, G. Geomicrobiology of sulfide mineral oxidation. In *Geomicrobiology: interactions between microbes and minerals*; Banfield, J.F., Nealson, K.H., Eds.; Reviews in Mineralogy. Min. Soc. Am.: Washington, DC, USA, 1997; Vol. 35, pp. 361-390. ISBN 9781501509247.

53. Silverman, M.P.; Ehrlich, H.L. Microbial formation and degradation of minerals. *Adv. Appl. Microbiol.* **1964**, *6*, 153–206, doi:10.1016/S0065-2164(08)70626-9.

54. Sand, W.; Gehrke, T.; Jozsa, P.G.; Schippers, A. (Bio)chemistry of bacterial leaching - direct vs. indirect bioleaching. *Hydrometallurgy* **2001**, *59*, 159–175, doi:10.1016/S0304-386X(00)00180-8.

55. Tributsch, H. Direct versus indirect bioleaching. *Hydrometallurgy* **2001**, *59*, 177–185, doi:10.1016/S0304-386X(00)00181-X.

56. Boon, M.; Heijnen, J.J. Chemical oxidation kinetics of pyrite in bioleaching processes. *Hydrometallurgy* **1998**, *48*, 27–41, doi:10.1016/S0304-386X(97)00072-8.

57. Fowler, T.A.; Holmes, P.R.; Crundwell, F.K. Mechanism of pyrite dissolution in the presence of thiobacillus ferrooxidans. *Appl. Environ. Microbiol.* **1999**, *65*, 2987–2993, doi:10.1128/aem.65.7.2987-2993.1999.

58. Vera, M.; Schippers, A.; Sand, W. Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation-part A. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 7529–7541, doi:10.1007/s00253-013-4954-2.

59. Schippers, A.; Rohwerder, T.; Sand, W. Intermediary sulfur compounds in pyrite oxidation: implications for bioleaching and biodepyritization of coal. *Appl. Microbiol. Biotechnol.* **1999**, *52*, 104–110, doi:10.1007/s002530051495.

60. Toniazzo, V.; Mustin, C.; Benoit, R.; Humbert, B.; Berthelin, J. Superficial compounds produced by Fe(III) mineral oxidation as essential reactants for bio-oxidation of pyrite by thiobacillus ferrooxidans. *Cultures* **1999**, *9*, 177–186.

61. Liu, C.; Jia, Y.; Sun, H.; Tan, Q.; Niu, X.; Leng, X.; Ruan, R. Limited role of sessile acidophiles in pyrite oxidation below redox potential of 650 mV. *Sci. Rep.* **2017**, *7*, 5032, doi:10.1038/s41598-017-04420-2.

62. Dong, B.; Jia, Y.; Tan, Q.; Sun, H.; Ruan, R. Contributions of microbial “contact leaching” to pyrite oxidation under different controlled redox potentials. *Minerals* **2020**, *10*, 856, doi:10.3390/min10100856.

63. Sánchez-Andrea, I.; Rodríguez, N.; Amils, R.; Sanz, J.L. Microbial diversity in anaerobic sediments at Río Tinto, a naturally acidic environment with a high heavy metal content. *Appl. Environ. Microbiol.* **2011**, *77*, 6085–6093, doi:10.1128/AEM.00654-11.

64. Johnson, D.B. Biodiversity and ecology of acidophilic microorganisms. *FEMS Microbiol. Ecol.* **1998**, *27*, 307–317, doi:10.1016/S0168-6496(98)00079-8.

65. Hedrich, S.; Schippers, A. Distribution of acidophilic microorganisms in natural and man-

made acidic environments. *Curr. Issues Mol. Biol.* **2020**, *40*, 25–48, doi:10.21775/CIMB.040.025.

66. Kucera, J.; Lochman, J.; Bouchal, P.; Pakostova, E.; Mikulasek, K.; Hedrich, S.; Janiczek, O.; Mandl, M.; Johnson, D.B. A model of aerobic and anaerobic metabolism of hydrogen in the extremophile acidithiobacillus ferrooxidans. *Front. Microbiol.* **2020**, *11*, 610836, doi:10.3389/fmicb.2020.610836.

67. Bridge, T.A.M.; Johnson, D.B. Reduction of soluble iron and reductive dissolution of ferric iron- containing minerals by moderately thermophilic iron-oxidizing bacteria. *Appl. Environ. Microbiol.* **1998**, *64*, 2181–2186, doi:10.1128/aem.64.6.2181-2186.1998.

68. Johnson, D.B. Acidophilic microbial communities: candidates for bioremediation of acidic mine effluents. *Int. Biodeterior. Biodegrad.* **1995**, *35*, 41–58, doi:10.1016/0964-8305(95)00065-D.

69. Johnson, D.B.; McGinness, S. Ferric iron reduction by acidophilic heterotrophic bacteria. *Appl. Environ. Microbiol.* **1991**, *57*, 207–211, doi:10.1128/aem.57.1.207-211.1991.

70. González-Toril, E.; Aguilera, Á. Microbial ecology in extreme acidic environments: use of molecular tools. In *Microbial Diversity in the Genomic Era*; Elsevier, 2019; pp. 227–238 ISBN 9780128148501.

71. Borilova, S.; Mandl, M.; Zeman, J.; Kucera, J.; Pakostova, E.; Janiczek, O.; Tuovinen, O.H. Can sulfate be the first dominant aqueous sulfur species formed in the oxidation of pyrite by acidithiobacillus ferrooxidans? *Front. Microbiol.* **2018**, *9*, 3134, doi:10.3389/fmicb.2018.03134.

72. Osorio, H.; Mangold, S.; Denis, Y.; Ñancucheo, I.; Esparza, M.; Johnson, D.B.; Bonnefoy, V.; Dopson, M.; Holmesa, D.S. Anaerobic sulfur metabolism coupled to dissimilatory iron reduction in the extremophile acidithiobacillus ferrooxidans. *Appl. Environ. Microbiol.* **2013**, *79*, 2172–2181, doi:10.1128/AEM.03057-12.

73. Mardanov, A. V.; Panova, I.A.; Beletsky, A. V.; Avakyan, M.R.; Kadnikov, V. V.; Antsiferov, D. V.; Banks, D.; Frank, Y.A.; Pimenov, N. V.; Ravin, N. V.; et al. Genomic insights into a new acidophilic, copper-resistant desulfosporosinus isolate from the oxidized tailings area of an abandoned gold mine. *FEMS Microbiol. Ecol.* **2016**, *92*, 1–14, doi:10.1093/femsec/fiw111.

74. Sela-Adler, M.; Ronen, Z.; Herut, B.; Antler, G.; Vigderovich, H.; Eckert, W.; Sivan, O. Co-existence of methanogenesis and sulfate reduction with common substrates in sulfate-rich estuarine sediments. *Front. Microbiol.* **2017**, *8*, 1–11, doi:10.3389/fmicb.2017.00766.

75. Blowes, D.W.; Ptacek, C.J.; Frind, E.O.; Johnson, R.H.; Robertson, W.D.; Molson, J.W. Acid-neutralization reactions in inactive mine tailings impoundments and their effect on the transport of dissolved metals. *J. Am. Soc. Min. Reclam.* **1994**, *1*, 429–438, doi:10.21000/JASMR94010429.

76. Sherlock, E.J.; Lawrence, R.W.; Poulin, R. On the neutralization of acid rock drainage by

carbonate and silicate minerals. *Environ. Geol.* **1995**, *25*, 43–54, doi:10.1007/BF01061829.

77. Strömberg, B.; Banwart, S. Weathering kinetics of waste rock from the Aitik copper mine, Sweden: scale dependent rate factors and pH controls in large column experiments. *J. Contam. Hydrol.* **1999**, *39*, 59–89, doi:10.1016/S0169-7722(99)00031-5.

78. Karlsson, T.; Räisänen, M.L.; Lehtonen, M.; Alakangas, L. Comparison of static and mineralogical ARD prediction methods in the Nordic environment. *Environ. Monit. Assess.* **2018**, *190*, doi:10.1007/s10661-018-7096-2.

79. Maest, A.S.; Nordstrom, D.K. A geochemical examination of humidity cell tests. *Appl. Geochemistry* **2017**, *81*, 109–131, doi:10.1016/j.apgeochem.2017.03.016.

80. US Environmental Protection Agency. Technical document acid mine drainage prediction 1994, EPA 530-R-94-036.

81. Kwong, Y.T. *Prediction and prevention of acid rock drainage from a geological and mineralogical perspective, MEND, Project 1.32.1.*; Canmet, Ottawa, Canada, 1993;

82. Dold, B. Acid rock drainage prediction: a critical review. *J. Geochemical Explor.* **2017**, *172*, 120–132, doi:10.1016/j.gexplo.2016.09.014.

83. Lüttge, A.; Conrad, P.G. Direct observation of microbial inhibition of calcite dissolution. *Appl. Environ. Microbiol.* **2004**, *70*, 1627–1632, doi:10.1128/AEM.70.3.1627-1632.2004.

84. Lüttge, A.; Zhang, L.; Nealson, K.H. Mineral surfaces and their implications for microbial attachment: results from Monte Carlo simulations and direct surface observations. *Am. J. Sci.* **2005**, *305*, 766–790, doi:10.2475/ajs.305.6-8.766.

85. Parbhakar-Fox, A.; Lottermoser, B.G. A critical review of acid rock drainage prediction methods and practices. *Miner. Eng.* **2015**, *82*, 107–124, doi:10.1016/j.mineng.2015.03.015.

86. Becker, M.; Dyantyi, N.; Broadhurst, J.L.; Harrison, S.T.L.; Franzidis, J.-P. A mineralogical approach to evaluating laboratory scale acid rock drainage characterisation tests. *Miner. Eng.* **2015**, *80*, 33–36, doi:10.1016/j.mineng.2015.06.015.

87. Luce, R.W.; Bartlett, R.W.; Parks, G.A. Dissolution kinetics of magnesium silicates. *Geochim. Cosmochim. Acta* **1972**, *36*, 35–50, doi:10.1016/0016-7037(72)90119-6.

88. Miller, S.D.; Stewart, W.S.; Rusdinar, Y.; Schumann, R.E.; Ciccarelli, J.M.; Li, J.; Smart, R.S.C. Methods for estimation of long-term non-carbonate neutralisation of acid rock drainage. *Sci. Total Environ.* **2010**, *408*, 2129–2135, doi:10.1016/j.scitotenv.2010.01.011.

89. McClelland, J.E. The effect of time, temperature, and particle size on the release of bases from some common soil-forming minerals of different crystal structure. *Soil Sci. Soc. Proc.* **1950**, *15*, 301–307, doi:10.2136/sssaj1951.036159950015000c0069x.

90. Huang, W.H.; Keller, W.D. Dissolution of rock-forming silicate minerals in organic acids:

simulated first-stage weathering of fresh mineral surfaces. *Am. Mineral.* **1970**, *55*, 2076–2094.

91. Malmström, M.; Banwart, S. Biotite dissolution at 25°C: the pH dependence of dissolution rate and stoichiometry. *Geochim. Cosmochim. Acta* **1997**, *61*, 2779–2799, doi:10.1016/S0016-7037(97)00093-8.

92. Ye, L.; Wang, L.; Jing, C. Biotransformation of adsorbed arsenic on iron minerals by coexisting arsenate-reducing and arsenite-oxidizing bacteria. *Environ. Pollut.* **2020**, *256*, 113471, doi:10.1016/j.envpol.2019.113471.

93. White, A.F.; Bullen, T.D.; Schulz, M.S.; Blum, A.E.; Huntington, T.G.; Peters, N.E. Differential rates of feldspar weathering in granitic regoliths. *Geochim. Cosmochim. Acta* **2001**, *65*, 847–869, doi:10.1016/S0016-7037(00)00577-9.

94. Blackmore, S.; Vriens, B.; Sorensen, M.; Power, I.M.; Smith, L.; Hallam, S.J.; Mayer, K.U.; Beckie, R.D. Microbial and geochemical controls on waste rock weathering and drainage quality. *Sci. Total Environ.* **2018**, *640–641*, 1004–1014, doi:10.1016/j.scitotenv.2018.05.374.

95. Bennett, P.C.; Rogers, J.R.; Choi, W.J.; Hiebert, F.K. Silicates, silicate weathering, and microbial ecology. *Geomicrobiol. J.* **2001**, *18*, 3–19, doi:10.1080/01490450151079734.

96. Ivanova, E.; Chizhikova, N. Degradative crystal–chemical transformations of clay minerals under the influence of cyanobacterium-actinomycetal symbiotic associations. *Eurasian J. Soil Sci.* **2014**, *3*, 116, doi:10.18393/ejss.79975.

97. Samuels, T.; Bryce, C.; Landenmark, H.; Marie-Loudon, C.; Nicholson, N.; Stevens, A.H.; Cockell, C. Microbial weathering of minerals and rocks in natural environments. In *Biogeochemical Cycles: Ecological Drivers and Environmental Impact.*; American Geophysical Union (AGU), 2020; pp. 59–79 ISBN 9781119413332.

98. Fomina, M.; Skorochod, I. Microbial interaction with clay minerals and its environmental and biotechnological implications. *Minerals* **2020**, *10*, 861, doi:10.3390/min10100861.

99. Ahmed, E.; Holmström, S.J.M. Microbe-mineral interactions: the impact of surface attachment on mineral weathering and element selectivity by microorganisms. *Chem. Geol.* **2015**, *403*, 13–23, doi:10.1016/j.chemgeo.2015.03.009.

100. Balland, C.; Poszwa, A.; Leyval, C.; Mustin, C. Dissolution rates of phyllosilicates as a function of bacterial metabolic diversity. *Geochim. Cosmochim. Acta* **2010**, *74*, 5478–5493, doi:10.1016/j.gca.2010.06.022.

101. Uroz, S.; Calvaruso, C.; Turpault, M.P.; Frey-Klett, P. Mineral weathering by bacteria: ecology, actors and mechanisms. *Trends Microbiol.* **2009**, *17*, 378–387, doi:10.1016/j.tim.2009.05.004.

102. Stranghoener, M.; Schippers, A.; Dultz, S.; Behrens, H. Experimental microbial alteration and Fe mobilization from basaltic rocks of the ICDP HSDP2 drill core, Hilo, Hawaii. *Front.*

Microbiol. **2018**, *9*, 1252, doi:10.3389/fmicb.2018.01252.

103. Kalinowski, B.E.; Liermann, L.J.; Givens, S.; Brantley, S.L. Rates of bacteria-promoted solubilization of Fe from minerals: a review of problems and approaches. *Chem. Geol.* **2000**, *169*, 357–370, doi:10.1016/S0009-2541(00)00214-X.

104. Hutchens, E. Microbial selectivity on mineral surfaces: Possible implications for weathering processes. *Fungal Biol. Rev.* **2009**, *23*, 115–121, doi:10.1016/j.fbr.2009.10.002.

105. Vandevivere, P.; Welch, S.A.; Ullman, W.J.; Kirchman, D.L. Enhanced dissolution of silicate minerals by bacteria at near-neutral pH. *Microb. Ecol.* **1994**, *27*, 241–251, doi:10.1007/BF00182408.

106. Rogers, J.R.; Bennett, P.C.; Choi, W.J. Feldspars as a source of nutrients for microorganisms. *Am. Mineral.* **1998**, *83*, 1532–1540, doi:10.2138/am-1998-11-1241.

107. Bonneville, S.; Morgan, D.J.; Schmalenberger, A.; Bray, A.; Brown, A.; Banwart, S.A.; Benning, L.G. Tree-mycorrhiza symbiosis accelerate mineral weathering: evidences from nanometer-scale elemental fluxes at the hypha-mineral interface. *Geochim. Cosmochim. Acta* **2011**, *75*, 6988–7005, doi:10.1016/j.gca.2011.08.041.

108. Bonneville, S.; Smits, M.M.; Brown, A.; Harrington, J.; Leake, J.R.; Brydson, R.; Benning, L.G. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology* **2009**, *37*, 615–618, doi:10.1130/G25699A.1.

109. Bennett, P.C.; Hiebert, F.K.; Choi, W.J. Microbial colonization and weathering of silicates in a petroleum-contaminated groundwater. *Chem. Geol.* **1996**, *132*, 45–53, doi:10.1016/s0009-2541(96)00040-x.

110. Roberts, J.A.; Fowle, D.A.; Hughes, B.T.; Kulczycki, E. Attachment behavior of Shewanella putrefaciens onto magnetite under aerobic and anaerobic conditions. *Geomicrobiol. J.* **2006**, *23*, 631–640, doi:10.1080/01490450600964441.

111. Rogers, J.R.; Bennett, P.C. Mineral stimulation of subsurface microorganisms: release of limiting nutrients from silicates. *Chem. Geol.* **2004**, *203*, 91–108, doi:10.1016/j.chemgeo.2003.09.001.

112. Liu, W.; Xu, X.; Wu, X.; Yang, Q.; Luo, Y.; Christie, P. Decomposition of silicate minerals by bacillus mucilaginosus in liquid culture. *Environ. Geochem. Health* **2006**, *28*, 133–140, doi:10.1007/s10653-005-9022-0.

113. Hoffland, E.; Kuyper, T.W.; Wallander, H.; Plassard, C.; Gorbushina, A.A.; Haselwandter, K.; Holmström, S.; Landeweert, R.; Lundström, U.S.; Rosling, A.; et al. The role of fungi in weathering. *Front. Ecol. Environ.* **2004**, *2*, 258–264, doi:https://doi.org/10.1890/1540-9295(2004)002[0258:TROFIW]2.0.CO;2.

114. Welch, S.A.; Ullman, W.J. The effect of microbial glucose metabolism on bytownite feldspar dissolution rates between 5° and 35°C. *Geochim. Cosmochim. Acta* **1999**, *63*,

3247–3259, doi:10.1016/S0016-7037(99)00248-3.

115. Bigham, J.M.; Nordstrom, D.K. Iron and aluminum hydroxysulfates from acid sulfate waters. *Rev. Mineral. Geochemistry* **2000**, *40*, 351–403, doi:10.2138/rmg.2000.40.7.

116. Dutrizac, J.E.; Jambor, J.L. Jarosites and their application in hydrometallurgy. *Rev. Mineral. Geochemistry* **2000**, *40*, 405–452, doi:10.2138/rmg.2000.40.8.

117. Dold, B. Evolution of acid mine drainage formation in sulphidic mine tailings. *Minerals* **2014**, *4*, 621–641, doi:10.3390/min4030621.

118. Kocourková, E.; Sracek, O.; Houzar, S.; Cempírek, J.; Losos, Z.; Filip, J.; Hršelová, P. Geochemical and mineralogical control on the mobility of arsenic in a waste rock pile at Dlouhá Ves, Czech Republic. *J. Geochemical Explor.* **2011**, *110*, 61–73, doi:10.1016/j.gexplo.2011.02.009.

119. Lindsay, M.B.J.; Moncur, M.C.; Bain, J.G.; Jambor, J.L.; Ptacek, C.J.; Blowes, D.W. Geochemical and mineralogical aspects of sulfide mine tailings. *Appl. Geochemistry* **2015**, *57*, 157–177, doi:10.1016/j.apgeochem.2015.01.009.

120. Cravotta, C.A.I. Secondary iron-sulfate minerals as sources of sulfate and acidity. In *Environmental geochemistry of sulfide oxidation*; Alpers, C.N., Blowes, D.W., Eds.; American Chemical Society: Washington, DC, USA, 1994; pp. 345–364.

121. Harris, D.L.; Lottermoser, B.G.; Duchesne, J. Ephemeral acid mine drainage at the Montalbion silver mine, north Queensland. *Aust. J. Earth Sci.* **2003**, *50*, 797–809, doi:10.1111/j.1440-0952.2003.01029.x.

122. Sáinz, A.; Grande, J.A.; De La Torre, M.L.; Sánchez-Rodas, D. Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. *J. Environ. Manage.* **2002**, *64*, 345–353, doi:10.1006/jema.2001.0497.

123. Douglas, S.; Beveridge, T.J. Mineral formation by bacteria in natural microbial communities. *FEMS Microbiol. Ecol.* **1998**, *26*, 79–88, doi:10.1016/S0168-6496(98)00027-0.

124. Bigham, J.M.; Schwertmann, U.; Traina, S.J.; Winland, R.L.; Wolf, M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* **1996**, *60*, 2111–2121, doi:10.1016/0016-7037(96)00091-9.

125. Walker, S.R.; Parsons, M.B.; Jamieson, H.E.; Lanzirotti, A. Arsenic mineralogy of near-surface tailings and soils: influences on arsenic mobility and bioaccessibility in the Nova Scotia gold mining districts. *Can. Mineral.* **2009**, *47*, 533–556, doi:10.3749/canmin.47.3.533.

126. Xie, Y.; Lu, G.; Yang, C.; Qu, L.; Chen, M.; Guo, C.; Dang, Z. Mineralogical characteristics of sediments and heavy metal mobilization along a river watershed affected by acid mine drainage. *PLoS One* **2018**, *13*, e0190010, doi:10.1371/journal.pone.0190010.

127. Yu, J.Y.; Heo, B.; Choi, I.K.; Cho, J.P.; Chang, H.W. Apparent solubilities of schwertmannite

and ferrihydrite in natural stream waters polluted by mine drainage. *Geochim. Cosmochim. Acta* **1999**, *63*, 3407–3416, doi:10.1016/S0016-7037(99)00261-6.

128. Nordstrom, D.K.; Plummer, L.N.; Langmuir, D.; Busenberg, E.; May, H.M.; Jones, B.F.; Parkhurst, D.L. Revised chemical equilibrium data for major water—mineral reactions and their limitations. In *Chemical modeling of aqueous systems II*; Bassett, R.L., Melchior, D.C., Eds.; ACS Symposium Series 416: Washington, DC, USA, 1990; Vol. 416, pp. 398–413.

129. Baron, D.; Palmer, C.D. Solubility of jarosite at 4-35°C. *Geochim. Cosmochim. Acta* **1996**, *60*, 185–195, doi:10.1016/0016-7037(95)00392-4.

130. Acero, P.; Ayora, C.; Torrentó, C.; Nieto, J.M. The behavior of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. *Geochim. Cosmochim. Acta* **2006**, *70*, 4130–4139, doi:10.1016/j.gca.2006.06.1367.

131. Burton, E.D.; Bush, R.T.; Sullivan, L.A.; Mitchell, D.R.G. Schwertmannite transformation to goethite via the Fe(II) pathway: reaction rates and implications for iron-sulfide formation. *Geochim. Cosmochim. Acta* **2008**, *72*, 4551–4564, doi:10.1016/j.gca.2008.06.019.

132. Liu, H.; Li, P.; Zhu, M.; Wei, Y.; Sun, Y. Fe(II)-induced transformation from ferrihydrite to lepidocrocite and goethite. *J. Solid State Chem.* **2007**, *180*, 2121–2128, doi:10.1016/j.jssc.2007.03.022.

133. Fortin, D.; Langley, S. Formation and occurrence of biogenic iron-rich minerals. *Earth-Science Rev.* **2005**, *72*, 1–19, doi:10.1016/j.earscirev.2005.03.002.

134. Huang, S.; Zhou, L. Fe^{2+} oxidation rate drastically affect the formation and phase of secondary iron hydroxysulfate mineral occurred in acid mine drainage. *Mater. Sci. Eng. C* **2012**, *32*, 916–921, doi:10.1016/j.msec.2012.02.012.

135. Zhu, J.; Gan, M.; Zhang, D.; Hu, Y.; Chai, L. The nature of schwertmannite and jarosite mediated by two strains of acidithiobacillus ferrooxidans with different ferrous oxidation ability. *Mater. Sci. Eng. C* **2013**, *33*, 2679–2685, doi:10.1016/j.msec.2013.02.026.

136. Hedrich, S.; Lünsdorf, H.; Kleeberg, R.; Heide, G.; Seifert, J.; Schlömann, M. Schwertmannite formation adjacent to bacterial cells in a mine water treatment plant and in pure cultures of ferrovum myxofaciens. *Environ. Sci. Technol.* **2011**, *45*, 7685–7692, doi:10.1021/es201564g.

137. Tischler, J.S.; Wiacek, C.; Janneck, E.; Schlömann, M. Microbial abundance in the schwertmannite formed in a mine water treatment plant. *Mine Water Environ.* **2013**, *32*, 258–265, doi:10.1007/s10230-013-0250-8.

138. Feng, K.; Wang, X.; Zhou, B.; Xu, M.; Liang, J.; Zhou, L. Hydroxyl, Fe^{2+}, and acidithiobacillus ferrooxidans jointly determined the crystal growth and morphology of schwertmannite in a sulfate-rich acidic environment. *ACS Omega* **2021**, *6*, 3194–3201, doi:10.1021/acsomega.0c05606.

139. O'Loughlin, E.J.; Gorski, C.A.; Flynn, T.M.; Scherer, M.M. Electron donor utilization and secondary mineral formation during the bioreduction of lepidocrocite by shewanella putrefaciens CN32. *Minerals* **2019**, *9*, 434, doi:10.3390/min9070434.

140. O'Reilly, S.E.; Watkins, J.; Furukawa, Y. Secondary mineral formation associated with respiration of nontronite, NAu-1 by iron reducing bacteria. *Geochem. Trans.* **2005**, *6*, 67–76, doi:10.1063/1.2084787.

141. Bayliss, P.; Kolitsch, U.; Nickel, E.H.; Pring, A. Alunite supergroup: recommended nomenclature. *Mineral. Mag.* **2010**, *74*, 919–927, doi:10.1180/minmag.2010.074.5.919.

142. Qian, G.; Fan, R.; Short, M.D.; Schumann, R.C.; Li, J.; Li, Y.; Smart, R.S.C.; Gerson, A.R. Evaluation of the rate of dissolution of secondary sulfate minerals for effective acid and metalliferous drainage mitigation. *Chem. Geol.* **2019**, *504*, 14–27, doi:10.1016/j.chemgeo.2018.12.003.

143. Jones, F. Crystallization of jarosite with variable Al^{3+} content: the transition to alunite. *Minerals* **2017**, *7*, 90, doi:10.3390/min7060090.

144. Potter-McIntyre, S.L.; McCollom, T.M. Jarosite and alunite in ancient terrestrial sedimentary rocks: reinterpreting martian depositional and diagenetic environmental conditions. *Life* **2018**, *8*, 32, doi:10.3390/life8030032.

145. Wray, R.A.L. Alunite formation within silica stalactites from the Sydney Region, South-Eastern Australia. *Int. J. Speleol.* **2011**, *40*, 109–116, doi:10.5038/1827-806X.40.2.3.

146. Nazari, B.; Jorjani, E.; Hani, H.; Manafi, Z.; Riahi, A. Formation of jarosite and its effect on important ions for acidithiobacillus ferrooxidans bacteria. *Trans. Nonferrous Met. Soc. China* **2014**, *24*, 1152–1160, doi:10.1016/S1003-6326(14)63174-5.

147. Dockrey, J.W.; Lindsay, M.B.J.; Mayer, K.U.; Beckie, R.D.; Norlund, K.L.I.; Warren, L.A.; Southam, G. Acidic microenvironments in waste rock characterized by neutral drainage: bacteria–mineral interactions at sulfide surfaces. *Minerals* **2014**, *4*, 170–190, doi:10.3390/min4010170.

148. Fortin, D.; Davis, B.; Southam, G.; Beveridge, T.J. Biogeochemical phenomena induced by bacteria within sulfidic mine tailings. *J. Ind. Microbiol.* **1995**, *14*, 178–185, doi:10.1007/BF01569901.

149. Castro, L.; Blázquez, M.L.; González, F.; Muñoz, J.A.; Ballester, A. Anaerobic bioreduction of jarosites and biofilm formation by a natural microbial consortium. *Minerals* **2019**, *9*, 81, doi:10.3390/min9020081.

150. Antelo, J.; Fiol, S.; Gondar, D.; Pérez, C.; López, R.; Arce, F. Cu(II) incorporation to schwertmannite: effect on stability and reactivity under AMD conditions. *Geochim. Cosmochim. Acta* **2013**, *119*, 149–163, doi:10.1016/j.gca.2013.05.029.

151. Maillot, F.; Morin, G.; Juillot, F.; Bruneel, O.; Casiot, C.; Ona-Nguema, G.; Wang, Y.; Lebrun, S.; Aubry, E.; Vlaic, G.; et al. Structure and reactivity of As(III)- and As(V)-rich

schwertmannites and amorphous ferric arsenate sulfate from the Carnoulès acid mine drainage, France: comparison with biotic and abiotic model compounds and implications for As remediation. *Geochim. Cosmochim. Acta* **2013**, *104*, 310–329, doi:10.1016/j.gca.2012.11.016.

152. Morin, G.; Calas, G. Arsenic in soils, mine tailings, and former industrial sites. *Elements* **2006**, *2*, 97–101, doi:10.2113/gselements.2.2.97.

153. Peterson, R.C. The relationship between Cu content and distortion in the atomic structure of melanterite from the Richmond mine, Iron Mountain, California. *Can. Mineral.* **2003**, *41*, 937–949, doi:10.2113/gscanmin.41.4.937.

154. Martínez, C.E.; McBride, M.B. Cd, Cu, Pb, and Zn coprecipitates in Fe oxide formed at different pH: aging effects on metal solubility and extractability by citrate. *Environ. Toxicol. Chem.* **2001**, *20*, 122–126, doi:10.1002/etc.5620200112.

155. Fitzpatrick, R.W.; Mosley, L.M.; Raven, M.D.; Shand, P. Schwertmannite formation and properties in acidic drain environments following exposure and oxidation of acid sulfate soils in irrigation areas during extreme drought. *Geoderma* **2017**, *308*, 235–251, doi:10.1016/j.geoderma.2017.08.012.

156. Paikaray, S.; Göttlicher, J.; Peiffer, S. Removal of As(III) from acidic waters using schwertmannite: surface speciation and effect of synthesis pathway. *Chem. Geol.* **2011**, *283*, 134–142, doi:10.1016/j.chemgeo.2010.08.011.

157. Paikaray, S.; Göttlicher, J.; Peiffer, S. As(III) retention kinetics, equilibrium and redox stability on biosynthesized schwertmannite and its fate and control on schwertmannite stability on acidic (pH 3.0) aqueous exposure. *Chemosphere* **2012**, *86*, 557–564, doi:10.1016/j.chemosphere.2011.07.055.

158. Peak, D.; Sparks, D.L. Mechanisms of selenate adsorption on iron oxides and hydroxides. *Environ. Sci. Technol.* **2002**, *36*, 1460–1466, doi:10.1021/es0156643.

159. Wijnja, H.; Schulthess, C.P. Vibrational spectroscopy study of selenate and sulfate adsorption mechanisms on Fe and Al (hydr)oxide surfaces. *J. Colloid Interface Sci.* **2000**, *229*, 286–297, doi:10.1006/jcis.2000.6960.

160. Xu, Z.; Lçš, B.; Wu, J.; Zhou, L.; Lan, Y. Reduction of Cr(VI) facilitated by biogenetic jarosite and analysis of its influencing factors with response surface methodology. *Mater. Sci. Eng. C* **2013**, *33*, 3723–3729, doi:10.1016/j.msec.2013.05.006.

161. Zhou, P.; Li, Y.; Shen, Y.; Lan, Y.; Zhou, L. Facilitating role of biogenetic schwertmannite in the reduction of Cr(VI) by sulfide and its mechanism. *J. Hazard. Mater.* **2012**, *237–238*, 194–198, doi:10.1016/j.jhazmat.2012.08.024.

162. Baker-Austin, C.; Dopson, M.; Wexler, M.; Sawers, R.G.; Stemmler, A.; Rosen, B.P.; Bond, P.L. Extreme arsenic resistance by the acidophilic archaeon “ferroplasma acidarmanus” Fer1. *Extremophiles* **2007**, *11*, 425–434, doi:10.1007/s00792-006-0052-z.

163. Banerjee, P.C. Genetics of metal resistance in acidophilic prokaryotes of acidic mine environments. *Indian J. Exp. Biol.* **2004**, *42*, 9–25.

164. Navarro, C.A.; von Bernath, D.; Jerez, C.A. Heavy metal resistance strategies of acidophilic bacteria and their acquisition: importance for biomining and bioremediation. *Biol. Res.* **2013**, *46*, 363–371, doi:10.4067/S0716-97602013000400008.

165. Dopson, M.; Ossandon, F.J.; Lövgren, L.; Holmes, D.S. Metal resistance or tolerance? acidophiles confront high metal loads via both abiotic and biotic mechanisms. *Front. Microbiol.* **2014**, *5*, 10–13, doi:10.3389/fmicb.2014.00157.

166. Churchman, G.J.; Lowe, D.J. Alteration, formation, and occurrence of minerals in soils. In *Handbook of soil sciences. 2nd edition.*; Huang, P.M., Summer, M.E., Eds.; Taylor & Francis: Boca Ratón, FL, 2012; Vol. 1, pp. 29.1–20.72.

167. Claridge, G.G.C.; Campbell, I.B. Mineral transformation during the weathering of dolerite under cold arid conditions in Antarctica. *New Zeal. J. Geol. Geophys.* **1984**, *27*, 537–545, doi:10.1080/00288306.1984.10422271.

168. Lovley, D.R. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol. Rev.* **1991**, *55*, 259–287, doi:10.1016/S0065-2911(04)49005-5.

169. Wielinga, B.; Lucy, J.K.; Moore, J.N.; Seastone, O.F.; Gannon, J.E. Microbiological and geochemical characterization of fluvially deposited sulfidic mine tailings. *Appl. Environ. Microbiol.* **1999**, *65*, 1548–1555, doi:10.1128/aem.65.4.1548-1555.1999.

170. Bao, Y.; Guo, C.; Lu, G.; Yi, X.; Wang, H.; Dang, Z. Role of microbial activity in Fe(III) hydroxysulfate mineral transformations in an acid mine drainage-impacted site from the Dabaoshan Mine. *Sci. Total Environ.* **2018**, *616–617*, 647–657, doi:10.1016/j.scitotenv.2017.10.273.

171. Ouyang, B.; Lu, X.; Liu, H.; Li, J.; Zhu, T.; Zhu, X.; Lu, J.; Wang, R. Reduction of jarosite by shewanella oneidensis MR-1 and secondary mineralization. *Geochim. Cosmochim. Acta* **2014**, *124*, 54–71, doi:10.1016/j.gca.2013.09.020.

172. Paikaray, S.; Peiffer, S. Abiotic schwertmannite transformation kinetics and the role of sorbed As(III). *Appl. Geochemistry* **2012**, *27*, 590–597, doi:10.1016/j.apgeochem.2011.12.013.

173. Paikaray, S.; Schröder, C.; Peiffer, S. Schwertmannite stability in anoxic Fe(II)-rich aqueous solution. *Geochim. Cosmochim. Acta* **2017**, *217*, 292–305, doi:10.1016/j.gca.2017.08.026.

174. Burton, E.D.; Johnston, S.G.; Watling, K.; Bush, R.T.; Keene, A.F.; Sullivan, L.A. Arsenic effects and behavior in association with the Fe(II)-catalyzed transformation of schwertmannite. *Environ. Sci. Technol.* **2010**, *44*, 2016–2021, doi:10.1021/es903424h.

175. Fan, C.; Guo, C.; Zeng, Y.; Tu, Z.; Ji, Y.; Reinfelder, J.R.; Chen, M.; Huang, W.; Lu, G.; Yi, X.; et al. The behavior of chromium and arsenic associated with redox transformation of

schwertmannite in AMD environment. *Chemosphere* **2019**, *222*, 945–953, doi:10.1016/j.chemosphere.2019.01.142.

176. Karn, S.K.; Pan, X.; Jenkinson, I.R. Bio-transformation and stabilization of arsenic (As) in contaminated soil using arsenic oxidizing bacteria and $FeCl_3$ amendment. *3 Biotech* **2017**, *7*, 50, doi:10.1007/s13205-017-0681-1.

177. Johnston, S.G.; Burton, E.D.; Keene, A.F.; Planer-Friedrich, B.; Voegelin, A.; Blackford, M.G.; Lumpkin, G.R. Arsenic mobilization and iron transformations during sulfidization of As(V)-bearing jarosite. *Chem. Geol.* **2012**, *334*, 9–24, doi:10.1016/j.chemgeo.2012.09.045.

178. Vithana, C.L.; Sullivan, L.A.; Burton, E.D.; Bush, R.T. Stability of schwertmannite and jarosite in an acidic landscape: prolonged field incubation. *Geoderma* **2015**, *239*, 47–57, doi:10.1016/j.geoderma.2014.09.022.

179. Thomasarrigo, L.K.; Bouchet, S.; Kaegi, R.; Kretzschmar, R. Organic matter influences transformation products of ferrihydrite exposed to sulfide. *Environ. Sci. Nano* **2020**, *7*, 3405–3418, doi:10.1039/d0en00398k.

180. Zeng, Y.; Wang, H.; Guo, C.; Wan, J.; Fan, C.; Reinfelder, J.R.; Lu, G.; Wu, F.; Huang, W.; Dang, Z. Schwertmannite transformation via direct or indirect electron transfer by a sulfate reducing enrichment culture. *Environ. Pollut.* **2018**, *242*, 738–748, doi:10.1016/j.envpol.2018.07.024.

181. Drewniak, L.; Sklodowska, A. Arsenic-transforming microbes and their role in biomining processes. *Environ. Sci. Pollut. Res.* **2013**, *20*, 7728–7739, doi:10.1007/s11356-012-1449-0.

182. Courchesne, B.; Schindler, M.; Mykytczuk, N.C.S. Relationships between the microbial composition and the geochemistry and mineralogy of the cobalt-bearing legacy mine tailings in northeastern Ontario. *Front. Microbiol.* **2021**, *12*, 660190, doi:10.3389/fmicb.2021.660190.

183. Huang, L.N.; Zhou, W.H.; Hallberg, K.B.; Wan, C.Y.; Li, J.; Shu, W.S. Spatial and temporal analysis of the microbial community in the tailings of a Pb-Zn mine generating acidic drainage. *Appl. Environ. Microbiol.* **2011**, *77*, 5540–5544, doi:10.1128/AEM.02458-10.

184. Londry, K.L.; Sherriff, B.L. Comparison of microbial biomass, biodiversity, and biogeochemistry in three contrasting gold mine tailings deposits. *Geomicrobiol. J.* **2005**, *22*, 237–247, doi:10.1080/01490450590947797.

185. Rosario, K.; Iverson, S.L.; Henderson, D.A.; Chartrand, S.; McKeon, C.; Glenn, E.P.; Maier, R.M. Bacterial community changes during plant establishment at the San Pedro river mine tailings site. *J. Environ. Qual.* **2007**, *36*, 1249–1259, doi:10.2134/jeq2006.0315.

186. Schippers, A.; Jozsa, P.G.; Sand, W.; Kovacs, Z.M.; Jelea, M. Microbiological pyrite oxidation in a mine tailings heap and its relevance to the death of vegetation. *Geomicrobiol. J.* **2000**, *17*, 151–162, doi:10.1080/01490450050023827.

187. Johnson, D.B.; Hallberg, K.B. Acid mine drainage remediation options: a review. *Sci. Total Environ.* **2005**, *338*, 3–14, doi:10.1016/j.scitotenv.2004.09.002.

188. Ayangbenro, A.S.; Olanrewaju, O.S.; Babalola, O.O. Sulfate-reducing bacteria as an effective tool for sustainable acid mine bioremediation. *Front. Microbiol.* **2018**, *9*, 1–10, doi:10.3389/fmicb.2018.01986.

189. Malki, M.; González-Toril, E.; Sanz, J.L.; Gómez, F.; Rodríguez, N.; Amils, R. Importance of the iron cycle in biohydrometallurgy. *Hydrometallurgy* **2006**, *83*, 223–228, doi:10.1016/j.hydromet.2006.03.053.

190. Martinez, P.; Vera, M.; Bobadilla-Fazzini, R.A. Omics on bioleaching: current and future impacts. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 8337–8350, doi:10.1007/s00253-015-6903-8.

191. Phyo, A.K.; Jia, Y.; Tan, Q.; Sun, H.; Liu, Y.; Dong, B.; Ruan, R. Competitive growth of sulfate-reducing bacteria with bioleaching acidophiles for bioremediation of heap bioleaching residue. *Int. J. Environ. Res. Public Health* **2020**, *17*, 2715, doi:10.3390/ijerph17082715.