



# What Do We Really Know about the Role of Microorganisms in Iron Sulfide Mineral Formation?

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Iron sulfide mineralization in low-temperature systems is a result of biotic and abiotic processes, though the delineation between these two modes of formation is not always straightforward. Here we review the role of microorganisms in the precipitation of extracellular iron sulfide minerals. We summarize the evidence that links sulfur-metabolizing microorganisms and sulfide minerals in nature and we present a critical overview of laboratory-based studies of the nucleation and growth of iron sulfide minerals in microbial cultures. We discuss whether biologically derived minerals are distinguishable from abiotic minerals, possessing attributes that are uniquely diagnostic of biomineralization. These inquiries have revealed the need for additional thorough, mechanistic and high-resolution studies to understand microbially mediated formation of a variety of sulfide minerals across a range of natural environments.

**Keywords:** iron sulfide mineral, biomineralization, pyrite, mackinawite, greigite, microbial sulfate reduction, microbial sulfur disproportionation, sulfate-reducing prokaryotes

## CO-OCCURENCE OF MICROORGANISMS AND SULFIDE MINERALS IN NATURE

Throughout Earth's history the burial of solid phases of Fe and S has controlled the redox state of Earth's surface environments (Berner, 1984). While iron is one of the most abundant elements on Earth, sulfur represents <1% of the Earth by mass (Allègre et al., 1995), although its importance to life and earth systems is greater than its abundance would suggest. Though the sulfur cycle was the first elemental cycle to be studied (Beijerinck, 1895), research on sulfur biogeochemistry is far from complete, and novel aspects of sulfur's transformations on Earth are still being discovered (Canfield et al., 2010). In Earth's biosphere, sulfur may be gaseous (e.g., sulfur dioxide), dissolved (e.g., sulfide, polysulfides, thiosulfate, sulfite, or sulfate) or solid (e.g., metal sulfides, elemental sulfur). Much of the interest in sulfur is due to its redox versatility—from sulfide (−2) to sulfate (+6), with numerous redox transformations possible in between (Zopfi et al., 2004). Microorganisms can take advantage of this diversity of oxidation states for energy conservation, which can be achieved by: (1) coupling the oxidation of organic compounds or dihydrogen to the reduction of oxidized organic and inorganic sulfur compounds (e.g., dimethyl sulfoxide, sulfate, elemental sulfur, and thiosulfate) (Widdel and Bak, 1992; Rabus et al., 2013); (2) disproportionating elemental sulfur, thiosulfate and sulfite (Bak and Pfennig, 1987; Thamdrup et al., 1993); and (3) oxidizing organosulfur compounds, hydrogen sulfide, sulfur, sulfite, and thiosulfate chemosynthetically with oxygen and nitrate during respiration, or by anoxygenic photosynthesis (Jørgensen and Nelson, 2004). Sulfate is the dominant sulfur species at 28 mM in

the modern oxic oceans, while reduced sulfur species, including hydrogen sulfide and organosulfur compounds, are often abundant where oxygen is low or absent. In these low-oxygen environments, sulfur and iron can be immobilized in the form of iron sulfide minerals, primarily the iron(II) monosulfide mackinawite (tetragonal FeS), the iron(II,III) sulfide greigite (Fe<sub>3</sub>S<sub>4</sub>), and the iron (II) disulfide pyrite (FeS<sub>2</sub>) (Schoonen, 2004; Rickard, 2012a,c).

Ninety-seven percent of the sulfide produced on Earth is attributable to the activity of sulfate-reducing prokaryotes (SRP) in low-temperature environments (Trudinger et al., 1985; Rickard, 2012b), while the remaining three percent are produced at volcanoes and deep-sea hydrothermal vents (Elderfield and Schultz, 1996; Andres and Kasgnoc, 1998). SRP are present in an enormous diversity of environments including freshwater (Ramamoorthy et al., 2009; Sass et al., 2009), hypersaline (Foti et al., 2007), hydrothermal sediment (Jørgensen et al., 1992), polar (Ravenschlag et al., 2000; Karr et al., 2006), and oceanic crust (Robador et al., 2015) habitats. Although black sulfide precipitates in anoxic sediments are used as an indicator for the presence of SRP, their abundance isn't necessarily linked to large metal sulfide deposits. There are few environmental studies closely linking microbial sulfate-reducing activity and specific sulfide minerals, even though it has been 100 years since the first suggestion that SRP might be responsible for metal sulfide ore formation (Siebenthal, 1915). In the Cu-Zn Kidd Creek Mine, the presence of SRP corresponded to the enrichment of pyrite in the sediments (Fortin and Beveridge, 1997), while in the Zn-Pb Piquette mine, only sphalerite (ZnS) precipitated in a SRP-rich biofilm to the exclusion of other metal sulfides (Labrenz et al., 2000; Druschel et al., 2002; Labrenz and Banfield, 2004). In the Evander Au mine, ZnS rich biofilms were observed in association with pyrite framboids, and the minerals occurred inside organic matrices such as exopolysaccharides (Maclean et al., 2007, 2008). In sediments contaminated by mine tailing drainage, microbial cell surfaces were associated with FeS and NiS (Ferris et al., 1987). In hydrothermal vents, which result in the formation of submarine ores, both metabolically active SRP and dissimilatory sulfite reductase (*dsr*) genes have been found in the outer walls of chimneys and in seafloor massive sulfide deposits, where seawater sulfate is entrained (Nakagawa et al., 2004; Kormas et al., 2006; Frank et al., 2013; Kato et al., 2015). Nonetheless, the role of microorganisms in sulfide mineral formation at vents is considered quantitatively unimportant, due to the abundant abiotic sulfide provided by the vents.

In low-temperature sedimentary marine environments, where microbial sulfate reduction is the most important pathway for organic matter remineralization (Jørgensen, 1982), the biogeochemical cycles of iron and sulfur are intimately linked to carbon cycling (Bernier, 1982). The interactions between extracellular sulfide mineral precipitates and microorganisms are thus of great interest to understand the pathways of organic matter preservation in modern and ancient systems. For example, studies of marine sediments in Aarhus Bay in Denmark found that the highest sulfide production rates are attributed to members of the *Desulfobacteraceae* and that Fe<sub>3</sub>S<sub>4</sub> is most abundant in the sediment just below these communities (Leloup

et al., 2009; Holmkvist et al., 2011). Although the focus of this mini review is on extracellular iron sulfide minerals, it should be noted that some magnetotactic bacteria (MTB) form intracellular iron sulfides ranging in size 35–120 nm, that are contained in bilayer membranes within an organelle called the magnetosome (Lefevre and Bazylinski, 2013). These sulfide-mineral-forming MTB are typically found below the oxic-anoxic interface both in marine and freshwater environments, where sulfide is found in the millimolar range (Farina et al., 1990; Bazylinski et al., 1995; Simmons et al., 2004; Lefevre et al., 2011). The intracellular mineral primarily formed is Fe<sub>3</sub>S<sub>4</sub> (Posfai et al., 2013b), but tetragonal and cubic FeS have also been described as intermediate phases in the formation of greigite (Posfai et al., 1998).

Despite these discoveries in intracellular sulfide biomineralization, the role of microorganisms in the nucleation and growth of extracellular sulfide minerals is still ripe for exploration and explanation. In the next section, we examine the efforts made to understand the potential microbial mechanisms and pathways of sulfide mineral formation through laboratory experiments.

## EXAMINING THE ROLE OF MICROORGANISMS IN EXTRACELLULAR IRON SULFIDE MINERAL FORMATION VIA LABORATORY STUDIES

SRP are the major producers of free sulfide in low-temperature environments, and thus have been the subject of most laboratory studies considering extracellular iron sulfide mineralization. Early studies demonstrated that Fe(II) salts react with sulfide produced in cultures of SRP, forming black precipitates, without further mineralogical characterization (Miller, 1950; Baas Becking and Moore, 1961; Freke and Tate, 1961; Temple and Le Roux, 1964). Later studies used energy-dispersive spectroscopy (EDS) in association with scanning electron microscopy (SEM) to identify the elemental ratios of iron sulfide precipitates (**Table 1**) (Fortin et al., 1994; Herbert et al., 1998; Benning et al., 1999; Donald and Southam, 1999; Li et al., 2004, 2006; Williams et al., 2005; Kim et al., 2015). However, determining mineralogy using EDS only can be contentious, as hydrogen sulfide can potentially adsorb onto iron sulfide aggregates, and thus alter the measured Fe:S ratio of the precipitates. X-ray diffraction (XRD), selected area electron diffraction (SAED), or X-ray absorption spectroscopy (XAS), revealed primarily the formation of mackinawite and greigite in microbial cultures to which Fe has been provided as soluble Fe(II) (**Table 1**) (Rickard, 1969; Herbert et al., 1998; Benning et al., 1999; Watson et al., 2000; Neal et al., 2001; Li et al., 2004; Williams et al., 2005; Gramp et al., 2009, 2010; Zhou et al., 2014). While greigite is typically found as rod-shaped and 100- to 300-nm platelet structures (Herbert et al., 1998; Gramp et al., 2010), mackinawite does not have a specific morphology, and both minerals appear (via XRD and SEM) to be disordered and poorly crystalline and tend to assemble in μm-sized aggregates (Fortin et al., 1994; Herbert et al., 1998; Benning et al., 1999; Watson et al., 2000; Kim et al., 2015). Additionally, using X-ray photoelectron

spectroscopy (XPS), pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ,  $0 < x < 0.2$ ) has been detected in association with mackinawite (Herbert et al., 1998) or at the surface of iron oxides, when these were used in culture medium as a source of iron (Neal et al., 2001). Notably, the formation of pyrite in microbial cultures has been reported only in two instances (Rickard, 1969; Donald and Southam, 1999).

Given the limited variety of isolates investigated in these studies (Table 1), it is unclear if there is a relationship between the type of SRP and the iron sulfide minerals that form in microbial cultures. The mineralogy of iron sulfide minerals seems to differ when Fe is provided as soluble Fe(II) vs. when it is provided as Fe(III) minerals (Rickard, 1969; Neal et al., 2001). Also, in microbial cultures, the crystallinity of iron sulfide minerals, in particular mackinawite and greigite, increases with incubation time (Rickard, 1969; Gramp et al., 2010; Zhou et al., 2014), and with increasing incubation temperature (Gramp et al., 2010). The size of mackinawite crystals decreases when initial pH deviates from the optimal pH for growth of the strain, and the largest crystals form when the sulfide production rates are highest (Zhou et al., 2014). However, to establish whether microorganisms have a more specific role in sulfide mineral nucleation and growth, it is essential to perform control experiments by reacting free sulfide with Fe in the culture medium in the absence of microorganisms. Among the few studies that did such controls, sulfide was not added at concentrations or rates similar to those occurring in microbial cultures (Rickard, 1969; Donald and Southam, 1999; Neal et al., 2001; Li et al., 2004, 2006; Gramp et al., 2010). Based on comparative XRD data for biotic and abiotic control experiments, Rickard (1969) concluded that no differences can be observed between synthetic and biotic mackinawite formed extracellularly in cultures of SRP. However, when pyrite and marcasite formed in cultures, he noted the association of an oil-like material, assumed to derive from the decomposition of cells, with the minerals. Gramp et al. (2010) found no difference in the mineralogy of abiotic vs. biotic metal sulfides, but reported differences in the morphology of the iron sulfide precipitates, suggesting a role of extracellular microbial substances. Finally, Donald and Southam (1999) proposed the involvement of organic sulfur, released during cell autolysis, in the formation of iron sulfide minerals.

Microbial cell walls are highly reactive and have a net negative charge at circumneutral pH, due to deprotonation of organic ligands contained in various polymers, such as peptidoglycan, lipopolysaccharides, teichoic acid, or murein (Beveridge, 1989). They can provide templates for metal binding and/or microenvironments for supersaturation of elements, leading to the nucleation and growth of minerals (Beveridge, 1989). Very few sulfide biomineralization studies have investigated cell-mineral associations (Table 1). Cells appear encrusted in sulfide minerals only in a few cases (Figure 1) (Fortin et al., 1994; Herbert et al., 1998; Donald and Southam, 1999; Watson et al., 2000; Williams et al., 2005). If cells interact with Fe while being metabolically inactive, then soluble Fe(II) could bind to reactive groups at the surface of cells (Figure 1A). Sulfide produced afterwards will then be able to react with iron, forming a crust of extracellular iron sulfides (Figure 1A). The apparent differences observed between Gram + and Gram -

bacteria (Figure 1A) could be explained by variations among cell envelope structure and composition. Alternatively, if Fe is at distance from metabolically active cells, or is provided when cells have already produced sulfide, then iron sulfide minerals could precipitate away from the cells (Figure 1B). The underlying causes of the variability of cell encrustation generally remain to be addressed.

## UNRESOLVED QUESTIONS AND FUTURE DIRECTIONS

If the role of microbes in metal sulfide formation is to be assessed on a broader scale, and with greater depth, the field must use microbial isolates and enrichments whose phylogeny and physiology are well characterized. Future studies should use defined rather than organic-rich and strongly buffered cultivation media, in order to mimic more closely conditions of natural environments. Additionally, while SRP essentially occupy the entire range of temperatures at which life exists, sulfide biomineralization studies have been limited to ambient pressure and temperature conditions. For example, while most sulfide mineral formation in hydrothermal environments is likely abiotically derived, the extent to which thermophilic SRP are involved remains unknown. Studies of other mineral systems suggest additional possibilities for SRP mediated mineral formation (Burns et al., 2000; Braissant et al., 2007; Gallagher et al., 2012; Zammit et al., 2015). For example, the localized microenvironments which result from SRP metabolism cause increases in pH and production of exopolymeric substances (EPS), which have been demonstrated to affect the morphology and mineralogy of carbonate minerals (Braissant et al., 2007). EPS may locally bind metal ions to a number of functional groups such as carboxylic acids, sulfinic or sulfonic acids, or amino acids, and the presence of metal ions in solution may also affect EPS production, resulting in a feedback between soluble metals and EPS binding (Braissant et al., 2007). In addition, SRP are not the only microorganisms that may contribute to metal sulfide mineralization. Sulfur-disproportionating bacteria that can produce sulfide and sulfate from thiosulfate, sulfite (Bak and Pfennig, 1987), or elemental sulfur (Thamdrup et al., 1993), as well as sulfide oxidizing bacteria that can excrete polysulfides (Griesbeck et al., 2000; Prange et al., 2004), both produce reduced sulfur products that may contribute to sulfide mineralization. Iron sulfides, notably pyrite, can indeed form as a result of S(0)-disproportionation in microbial cultures and in marine sediments (Canfield et al., 1998; Finster et al., 1998; Zopfi et al., 2008). Microbially produced organosulfides and even complexation of metals by microbially-produced organic matter may also be relevant, including at conditions where high temperatures preclude direct microbial involvement.

The correct application of methods can aid in resolving the spatial distribution of microorganisms and iron sulfide minerals. The use of bulk methods, like XRD, for mineralogical characterization will remove ambiguities inherent in elemental ratio analyses such as EDS. Besides XRD, Raman spectroscopy is a powerful method for the identification of sulfide minerals

TABLE 1 | Laboratory studies investigating the formation of extracellular Fe sulfide minerals in microbial cultures of sulfate-reducing bacteria.

| Inoculum (origin)   | Type of incubation<br>Culture medium<br>Carbon source<br>Temperature | Metal provided<br>Concentration<br>Fe:S ratio            | Analytical methods<br>(mineralogy and morphology) | Composition, mineralogy and properties of precipitates<br>Morphology of minerals  | Interactions with cells                                   | References                |
|---|--|--|---|---|---|---------------------------|
| <i>Desulfovibrio desulfuricans</i> strain Canet 41            | Batch<br>Mineral medium<br>Lactate<br>30°C                           | Hexagonal green rust 2<br>182 mM<br>S in excess          | XRD   | At pH 6-8: initial precipitate = M<br>At pH 6: 3 m. = G+M, 6 m. = G+M<br>At pH 7: 3 m. = G+M, 6 m. = G<br>At pH 8: 3 m. = M, 6 m. = M, 9 m. = pyrrhotite  | ND  | Rickard, 1969             |
| <i>Desulfovibrio desulfuricans</i> strain Canet 41            | Batch<br>Mineral medium<br>Lactate<br>30°C                           | Goethite<br>NI<br>S in excess                            | XRD   | At pH 6-8: initial precipitate = M<br>At pH 6: 3 m. = marcasite + pyrite, 6 m. = marcasite + pyrite<br>At pH 7: 3 m. = marcasite + pyrite + M, 6 m. = marcasite + pyrite<br>At pH 8: 3 m. = M, 6 m. = pyrite + marcasite<br>Minerals are all fine-grained<br>Pyrite is floating in "oily" phase | ND  | Rickard, 1969             |
| <i>Desulfohalobium</i> sp. strain DF-1 (metal refining plant) | Batch<br>Freshwater medium<br>Tryptone<br>RT                         | Fe(II) sulfate<br>0.1–0.5 g/l<br>S in excess             | TEM-EDS   | FeS aggregates with no specific morphology  | Extensive mineralization of the surface of the cells      | Fortin et al., 1994       |
| Enrichment (aquifer)  | Batch<br>Postgate medium C<br>Lactate + acetate<br>RT                | Fe(II) sulfate<br>18 μM + 1 Fe(0)<br>nail<br>S in excess | SEM-EDS<br>XRD<br>XPS                             | Disordered M (XRD)<br>Potentially G, oxidized M and/or pyrrhotite (XPS)<br>Platy particles (100–300 nm) aggregating in rosettes (1–2 μm)  | No precipitates at the cell surface visible in SEM images | Herbert et al., 1998      |
| Enrichment (sediment)   | Batch<br>Defined medium<br>Lactate<br>25°C                           | Fe(II) sulfate<br>0.5 g/l (1.62 mM)<br>S in excess       | SEM-EDS<br>TEM                                    | Cubic and hexagonal crystals of FeS <sub>2</sub> assigned as pyrite/marcasite (based on EDS data)   | Precipitates at the cell surface                          | Donald and Southern, 1999 |
| <i>Desulfovibrio desulfuricans</i> ATCC 29578                 | Batch<br>Seawater medium<br>Lactate<br>34°C                          | Fe(II)<br><1 mM<br>S in excess                           | SEM-EDS<br>XRD                                    | Aggregates of M and G (15 w)  | No precipitates at the cell surface visible in SEM images | Benning et al., 1999      |

(Continued)

TABLE 1 | Continued

| Inoculum (origin)  | Type of incubation<br>Culture medium<br>Carbon source<br>Temperature             | Metal provided<br>Concentration<br>Fe:S ratio   | Analytical methods<br>(mineralogy and morphology) | Composition, mineralogy and properties of precipitates<br>Morphology of minerals  | Interactions with cells   | References            |
|--|--|---|---|---|---|-----------------------|
| Enrichment ("natural source")                              | Chemostat<br>Dilution rate 0.1<br>h-1<br>Postgate medium<br>C<br>Lactate<br>32°C | Fe<br>"sufficient to maximize the production of iron sulfide"                                 | TEM-SAED<br>XANES<br>EXAFS                        | Very small and irregular particles or clusters of particles of amorphous M and G (strongly magnetic)  | 100-nm thick layer of fine-grained precipitates at the cell surface               | Watson et al., 2000   |
| <i>Desulfovibrio desulfuricans</i> strains G-20 and Essex6 | Batch<br>Postgate medium<br>C<br>Lactate<br>RT                                   | Hematite<br>NI<br>S in excess   | TEM<br>Fluorescence microscopy<br>XRD<br>XPS      | FeS precipitates at the surface of hematite assigned as pyrrhotite  | ND<br>Cells attached to hematite  | Neal et al., 2001     |
| <i>Desulfovibrio</i> sp. strain G-11                       | Batch<br>PHELPS medium<br>Lactate<br>30°C  | Nontronite NAU-2<br>30 mM Fe (mineral)<br>S in excess   | TEM-EDS<br>XRD                                    | Textural and structural alterations of nontronite<br>Aggregates of FeS (mineralogy not characterized), calcium carbonates                                 | No precipitates at the cell surface visible in SEM images                         | Li et al., 2004       |
| <i>Desulfovibrio vulgaris</i>                              | Sand-packed column<br>Anoxic feed solution<br>Lactate<br>RT                      | Fe(II) sulfate<br>360 µM<br>S in excess   | TEM-EDS<br>TEM-SAED<br>Geophysical methods        | M, 3-nm average crystal size forming 10–20 µm aggregates/clusters—phase shift in resistivity and acoustic wave deviation at the site of biomineralization | Sulfide-encrusted cells coating sand grains and cementing the pores of the column | Williams et al., 2005 |
| <i>Desulfovibrio desulfuricans</i> strain G-20             | Batch<br>Caccavo's medium<br>Lactate<br>30°C                                     | Ferrihydrite,<br>goethite, hematite,<br>magnetite   | TEM-EDS   | FeS with no specific morphology   | Mineral precipitates surrounding cells, EPS and Fe oxides                         | Li et al., 2006       |
| Enrichments (acid mine drainage and compost)               | Batch<br>Baar's medium<br>Lactate<br>22, 45, 60°C                                | Fe(II) chloride<br>8.95 mM<br>Fe probably in excess<br>(Sulfate provided as sulfate minerals) | XRD   | At 60°C: (2 w. with schwertmannite, jarosite and gypsum): G   | ND  | Gramp et al., 2009    |

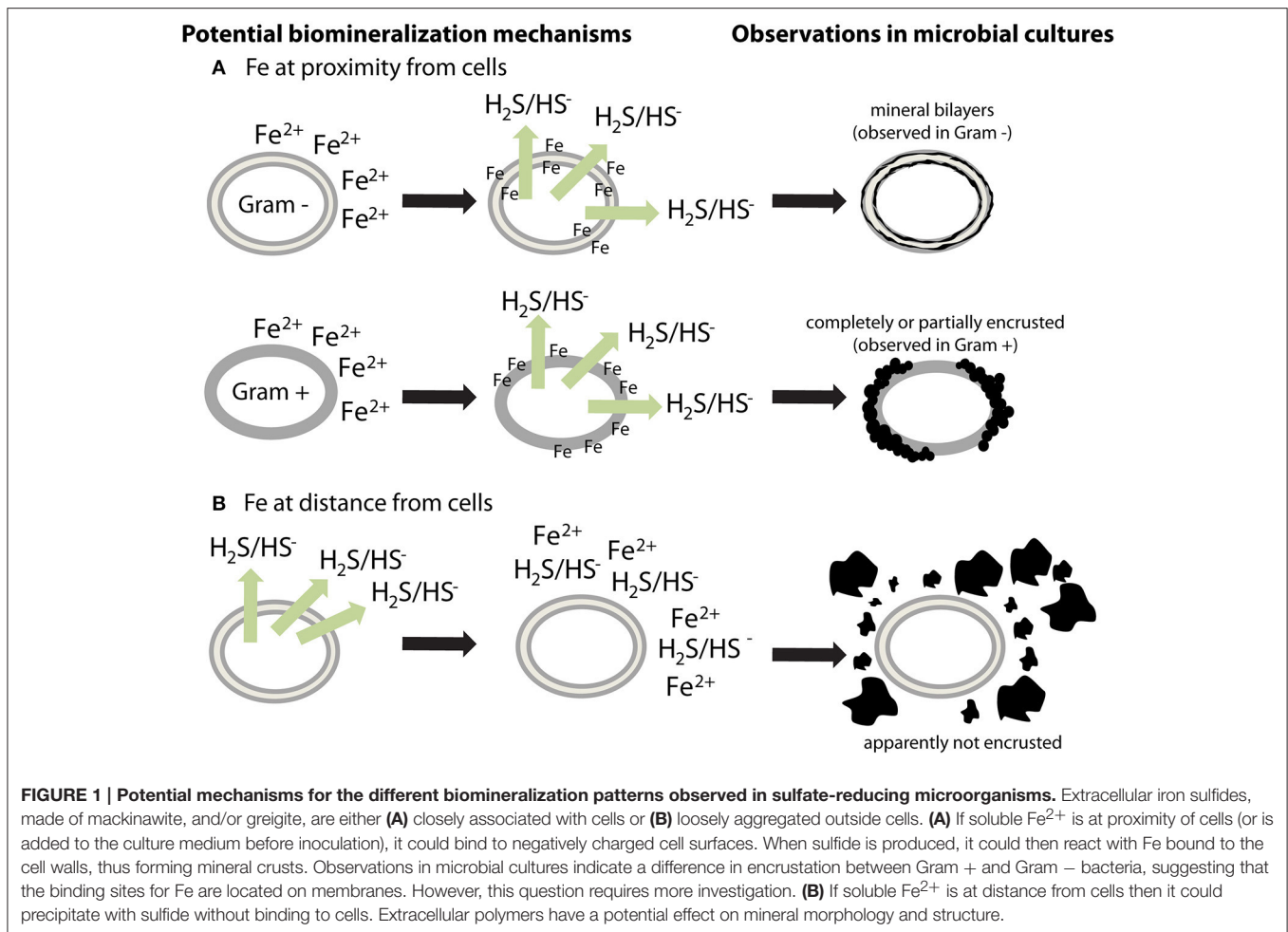
(Continued)

TABLE 1 | Continued

| Inoculum (origin)  | Type of incubation<br>Culture medium<br>Carbon source<br>Temperature | Metal provided<br>Concentration<br>Fe:S ratio  | Analytical methods<br>(mineralogy and morphology) | Composition, mineralogy and properties of precipitates<br>Morphology of minerals  | Interactions with cells | References         |
|--|--|--|---|---|-------------------------|--------------------|
| Enrichments (acid mine drainage and compost)   | Batch<br>Baat's medium<br>Lactate<br>22, 45 and 60°C                 | Fe(II) chloride<br>Variable to adjust to the Fe:S ratios<br>1:0.5, 1:0.65,<br>1:1.3, 1:3.25,<br>1:10, 1:20 and<br>1:50 | XRD<br>SEM  | M at 22°C<br>M and G at 45 and 60°C<br>Disordered morphology for both M and G<br>Fine particles of M without specific pattern, rod-shaped aggregates and encrusted platelet structures of G | ND                      | Gramp et al., 2010 |
| <i>Desulfovibrio vulgaris</i>  | Batch<br>ATCC 1249<br>medium<br>Lactate<br>30°C                      | Fe(II) ammonium sulfate<br>3.5 mM<br>S in excess   | XRD   | Crystalline M, G when sulfide is in excess  | ND                      | Zhou et al., 2014  |
| Biofilm containing<br><i>Desulfovibrio</i> and<br><i>Desulfuromonas</i> (acid mine drainage) | Batch<br>Biofilm+fluids<br>Glucose<br>RT                             | Akaganeite and schwertmannite (contained in biofilm)<br>NI   | TEM-EDS   | 40–60 nm rod-shaped FeS particles   | ND                      | Kim et al., 2015   |

Technical abbreviations: TEM, transmission electron microscopy; SEM, scanning electron microscopy; SAED, selective area electron diffraction; EDS, electron dispersive spectroscopy; XRD, X-ray diffraction; XPS, X-ray photon spectroscopy; XANES, X-ray absorption near-edge structure; EXAFS, extended X-ray absorption fine structure. Other abbreviations: M, mackinawite; G, greigite; RT, Room temperature; NI, not indicated; ND, not determined; w., weeks; m., months.





(White, 2009), as well as for the distinction between different various compositions of mackinawite and greigite (Bourdoiseau et al., 2008, 2011). Synchrotron X-ray methods, such as X-ray microscopy coupled to XAS may provide details about the microbe-mineral interface at the microscale that are overlooked in bulk studies (Templeton and Knowles, 2009). In the specific case of iron sulfide minerals, soft X-ray scanning transmission X-ray microscopy (STXM) can provide the distribution of C, Fe, and S (Behrens et al., 2012; Cosmidis and Benzerara, 2014). Using soft or hard X-rays, X-ray absorption near-edge structure (XANES), also called near-edge x-ray absorption fine structure (NEXAFS), spectroscopy can resolve the characterization of major biomolecules, such as lipids, polysaccharides and proteins, and the oxidation state of Fe and S and the associated mineralogy at the sub-micron scale, respectively (Templeton and Knowles, 2009). As newly precipitated iron sulfide particles are generally in the nm-size range, transmission electron microscopy (TEM) imaging and associated techniques, such as electron energy loss spectroscopy (EELS) and SAED, are essential to characterize the morphology and crystal structure of sulfide mineral crystals at the sub-micron scale (Posfai et al., 2013a). While bulk sulfur isotopic analyses provide the best line of evidence regarding the provenance of sulfide in sulfide minerals,

e.g., chemical sulfide vs. sulfide from sulfate reduction or from sulfur disproportionation (Chambers and Trudinger, 1979; Zopfi et al., 2008), considerable variations in isotopic compositions between—and even within—individual pyrite grains can occur (Kohn et al., 1998). In future studies, more spatially precise work using SIMS and nanoSIMS may provide critical information at the sub-micron scale to understand small spatial scale isotope fractionation and its possible causes (Fike et al., 2008; Orphan and House, 2009; Wacey et al., 2010). In highly resolved elemental analyses, co-localization of elements (especially C, N, Fe, S) must be considered. For example, nano-scale chemical mapping of organic carbon and nitrogen has detected relict pyrite framboids likely formed in microbial biofilms in larger pyrite grains (Wacey et al., 2015). In culture experiments, abiotic controls where pH, Eh, and reactant supply—including sulfide oxidation intermediates—are accurately controlled or quantified are critical to constraining unambiguous biotic influence on mineral rates of formation or morphology. Regarding rates of mineral formation, one study supports the conclusion that SRP may increase them (Mohagheghi et al., 1985), and that pyrite formation might be accelerated by  $\text{S}(0)$ -disproportionating microorganisms (Canfield et al., 1998). Nevertheless, more studies with a greater variety of microorganisms and

conditions should be performed to confirm or constrain this result.

If the goal is to arrive at a better understanding of the effects SRP and other microbes have on the formation of extracellular metal sulfides in natural environments, the “holy grail” could be described as studies that link microbial phylogeny and physiology with mineralogy, mineral morphology, rates of mineral formation, and isotope and element chemistry. Our understanding of the evolution of the Earth’s surface environment is mainly based on analyses of iron sulfides preserved in ancient or modern sediments. Additionally the presence of pyritized organisms in the sedimentary record of Archaean to Jurassic age implies a potential role for Fe sulfides in the preservation of micro- and microfossils (Sagemann et al., 1999; Grimes et al., 2001; Schieber, 2002; Cosmidis et al., 2013; Vietti et al., 2015). Deciphering the role of microorganisms in the formation of sulfide minerals is therefore crucial to better constrain the evolution of the biogeochemical cycles of Fe, S, and C.

## CONCLUDING REMARKS

Sulfide minerals are of great importance for diverse fields of research, e.g., paleontology and reconstruction of past environments, material sciences, and the potential use of sulfide minerals for industrial applications, and economic geology. Two mechanisms of extracellular, biologically induced mineralization have been established: (1) SRP, and potentially other microorganisms, produce free sulfide, which reacts abiotically with dissolved metals to form sulfide minerals, and

(2) the association of iron with their cell walls and EPS, which then react with sulfide on these surfaces to form metal sulfide minerals. These data, however, do not preclude the possibility that microbes play a more direct role in extracellular iron sulfide formation, perhaps in a manner similar to the intracellular metal sulfide formation found in MTB. The limits of analytical tools and resolution faced by previous investigators may have hindered their ability to better characterize the mineral phases observed during laboratory experiments, but recent advances may provide a timely opportunity to revisit this long-standing question. We suggest that in order to fully consider the microbial role in the formation of metal sulfides, a structured approach that queries both microbial processes and minerals in culture, looks for evidence in natural environments, and attempts to link microbial processes and metal sulfides across spatial scales should be followed. Such an approach is likely to be both challenging and enlightening.

## AUTHOR CONTRIBUTIONS

All authors listed, have made substantial, direct and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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