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Review

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

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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

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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].

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 the 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, such 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 and ferric iron reduction (Figure 1). Moreover, due to microbial oxygen consumption and pyrite dissolution, some typically aerobic species can be induced to grow anaerobically and use anaerobic sulfur oxidation as part of their metabolic activities. The synergy of the microbial communities controls flows of iron, sulfur, and carbon in AMD systems [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 ranged 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] (Figure 2). 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. [23] concluded that Fe(III) oxidized the majority of the sulfur intermediate species on pyrite surfaces at the Richmond Mine, which explains the much lower abundance of the sulfur-oxidizing microorganisms compared with the iron-oxidizers.

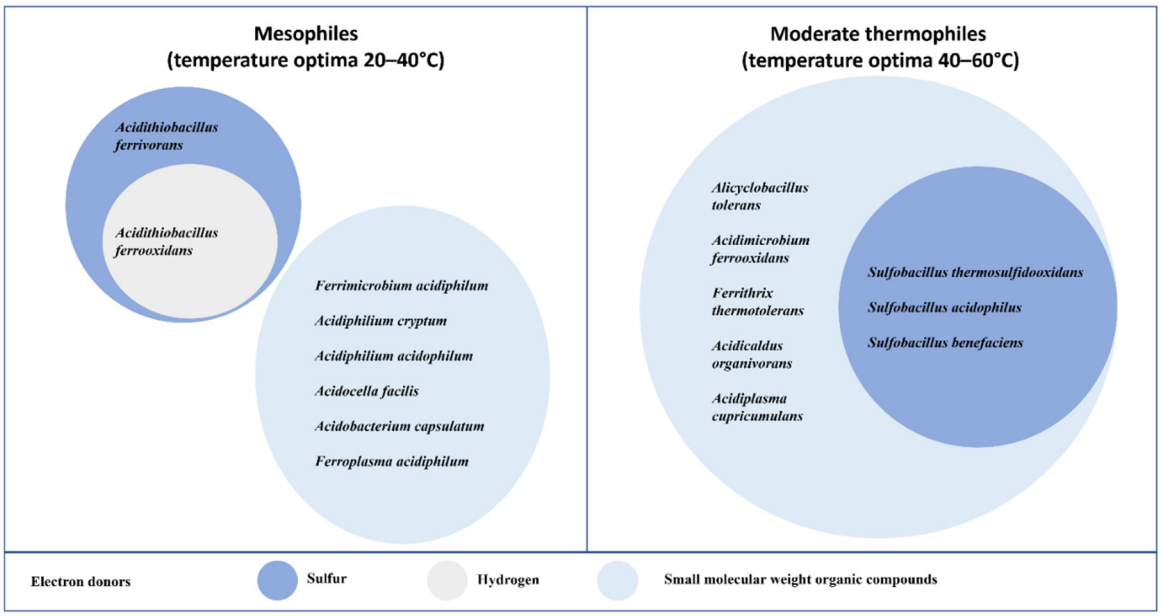


Figure 1. Acidophilic microorganisms catalyzing the dissimilatory reduction of ferric iron to ferrous. Adapted with permission from Johnson [28], published by Springer Netherlands, 2010.

Major factors influencing the size, composition, and activities of microbial communities include mineralogy and 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 affect 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 mod-

erately 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.

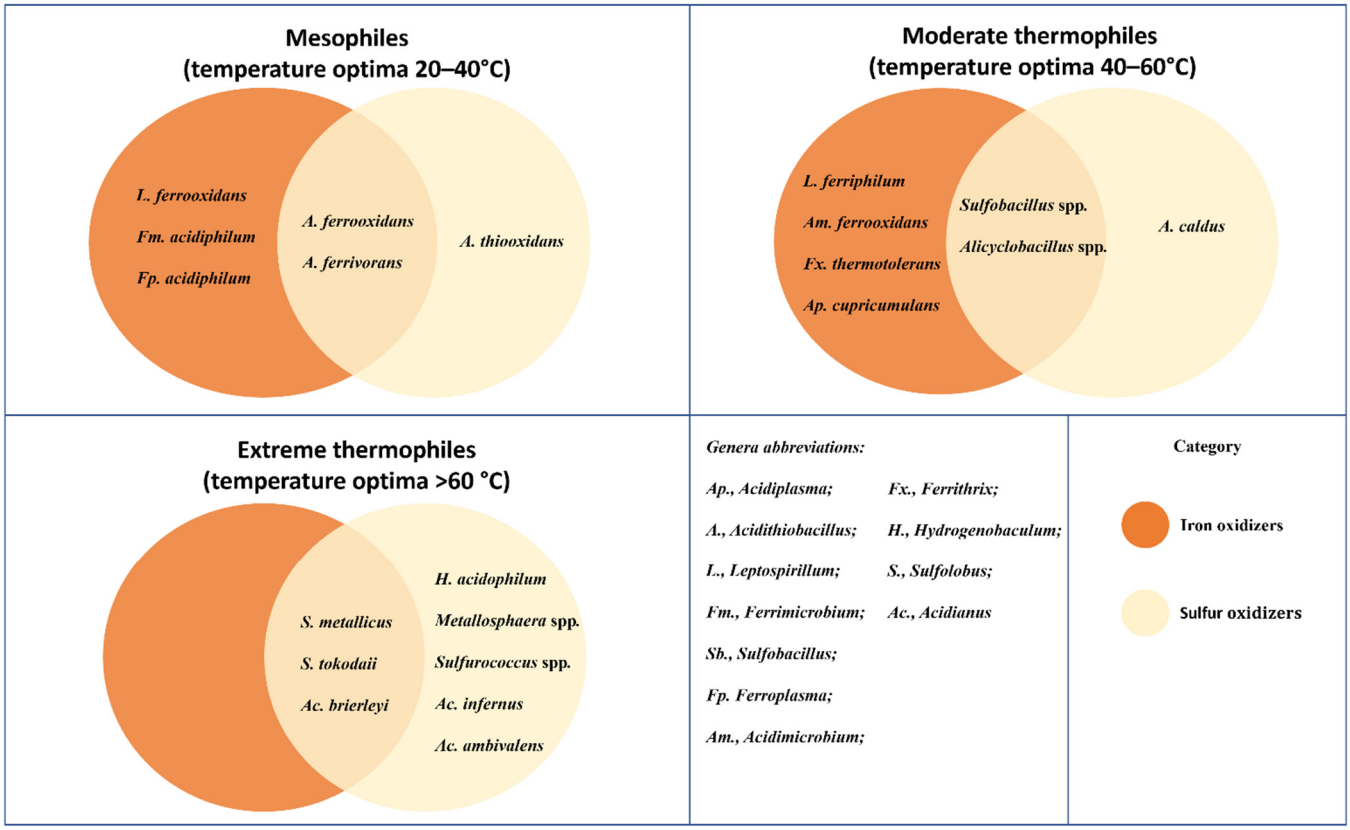


Figure 2. Acidophilic iron and sulfur-oxidizing microorganisms classified based on growth temperature optima. Adapted with permission from Johnson [28], published by Springer Netherlands, 2010.

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 Equation (1). The Fe(II) ions released are then oxidized by oxygen to Fe(III) via Equation (2). Ferric(III), under acidic conditions, is an important oxidant for most sulfide minerals. Pyrite oxidation by Fe(III) is shown in Equation (3). Another example is the oxidation of an iron-rich sphalerite by Fe(III) (Equation (4)), which is the main reason for elevated zinc concentrations in some mine drainage [41].

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \quad (1)$$

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

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

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

The rate of sulfide oxidation is influenced by the type of sulfides, its crystal structure, and the type of oxidant. Pyrrhotite oxidizes much faster than pyrite. Nicholson and Scharer [42] found that the rate of pyrrhotite oxidation by oxygen ranged from 6 to 14 $\times$ 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 $\times$ 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 $\times$ 10^{-10} to 6.3 $\times$ 10^{-7} mol·m^{-2}·s^{-1} by ferric and in the range of 2.9 $\times$ 10^{-11} to 3.3 $\times$ 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 (Equation (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 $\times$ 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 $\times$ 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 $\times$ 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) *A. ferrooxidans* (pH < 1.0, 42 °C) and concluded that the oxidation rate was approximately equivalent in both enrichments, the value being 2 $\times$ 10^{-14} g Fe(II) per min per bacterial cell. It has been found that pH inhibits the ferrous iron-oxidizing system of *A. 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 refers to 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 illustrates an example of a geomicrobiological model showing the role of microorganisms in the iron, sulfur and carbon cycling found in the natural acidic drainage environment of The Tinto River. While autotrophic iron-oxidizers use Fe(II) as a main source of energy, different heterotrophic and mixotrophic microorganisms (e.g., *Acidiphilium* spp., *Sulfobacillus* spp., *Acidobacterium* spp., and *Alicyclobacillus* spp.) can reduce Fe(III) with organic matter as the electron donor [63–65]. Under anoxic conditions, some iron-oxidizing microorganisms, such as *A. 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].

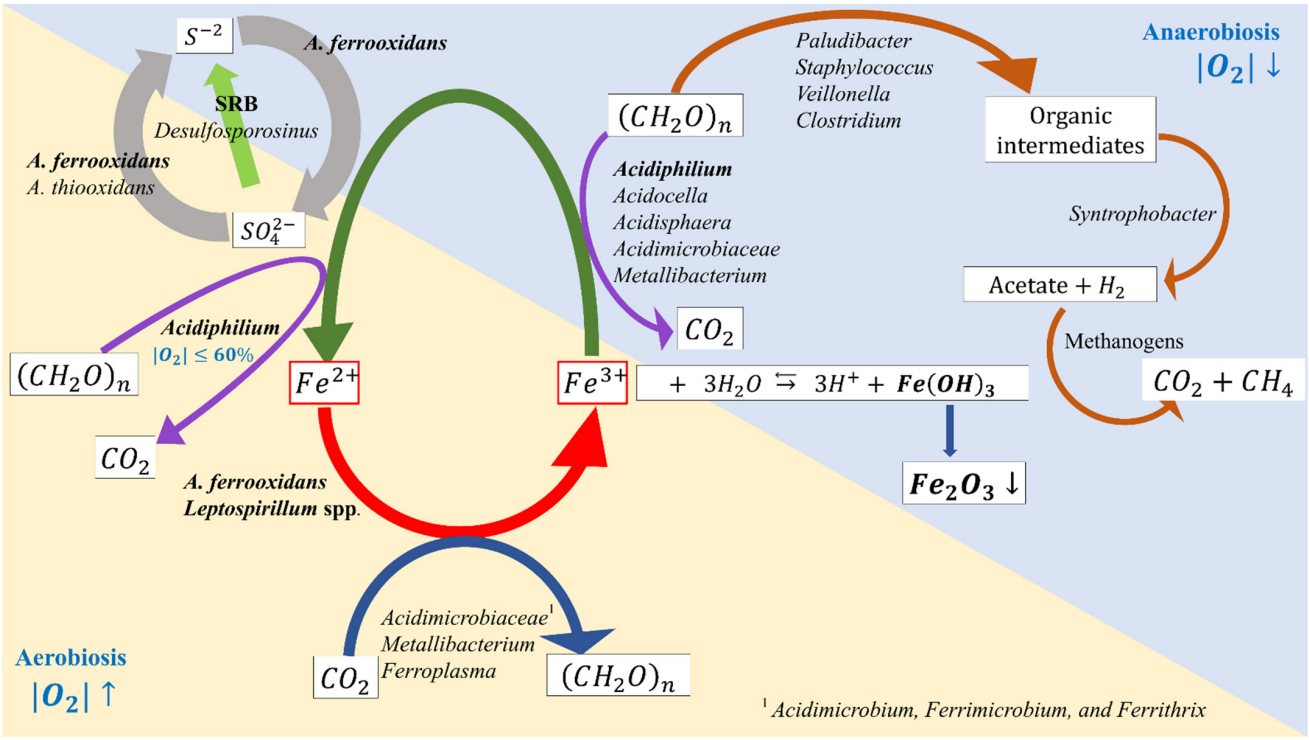


Figure 3. Geomicrobiological model of the role of microorganisms in iron, sulfur and carbon cycling in the natural acidic drainage environment of The Tinto River. *A. ferroxidans, Acidiphilium*, and *Leptospirillum* spp., represented in bold type are the microorganisms with the highest relative cell density in the model. Iron-oxidizing microorganisms participate in ferrous iron oxidation to ferric (blue and red arrow) represented by: *A. ferrooxidans*, *Leptospirillum* spp. *Acidimicrobiaceae* (*Acidimicrobium*, *Ferrimicrobium*, and *Ferrithrix*), *Metallibacterium*, and *Ferroplasma*. Iron-reducing microorganisms contribute towards ferric iron reduction to ferrous (purple arrow) and include: *Acidiphilium*, *Acidisphaera*, *Acidimicrobiaceae*, and *Metallibacterium*. SRB: sulfur-reducing microorganisms (e.g., *Desulfosporosinus*) participate in the sulfur reduction metabolic pathway. Sulfur-oxidizing microorganisms are represented by: *A. ferrooxidans* and *A. thiooxidans*. Microorganisms participating in microbial fermentation and respiration as part of carbon cycle (brown arrows) include: *Paludibacter*, *Staphylococcus*, *Veillonella*, *Clostridium*, *Synthrobacter*, and methanogens. Image adapted with permission from [70], published by Elsevier Inc, 2019.

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 mi-

croorganisms, 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 the mine permitting process, the design of 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 in which acid generation is not expected, but later developed, such as the 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 the 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 silicates (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 Equation (5), which provides neutralization potential [88].

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

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 play 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, and 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].

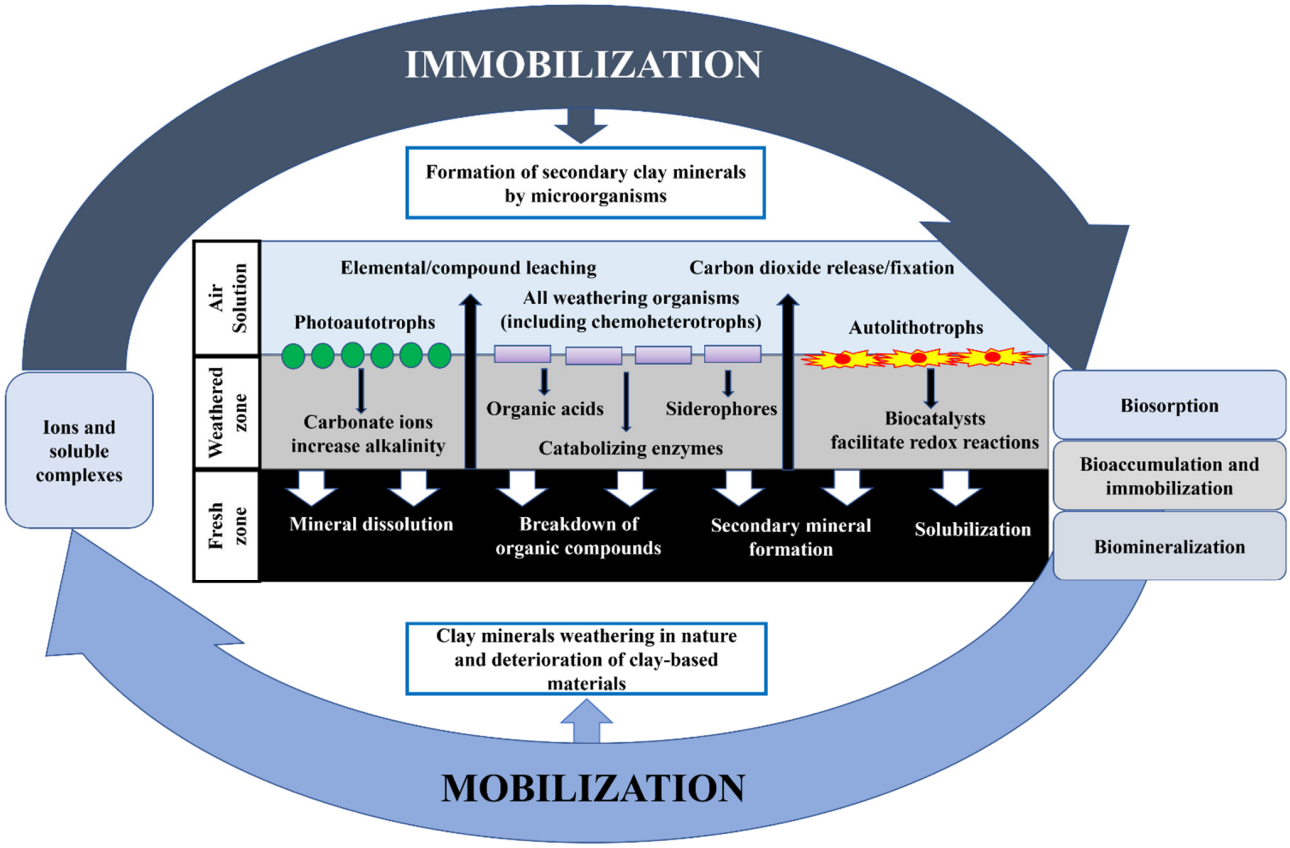


Figure 4. Diagram of biogeochemical processes involved in the transformation of clay minerals and weathering mechanisms on geological substrates. Images adapted from [97,98].

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 is 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 microorganisms 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 to 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 tends to release protons, sulfate, and a diversity of metal cations into the 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 ($Fe^{II}SO_4 \cdot 7H_2O$) (Equation (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 (Equation (6)), 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 (Equation (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].

$$FeS_2 + 3.5O_2 + 8H_2O = FeSO_4 \cdot 7H_2O + H_2SO_4 \quad (6)$$

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

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 Equation (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) (Equation (9)) generates acid, and the hydrolysis of SO_4^{2-} (Equation (10)) provides the buffering capacity. The equilibrium constants for Equations (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 the generation of acidity [41].

$$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O \quad (8)$$

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

$$SO_4^{2-} + H_2O = HSO_4^{-} + OH^{-} \quad (10)$$

The dissolution of melanterite is considered as the initiator of the so-called "propagation cycle", which 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 (Equation (11)) is accelerated by the hydrolysis of ferric and the flocculation of colloidal ferric. This oxidative dissolution reaction generates acid, which may decrease the pH to a level at which soluble ferric ions are available for pyrite oxidation. Pyrite oxidation generates acid, resulting in a further decrease of pH in the system. The creation of an acidic environment provides essential conditions for the growth of different acidophiles [15]. The presence of these microorganisms further accelerate pyrite oxidation and may serve as nucleation sites for the formation of secondary minerals [123].

$$FeSO_4 \cdot 7H_2O + 0.25O_2 = Fe(OH)_3 + H_2SO_4 + 4.5H_2O \quad (11)$$

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 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 $4.5 \leq x \leq 6$, $1.0 \leq y \leq 1.75$, and $8 - x = 2y$. The dissolution reaction and the solubility product K are shown as Equations (12) and (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 Equations (14) and (15).

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

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

$$FeOOH + 3H^+ = Fe^{3+} + 2H_2O \quad (14)$$

$$\log K = \log a_{Fe}{}^{3+} + 3pH \quad (15)$$

By comparing solubility products 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 Equation (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].

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

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 the 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 the weathering of clay minerals [9].

The formation of alunite and jarosite releases acid (Equations (17) and (18)). Their subsequent dissolution may further release latent acid depending on pH (Equations (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].

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

$$3Al^{3+} + K^+ + 2SO_4{}^{2-} + 6H_2O = KAl_3(SO_4)_2(OH)_6 + 6H^+ \quad (18)$$

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

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

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 *A. 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, and 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 acidophilic heterotrophs have one or more plasmids containing the genetic elements that encode metal-resistance (e.g., *Acidiphilium* and *Acidocella*).

For most chemolithoautotrophic and mixotrophic microorganisms, metal resistance is encoded by chromosomes and not by plasmids [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 Mediated by Microorganisms

Iron(II)-oxidizing and iron(III)-reducing microorganisms play important roles in the transformation of secondary minerals. On the one hand, iron(II)-oxidizing microorganisms participate in Fe(II) oxidation, leading to the precipitation of Fe(III) phases; on the other hand, iron(III)-reducing microorganisms use ferric as the electron acceptor and transform Fe(III)-bearing minerals to Fe(II) or Fe(II)-Fe(III) minerals [166]. Different in-situ experiments and characterization methods with isolated bacterial strains have been designed to elucidate the mechanisms of mineral transformation and the role of microorganisms [167].

Vithana et al. [168] proposed that the transformation of secondary minerals was driven by dissimilatory microbial reduction and Fe(II)-catalyzed conversion of schwertmannite and jarosite to goethite. The conditions that favor the transformation are anoxic, reducing, circumneutral, and rich in organic carbon [168]. Even in sulfidic mine rock and drainage environments often characterized by very low biodiversity [24], Bao et al. [169] 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 [170]. 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; indirect electron transfer by producing endogenous electron shuttles and Fe(III) complexing agents, e.g., quinones or siderophores [171]. Neal et al. [171] found that near-surface structure affected the initial cell attachment to iron oxide surfaces by electrostatic interactions [172]. The crystallinity of iron minerals has been reported to influence the rate of transformation, with more amorphous forms being more prone to be transformed than the less amorphous forms [169,173]. 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].

Anaerobic Fe(III)-reducing and aerobic Fe(II)-oxidizing bacteria are the most widely understood, but it has been increasingly appreciated that bacteria also facilitate oxidation of Fe(II) under anaerobic conditions [174]. Under anoxic conditions, two main pathways in which Fe(II) is oxidized have been identified [174]: (1) anoxygenic photosynthesis (Equation (21)) [175]; and (2) nitrate-dependent ferrous oxidation (Equation (22)) [176].

$$4Fe^{2+} + HCO_3^- + 10H_2O + hv = 4Fe(OH)_3 + CH_2O + 7H^+ \quad (21)$$

$$10Fe^{2+} + 2NO_3^- + 24H_2O = 10Fe(OH)_3 + N_2 + 18H^+ \quad (22)$$

Photoferrotrophy is the process in which reduced iron is used as an electron donor and light as an energy source by anoxygenic phototrophs to fix inorganic carbon into organic matter, leading to the formation of a different ferric iron phase [177]. Posth et al. [178] found that during anoxygenic phototrophic Fe(II) oxidation goethite was formed when a low concentration of phosphate (~40 μM) was present in the dissolved Fe(II) medium, whereas poorly ordered ferrihydrite was produced in the presence of a high concentration of phosphate (4.4 mM) and amorphous Fe(II) minerals. This was attributed to the initial

presence of phosphate at high concentrations, blocking the mineral surface and thus preventing the mineral transformation to goethite.

Nitrate-dependent ferrous oxidation is an anaerobic pathway in which nitrate is used as an electron acceptor [179]. Mejia et al. [180] observed a decrease in Fe(II) oxidation in the redox cycling of nitrate and the consequent lack of availability of Fe(III) for iron (III)-reducing bacteria. In this case, magnetite was the main product generated from the reduction of both lepidocrocite and ferrihydrite. On the other hand, aerobic conditions favor oxidation of Fe(II), promoting the formation of lepidocrocite and ferrihydrite. A wide diversity of minerals, including lepidocrocite, goethite, and Fe phosphate, have been found encrusting the periplasm of *Acidovorax* sp., a Fe(II) oxidizing nitrate-dependent bacteria [181]. The types of Fe-bearing phases formed depend on pH, Fe(II) precursor (solid or dissolved), and the type and concentration of the organic substrate [181].

6.3. Release of Toxic Elements during Secondary Mineral Transformation

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 [182]. Major factors that could influence secondary mineral transformation include chemical weathering, temperature, salt concentration around mineral grains, and microbial activities [183]. The release of trace elements, as demonstrated with goethite and hematite, depends on pH and mineral stability [184]. In addition, complexation, redox, and precipitation reactions play significant roles in facilitating the mobility and release of toxic elements [185]. Toxic elements can also be mobilized by advection without abiotic or microbial net iron reduction [184]. 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 [24,186,187]. Schwertmannite and jarosite are transformed to goethite by microorganisms in the presence of organic carbon, promoting the mobility of heavy metals [169,188]. For example, *Clostridium* sp. solubilizes Cd, Ni, Pb, and Zn elements that have coprecipitated with goethite via either direct action, i.e., enzymatic reduction of Fe(III) iron or indirect action resulting from metabolic products [189]. 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 [190,191]. Burton et al. [192] 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 [193]. 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 [92,194]. Arsenate co-precipitated with jarosite may be mobilized when jarosite encounters sulfide ions and undergoes the sulfidization process [195]. Metal-reducing microorganisms were found to participate in the reduction of Cr(VI) to Cr(III), most likely as a detoxification mechanism [21].

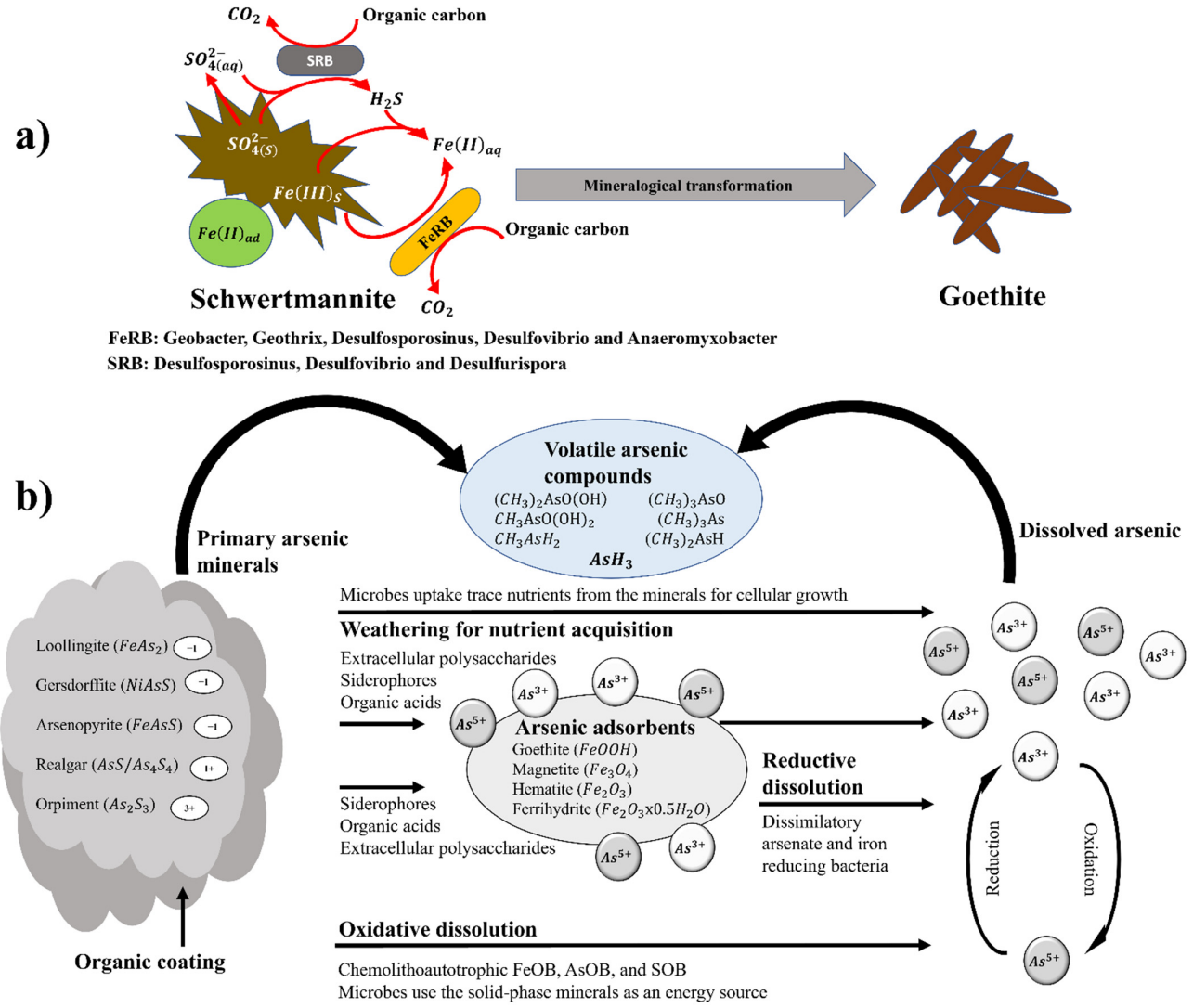


Figure 5. (**a**) Role of microorganisms in the transformation of schwertmannite to goethite. SRB: sulfur-reducing microorganisms; FeRB: iron-reducing microorganisms. Image adapted with permission from [169], published by Elsevier B.V., 2018; (**b**) Role of microorganisms in the mobilization of arsenic in mining environments. FeOB: iron-oxidizing microorganisms; AsOB: arsenic-oxidizing microorganisms; and SOB: sulfur-oxidizing microorganisms. Image adapted from [196].

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 [197]. 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 *A. ferrooxidans* and *Leptospirillum* spp. being consistently present in the acidic tailings and acidophilic archaea, mostly *Fp. acidiphilum*, being predominant in the oxidized zones [198]. (2) Act as a performance indicator of the remediation efforts. In phytoremediation, increases in autotrophic iron and sulfur oxidizing microorganisms were indicative of generation of acid drainage and vegetation death; on the other hand, increases in neutrophilic heterotrophic microbes were used as an indicator

of the establishment of plants [199–201]. (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 [202]. 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 [203]. 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; (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 [204]. 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 [205]. Microbial cell surfaces are largely negatively charged with functional groups, such as hydroxyl, carboxyl, and phosphoryl, that can directly adsorb metal cations, which can potentially be used for bioremediation [206]. The understanding of iron cycling in the presence of nitrate-dependent microorganisms (e.g., *Shewanella* sp.) may help develop remediation measures for handling water pollution by nitrate [166,207,208].

The formation, dissolution, and transformation of secondary minerals can potentially be studied at the nanoscale by bimodal microscopy, such as helium ion microscopy combined with scanning electron microscopy. These techniques could help elucidate with more precision the different mechanisms by which microorganisms interact with the mineral surfaces [209]. The current knowledge of microbial-mediated transformation of secondary minerals represents a starting point to design in-situ synthetic routes for synthesizing promising materials and nanomaterials. For instance, *Shewanella* sp. HN-41, a dissimilatory iron-reducing bacteria, has been used to produce various nanoscale materials, such as goethite nanowires, which can be further applied in the development of Li-rechargeable battery electrode materials [210]. Moreover, studies of microbial interactions with secondary minerals have facilitated the understanding of the extracellular electron transfer of iron(III)-reducing bacteria [166]. Some iron(III)-reducing bacteria are electroactive (e.g., *Geobacter sulfurreducens*) and therefore can be used to produce electrical current in bioelectrochemical systems. The design of engineered microorganisms and the exploration of electroactive iron(III)-reducing bacteria in natural biogeochemical environments can potentially be used to generate electricity (microbial fuel cells) or produce hydrogen and methane (microbial electrolysis cells) [211].

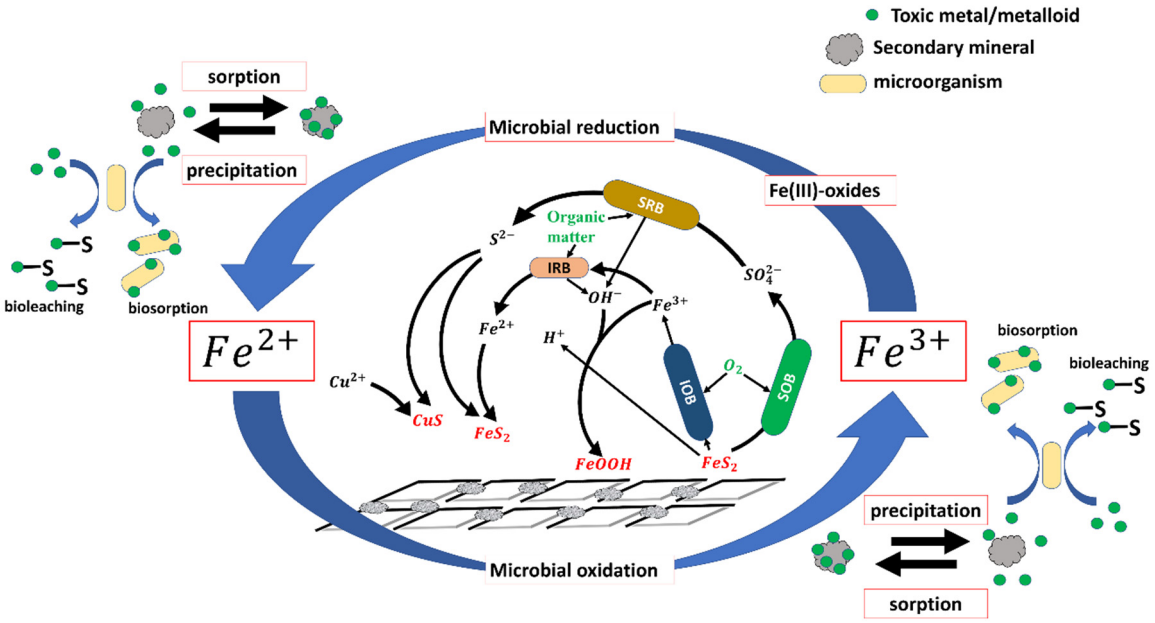


Figure 6. Schematic of the role of microorganisms in the bioremediation of pyritic mine rock. Adapted from [212]. SOB: sulfur-oxidizing microorganisms; IOB: iron-oxidizing microorganisms; IRB: iron-reducing microorganisms; SRB: sulfur-reducing microorganisms.

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