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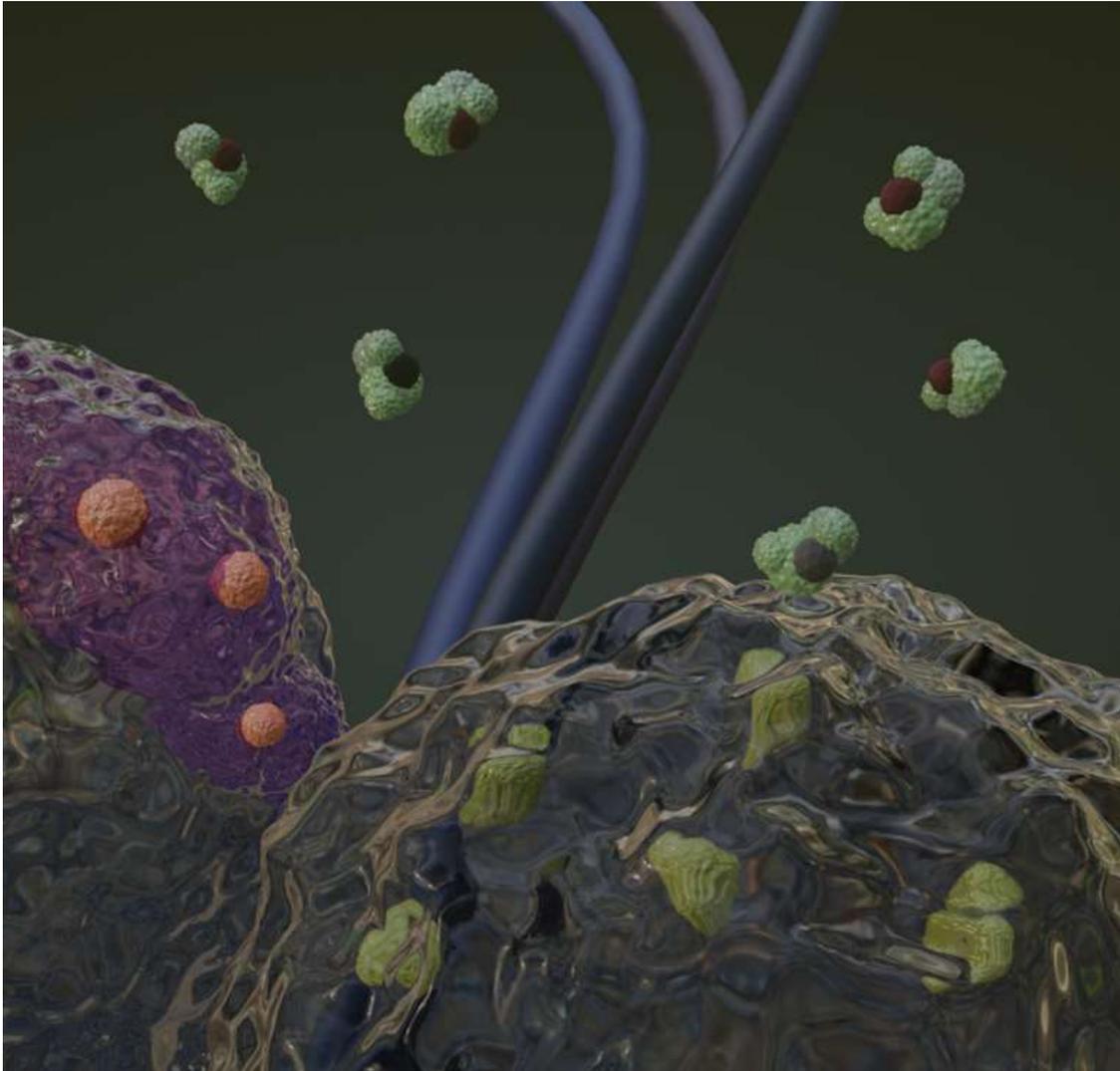
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Diversity of Microbial Metal Sulfide Biomineralization

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9 **Abstract**

10 Since the emergence of life on Earth, microorganisms have contributed to biogeochemical cycles.
11 Sulfate-reducing bacteria are an example of widespread microorganisms that participate in the metal
12 and sulfur cycles by biomineralization of biogenic metal sulfides. In this work, we review the microbial
13 biomineralization of metal sulfide particles and summarize distinctive features from exemplary cases.
14 We highlight that metal sulfide biomineralization is highly metal- and organism-specific. The properties
15 of metal sulfide biominerals depend on the degree of cellular control and on environmental factors, such
16 as pH, temperature, and concentration of metals. Moreover, biogenic macromolecules, including
17 peptides and proteins, help cells control their extracellular and intracellular environments that regulate
18 biomineralization. Accordingly, metal sulfide biominerals exhibit unique features when compared to
19 abiotic minerals or biominerals produced by dead cell debris.

20

21 **1. Introduction**

22 Metals are essential for most biochemical reactions and more generally for life-related activities in
23 microorganisms.^[1] Key processes in the biogeochemical cycle of metal elements are associated with
24 mineral immobilization and mobilization driven by microorganisms.^[2] Immobilization of metal species
25 involving biological processes is achieved through biomineralization, biosorption, and
26 bioaccumulation.^[3] Biomineralization is a metal precipitation process, in which inorganic particles are
27 formed by organisms. In turn, biosorption refers to a metabolically-passive process where metals are
28 bound to a cellular surface by simple adsorption. Finally, bioaccumulation involves energy-consuming
29 processes where active transport systems are often required.^[4] The biosorption and bioaccumulation
30 frequently occur ahead of biomineralization processes.

31 In contrast, biological mobilization of metal species occurs through reactions involving redox potential
32 changes, such as bioleaching and bioweathering. Mobilization of metal species commonly results in an
33 increase of bioavailability of metals.^[2] Bioleaching or biooxidation is a set of reactions in which
34 minerals are oxidized by organic acids and organic compounds typically secreted by acidophiles.^[5]
35 Bioweathering is biological dissolution of minerals through mechanical and chemical reactions.^[6] These
36 reactions can occur via different mechanisms, depending on the metal sulfide types and associated
37 microorganisms.^[7]

38 Metal sulfide is one of the major family of minerals. It is ubiquitously encountered in global
39 biogeochemical metal cycles.^[8,9] In general, metal sulfide nanoparticles are common metal reservoirs
40 and carriers in anoxic environments at low temperature.^[10,11] Natural metal sulfides generally have a
41 wide variation in chemical compositions, valence states, and crystal phases.^[9] Metal sulfides are
42 commonly divided into several categories depending on the structural features of the formed crystals,
43 but most of the sulfide crystals in nature are subordinate to simple binary or ternary systems and contain
44 impurities.^[8] Metal sulfide nanoparticles have interesting and useful properties and functions,^[13,14] in
45 particular high electric conductivity and thermal stability.^[15,16] Metal sulfides are typically diamagnetic,
46 paramagnetic or Pauli-paramagnetic but several transition-metal sulfides such as greigite (Fe_3S_4) and
47 pyrrhotite (Fe_7S_8) have a magnetic ordering leading to permanent magnetic moments.^[17-19] Such
48 magnetic property is used by organisms like magnetotactic bacteria that use intracellular magnetic
49 nanoparticles composed of greigite, in order to migrate to the optimal conditions for their growth and
50 proliferation by interacting with Earth's magnetic field lines.^[20,21]

51 Precipitation and dissolution of metal sulfide frequently occur by the above-mentioned microbial

52 reactions. For example, precipitation of metal sulfides is reported both in the extracellular and in the
53 intracellular space of sulfate-reducing organisms that produce reductive sulfur species. Metal sulfide
54 biominerals are also often produced by other species of bacteria, archaea, and fungi as we will see below.
55 The formation of metal sulfide nanoparticles is often correlated to metal detoxification, which is a
56 process used by microorganisms to decrease the concentration of metals from their environment to
57 reduce their toxicity.^[22,23] Biomineralization that occurs promoted by high concentrations of metal ions
58 as a microbial reaction to protect microorganisms from their toxicity is recently termed ‘forced
59 biomineralization’ by H.Ehrlich et al. Hence, metal sulfide biomineralization becomes a good example
60 of this biomineralization category.^[24] On the contrary, metal sulfides can be dissociated by sulfide-
61 oxidizing microorganisms in marine environments.^{[25][26,27]} The dissolution of metal sulfides is mostly
62 performed by biogenic oxidants at the exopolysaccharide (EPS) layer of microorganisms^[28] after the
63 cells attach on the mineral surface.^[29] Bioleaching of metal sulfides has been widely studied for its
64 significance and advantages in industrial purposes in the biomining industry.^[30,31] Metal sulfide
65 precipitation and dissolution also takes place by macroorganisms. For example, deep-sea gastropod
66 mulluscs biomineralize iron sulfides with organic substrates to make their outer shell composed of
67 pyrite or greigite. Bioleaching of pyrite is observed at plant roots of that secrete oxidant compounds.^[32]

68 Similar to their role in the metal cycle, biogenic metal sulfides play an important role in the global sulfur
69 cycle.^[33–36] A critical process in the sulfur cycle is sulfate reduction, which involves dissimilatory sulfate
70 reduction to sulfide, sulfur disproportionation, and sulfide oxidation.^[35] The main driving force for
71 sulfide generation in sediments is sulfate-reducing activities of microorganisms.^[33,37] Many heavy
72 metals can be sequestered by interactions among metal ions and biogenic molecules produced by sulfate
73 reducing prokaryotes (SRP). For example, Co, Ni, Cu, Zn, Cd, As, Hg, and Pb are reported to effectively
74 precipitate with sulfide anions.^[38,39]

75 So far, there have only been a few reviews that concentrated on metal sulfide biominerals.^[37,40,41]
76 Therefore, we focus here on the extensive diversity of microbial metal sulfide biomineralization, and
77 on important factors for each biomineral property, structuring the review based on the materials’
78 composition. In general, metal sulfide biominerals show characteristic features that are distinguishable
79 from abiotic precipitates. The types of metal sulfide biominerals are highly metal- and organism-
80 specific. We remarked that many organisms produce and use proteins or peptides as capping agents for
81 metal sulfide biomineralization. Capping agents are stabilizers of the surface of nanoparticles and
82 regulate their growth or agglomeration.^[42,43] Capping agents generally reduce the size of nanoparticles,
83 thus work against Ostwald ripening that consumes smaller particles to grow particles into a larger size
84 driven by surface energy. Throughout this review, we highlight the diversity in types and mechanisms
85 of biomineralization. We anticipate that a comprehensive understanding of distinctive features from
86 metal sulfide biomineralization will facilitate a systematic approach for understanding new types of
87 biogenic metal sulfides and potentially other types of biominerals.

88

89 **2. Classifications of biomineralization**

90 Biomineralization can be grouped into several categories based on different criteria. The most
91 commonly used criteria are (1) types of minerals based on chemical composition and crystal form of
92 minerals,^[44] (2) the degree of biological control,^[45] and (3) the location of mineralization.^[46] Metal
93 sulfide biomineralization shows a wide variety in the degree of biological control involved and in the
94 location of mineralization. In section 3, we organized different types of metal sulfide biominerals based
95 on the criteria (1) and examined each biomineralization case further based on the criteria (2) and (3).
96 Below is a summarized description of the last two criteria.

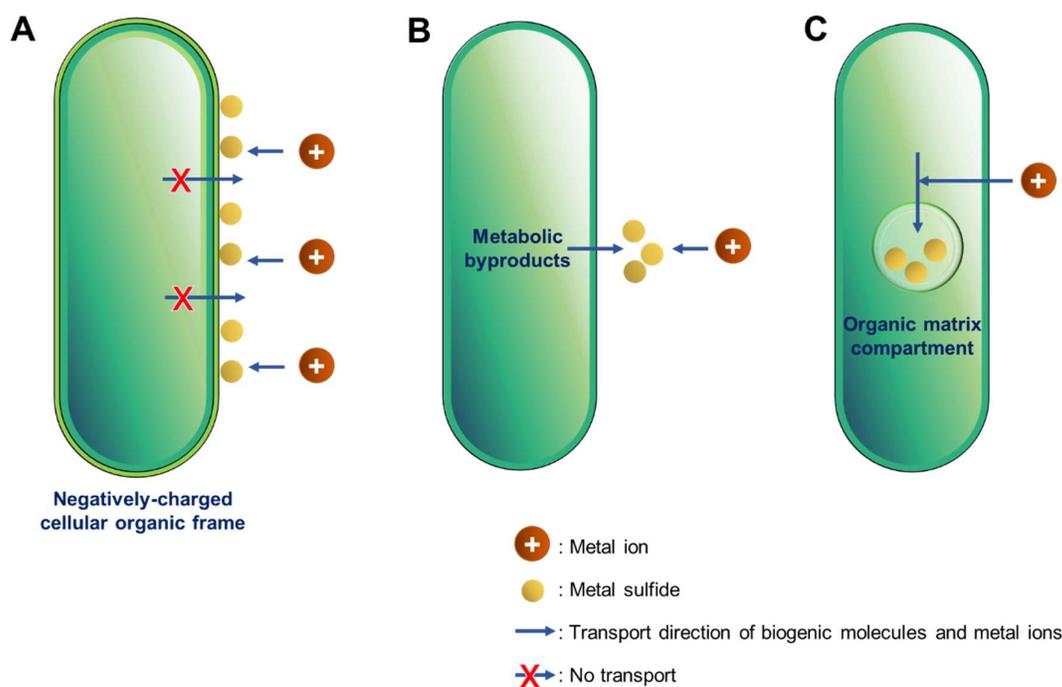
97 Based on the degree of biological control, biomineralization can be mainly categorized into three
98 following groups. First of all, biologically-influenced biomineralization (BFM, Figure 1A) is a passive
99 mineralization process occurring on cellular organic templates such as the bacterial cell wall and
100 extracellular polymeric substance (EPS).^[47,48] The main composition of EPS is polysaccharides, which
101 also comprises of other types of polymers, such as enzymatic proteins, lipids, and extracellular DNA.^[49]
102 The composition and structure of EPS varies according to the microorganisms, accordingly the function
103 as well.^[50,51] The function of EPS varies but is mainly responsible for protection of microbial cells.
104 Dependent on metal species, the contribution of polysaccharides or proteins for binding of metal ions
105 to EPS could be different.^[52] Cellular surface substrates commonly have a negative charge in both cases
106 of gram-positive and gram-negative bacteria.^[28,53] Positively-charged metal ions are easily stabilized
107 when they are bound to the surface and locally supersaturated by electrostatic interactions.^[54,55]
108 Macromolecular crowding effect also affects macromolecular stability, effectiveness in functions based
109 on alteration in protein folding and also mineralization behaviors both in promotion and inhibition of
110 nucleation.^[56] With the assist of organic substrates on the surface of bacteria, nucleation and
111 crystallization of amorphous minerals is several orders of magnitude faster than what it is for pure
112 inorganic mineralization.^[55] Even dead or disrupted debris from cells are sufficient to function as a
113 substrate that promotes supersaturation and further nucleation and growth of minerals.^[57]

114 Second, biologically-induced biomineralization (BIM, Figure 1B) is defined as the precipitation of
115 inorganic materials in the environment driven by cellular activities. This class of biomineralization
116 involves active reactions between metabolic byproducts and environmental solutes that lead to
117 nucleation and maturation of minerals in the environment.^[55] It has been proposed in the literature that
118 the end products formed by this type of biomineralization are not distinguishable from precipitates
119 produced by purely inorganic reactions and that the reaction typically occurs outside the cell but in the
120 close vicinity of the cell surface.^[55]

121 The last category, biologically-controlled biomineralization (BCM, Figure 1C), refers to the
122 precipitation of minerals by elaborate cellular control inside a separated compartment. The most
123 important feature found in this class of biomineralization is the association with an organic matrix that
124 forms an isolate intracellular environment, thus the group was formerly referred as organic matrix-
125 mediated biomineralization.^[58,59] The cellular compartment, such as a vacuole or an organelle like the
126 magnetosome, maintains a different condition from that recorded outside to facilitate supersaturation of
127 minerals. This is possible due to the guidance of proteins and macromolecules embedded in the
128 surrounding matrix. The biological control is applied in several processes: transport of the necessary
129 chemical elements to the nucleation site and direction of the precipitation to particular structures or
130 phases. To be more specific, the organisms control the crystal habit, the crystal organization, the
131 localization of nucleation, the chemical composition, and the crystal phase.^[60] However, only a few
132 reported cases found in microorganisms satisfy all the criteria for this biomineralization category.
133 Despite of the involvement of a biogenic organic matrix, many biomineralization cases show less
134 control over some material properties of the biomineral, such as calcium carbonate inclusions found in
135 cyanobacteria that shows amorphous crystal structures and no specific chemical composition.

136 Biomineralization can also be classified based on the location of mineralization. All reported cases are
137 broadly categorized into four groups as follows: extracellular, epicellular, intracellular, and
138 intercellular.^[46,61] These terms refer to biomineralization occurring outside the cell, on the surface of
139 cell, inside the cell, and in between cells, respectively.

140



141

142 **Figure 1. Schematic illustration of three major types of microbial biomineralization that are conventionally categorized**
 143 **by the degree of biological control.** (A) Biologically-influenced biomineralization (BFM) that primarily takes place through
 144 passive reactions between the cellular substrate and metal ions from environments. (B) Biologically-induced biomineralization
 145 (BIM) that occurs by metabolic byproducts reacting with environments. (C) Biologically-controlled biomineralization (BCM) that
 146 involves cellular compartments for the precipitation of biominerals in a controlled way that cannot be achieved by abiotic reactions.

147

148 3. Features of metal sulfide biomineralization cases

149 3.1. Iron sulfides

150 Iron sulfides are the most common metal sulfide species. They are typically found in anoxic
 151 sediments.^[62–64] Iron sulfide minerals can be produced by pure chemical reactions and include greigite
 152 (Fe_3S_4), pyrrhotite (Fe_7S_8), mackinawite (tetragonal FeS), pyrite (cubic FeS_2), marcasite (orthorhombic
 153 FeS_2), and amorphous FeS .^[55,65] Compared to these abiotic iron sulfides, those formed by SRB and
 154 anaerobic archaea are limited to amorphous FeS , mackinawite, greigite and rarely pyrite.^[37,66,67]

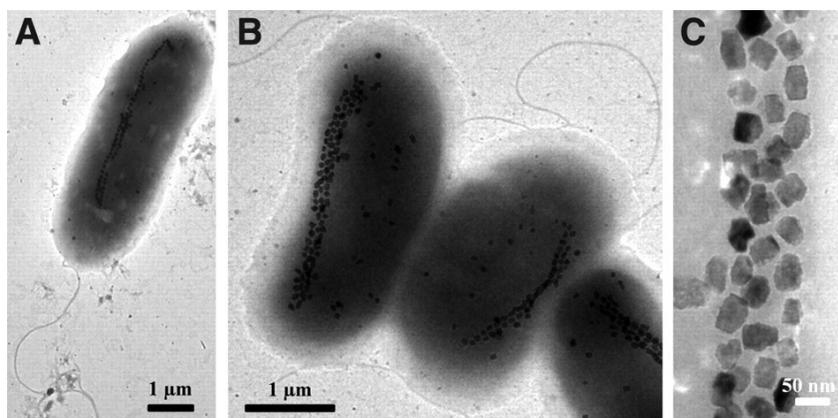
155 Microbial cultures have the ability to crystallize iron sulfide minerals much faster than what it is
 156 observed in abiotic conditions. For example, SRB culture produces crystalline mackinawite in a week,
 157 whereas abiotic experiments require several months.^[68] Rapid production of sedimentary pyrite is
 158 attributed to sulfate reduction by microorganisms as well, although pyritization is not common in
 159 bacterial culture and still requires several weeks at least.^[68,69] The kinetics of phase transformation from
 160 mackinawite to greigite is also influenced by microorganisms that accelerate the formation of greigite.^[70]
 161 As such, microorganisms play a significant role in the dynamics of iron sulfide mineralization.

162 Iron sulfide biominerals appear in various morphologies, especially when they are associated with
 163 cellular substrates. A few iron sulfide biomineralization cases were reported to encrust the cellular

164 substrates with different morphologies, with the biomineralization being dependent on the composition
165 of the cellular templates and the types of bacteria.^[37,70–72] Intracellular biomineralization of presumptive
166 amorphous iron sulfide particles has been observed in SRB *Desulfotomaculum nigrificans* and
167 *Desulfovibrio desulfuricans*, but not observed in the *Escherichia coli* at the same high iron
168 concentrations.^[73] Most of the intracellular particles appear to precipitate within the periplasmic area
169 and such a process shows features of both BIM and BCM.^[55]

170 The highest control in microbial metal sulfide biomineral formation is observed in greigite
171 magnetosome nanoparticles produced by magnetotactic bacteria (MTB).^[37,38] MTB form intracellular
172 magnetic nanoparticles composed of either magnetite (Fe_3O_4) or greigite (Fe_3S_4) to align themselves
173 along the Earth's magnetic field lines.^[74] MTB are single cells (Figure 2) or multicellular aggregates
174 named multicellular magnetotactic prokaryotes (MMP) (Figure 3). Greigite producing MTBs are
175 sulfate-reducers,^[75] which belong to the *Deltaproteobacteria* phylum.^[75] The material properties of the
176 iron sulfide particles are controlled by magnetosome proteins that are typically located in a specific
177 zone of a gene cluster called the magnetosome island.^{[76][77]} The proteins are either mostly embedded in
178 the membrane of an organelle called magnetosome or work together with the organelle to nucleate,
179 mature, and organize greigite magnetosome particles.^[40]

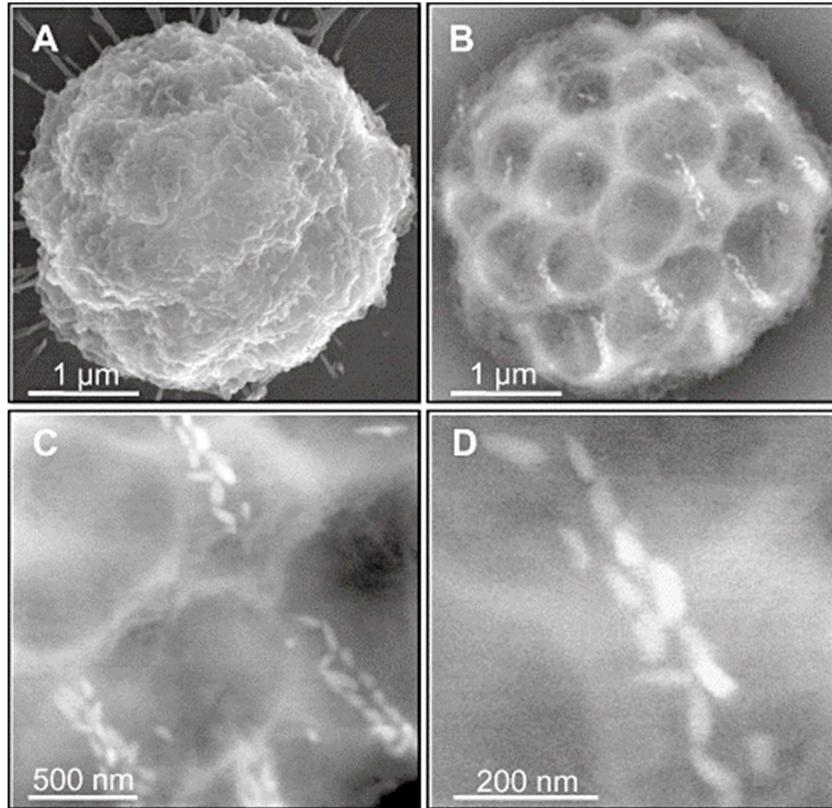
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181

182 **Figure 2. TEM images of uncultured magnetotactic bacteria (MTB) and greigite- and/or magnetite magnetosomes.** (A and
183 B) MTB cells collected from a spring in the Great Boiling Springs geothermal field in Gerlach, Nevada, USA. (C) High-
184 magnification image of greigite crystals from the cell shown in (B). (Figure adapted from ^[78] with permission)

185



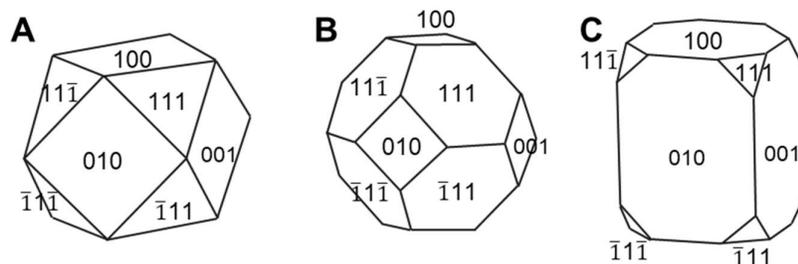
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187 **Figure 3. SEM images of an uncultured multicellular magnetotactic prokaryote (MMP) and greigite magnetosomes.** (A)
 188 Secondary electron image showing filamentous surface structures in a MMP. (B) Back-scattered electron image that reveals the
 189 arrangement of single cells within the individual MMP. The rows of magnetosomes can be distinguished based on their high yield
 190 of back-scattered electrons, which results in a bright signal. (C) Greigite magnetosomes are arranged in a few parallel chains.
 191 (D) Magnified image on two greigite magnetosome chains in (C). All magnetosome crystals are bullet-shaped, 91 ± 21 nm long
 192 and 40 ± 6 nm wide, and show a similar orientation. (Figure adapted from [79] with permission)

193

194 Greigite magnetosome particles show strict biological control over nearly all possible particle properties,
 195 including particular mineralization location, crystal dimension, chemical composition, as well as crystal
 196 organization. Magnetosome iron sulfide particles fall within the size of single domain state (less than
 197 120 nm).^[80] The ideal crystal habits of magnetosomes include cubo-octahedrons, truncated octahedrons,
 198 or rectangular prisms (Figure 4).^[81,82] Bullet-shaped or arrow-head greigite particles have also been
 199 reported in greigite magnetosomes (Figure 3).^[66,79] Finally, irregular shapes have also been observed.^[67]

200



201

202 **Figure 4. Crystal habits suggested as ideal greigite crystals found in magnetotactic bacteria.** (A) Cubo-octahedron. (B)
 203 Truncated octahedron. (C) Truncated rectangular prism.

204

205 Historically, pyrrhotite (Fe_{1-x}S) and pyrite (FeS_2) were proposed as possible phases of greigite
 206 magnetosome particles possibly originating from a misinterpretation of the electron diffraction data of
 207 the crystal structure.^[83,84] Indeed, M. Posfai et al. later examined several environmental samples and
 208 suggested that the diffraction data rather indicated greigite, mackinawite and cubic FeS of the sphalerite
 209 structure.^[85] They also observed crystal diffraction patterns of magnetosomes and found that a
 210 mackinawite particle inside a dead MTB cell transformed into greigite after several days of exposure to
 211 air, suggesting mackinawite as a precursor of greigite magnetosome particles. Accordingly, greigite is
 212 regarded as the final phase of greigite magnetosome nanocrystal after repeated phase transformation
 213 processes. The irregularity of the surfaces, stacking faults and lattice strains found on greigite particles
 214 also imply that they originate from the structural remnant of mackinawite during structural
 215 transformation.

216 As a summary, iron sulfide biomineralization occurs with varying degrees of biological control. Iron
 217 sulfide biomineralization can take place anywhere: on the cell wall, within biofilms, in the extracellular
 218 region, in the periplasmic space, and also in a cellular organelle in the cytoplasm (Table 1). Among the
 219 iron sulfide cases, the most striking case is the precipitation of greigite in magnetosomes, which
 220 represents one of the most highly controlled biomineralization pathways satisfying all of the aspects of
 221 biological control defined for BCM.^[40] In contrast, extracellular biomineralization of iron sulfides on
 222 the cell surface shows random properties corresponding to a combination of BFM and BIM. Each case
 223 shows distinguishable characteristics in morphology, phases, and size from minerals produced via
 224 abiotic processes.

225

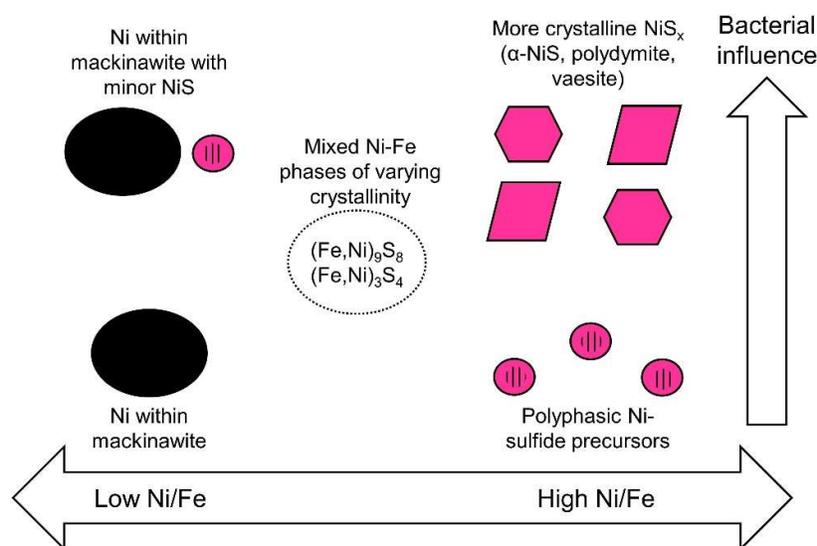
226 3.2. Mixed metal sulfides containing iron

227 In the environment, iron sulfide minerals typically contain different trace elements. One example is
 228 pyrite particles containing Ni, Cu, Zn, As, Mo, Ag, and Pb.^[86,87] Iron sulfide precursors incorporate
 229 other metal by adsorption, chemical substitution and coprecipitation.^[88] These additional elements can
 230 accelerate or inhibit the conversion to more stable structures, such as Fe-containing copper sulfides that
 231 transform into Fe-Cu-sulfides,^[10] or iron sulfides reacting with arsenic by sorption that are inhibited to
 232 convert to pyrite.^[89]

233 Dissolved iron in the microbial environments affect biomineralization of other metal sulfides and
 234 contrariwise. For example, the metal concentration needed for initial metal sulfide precipitation and the

235 properties of the biogenic materials are affected by the presence of other metal species: a high
 236 concentration of Ni in the *Desulfotomaculum* DF-1 culture hinders the formation of FeS since Fe-
 237 complexation is increased, while Ni remains soluble during the precipitation of FeS, because the
 238 bacterium also secretes Ni-binding proteins.^[90] The amount of iron species that adhere to the cell surface
 239 decreases when the concentration of nickel increases in the medium. M. Mansor et al. particularly
 240 investigated the influence of the ratio between the concentration of Ni and Fe on biomineral properties
 241 of mixed metal sulfides composed of Ni and/or Fe.^[91] Even trace amount of iron increases the time
 242 needed to develop crystallinity in nickel sulfide precipitates, which can cause better solubility of Ni to
 243 easily dissolve Ni back into the environment. On the contrary, Ni incorporation into mackinawite (FeS)
 244 enhances the stability of mackinawite. Figure 5 presents the influence of biological contribution on
 245 mineralization of mixed metal sulfides in conditions of different Ni / Fe concentrations. The phase,
 246 crystallinity, size and morphology differ according to the biological influence.

247



248

249 **Figure 5. Schematic diagram of the predicted Fe and Ni-hosting phases in environments of low redox potential and high**
 250 **concentration of sulfur.** The mineral properties are determined by the initial [Ni]_{aq}/[Fe]_{aq} ratios in solution and by the degree of
 251 bacterial influence. Bacterial culture influences on iron sulfide with different metals (Reproduced with permission from ^[91])

252

253 Following the same line, but with Fe and Cu, SRB produce Fe-Cu sulfides, of which the crystallinity is
 254 enhanced by the presence of dissolved Fe.^[37,92] It is an opposite tendency from nickel sulfide
 255 biominerals that shows less crystallinity in the presence of dissolved Fe. In comparison to abiotic
 256 systems, biogenic Fe-Cu sulfides show higher selectivity in particle composition, and crystal
 257 structure.^[10] SRB cultures also accelerate the transformation of Fe-rich copper sulfide to become mixed
 258 metal sulfides by atomic rearrangements, from covellite into chalcopyrite or nukundamite.^[10] Contrary
 259 to an earlier hypothesis that chalcopyrite is formed only by the reaction between iron sulfides and
 260 aqueous Cu,^[93] the transformation from covellite to chalcopyrite occur through redox reactions between
 261 aqueous Fe and S atoms present in covellite with the supply of sulfur from bisulfide ions (HS⁻).

262 Intracellular biomineralization of Fe-Cu sulfides have been reported in uncultured magnetotactic
 263 bacteria producing greigite magnetosome particles.^[66,94] Significant amounts of copper inclusion in
 264 greigite magnetosomes often occur in the microorganisms, of which the degree is variable roughly

265 between 0.1 to 10 atomic percent of iron content in magnetosome particles.^[66] M. Posfai et al. observed
266 that mackinawite converted to greigite from the same crystals when there was no significant amount of
267 Cu, while disordered mackinawite crystals containing Cu remained in the same crystal structure without
268 phase transition.^[66] Accordingly, it is speculated that the inclusion of copper affects the conversion rate
269 from mackinawite to greigite to inhibit the phase transformation. Besides, Bazylinski et al. suggested
270 that this copper inclusion could be related to heavy metal detoxification.^[94]

271 Biomineralization of mixed metal sulfides is more complicated than the single metal version since the
272 concentration of a metal influences the biomineralization of other metal sulfides. This directly
273 influences the properties of the formed biominerals, in terms of crystallinity, size, morphology, crystal
274 defects, and even phase. The variations originating from the inorganic factors seem based on BIM but
275 the biological control by metal-binding proteins is highly involved as well. Compared to magnetite
276 magnetosomes, greigite magnetosomes seem more affected by the influence of other metals, by copper,
277 in particular.

278

279 **3.3. Nickel sulfides**

280 All the cases of nickel sulfide biomineralization presented on Table 1 are based on extracellular
281 biomineralization achieved by metabolic activities of SRB. The structure of biominerals identified in
282 these studies include vaesite (α -NiS), heazelwoodite (Ni_3S_2), polydymite (Ni_3S_4), millerite (trigonal
283 NiS), or amorphous phase. In comparison with abiotic precipitates produced by sulfide sources, the
284 biomineralized nickel sulfide precipitates showed more ordered crystallinity, different size, as well as
285 different crystal phases (Table 1).^[91,95,96] The solubility and crystallinity change in nickel sulfide phases
286 is attributed to pH change and traces of other metals.^[91] The presence of organic capping agents also
287 influences the properties of nickel sulfide biominerals.^[90,97] The solubility of nickel sulfide indeed
288 increases in the microbial culture due to the organic capping agents that are secreted by bacteria. These
289 factors, as well as the slower release of biogenic sulfides responsible for the decreased reaction speed
290 of biomineralization, are recognized as the main contributors of the crystallinity of nickel sulfide
291 biominerals.

292 Nickel sulfide biomineralization commonly shows characteristics of BIM, as the biominerals are mainly
293 produced by reactions between metabolites and metal ions in the culture. However, SRB control the
294 solubility of nickel ions in the culture by secreting biomolecules. Accordingly, they control the
295 biomineralization processes, which in turn influences the biomineral properties as well.

296

297 **3.4. Copper sulfides**

298 Copper sulfide biomineralization is reported to efficiently remove dissolved copper from a microbial
299 culture.^[98] Extracellular copper sulfide biomineralization by SRB produces CuS (covellite) or Cu_2S
300 (chalcocite). Biogenic nanoparticles have a tissue-like morphology showing smaller size, less
301 crystallinity and less resistance to dissolution than abiotic counterparts.^[92] This tendency is opposite to
302 what has been observed in other types of biogenic metal sulfides that mostly show better crystallinity
303 and resistance against dissolution.^[91,99,100] Moreover, the tissue-like morphology may not be only
304 attributed to the slow speed of the reaction between metabolic byproducts and the environment. Other
305 biomolecules possibly work as a guiding substrate for the morphology. A particular case of extracellular
306 biomineralization of copper sulfide is seen in the culture of the fungus *Fusarium oxysporum* where
307 peptides are possibly helping produce spherical particles in the narrow size range of 2-5 nm.^[101] This

308 implies that also in this case, potential capping agents are involved in the control of the morphological
309 and chemical properties of biominerals, similarly to what is found in many other metal sulfide
310 biominerals.

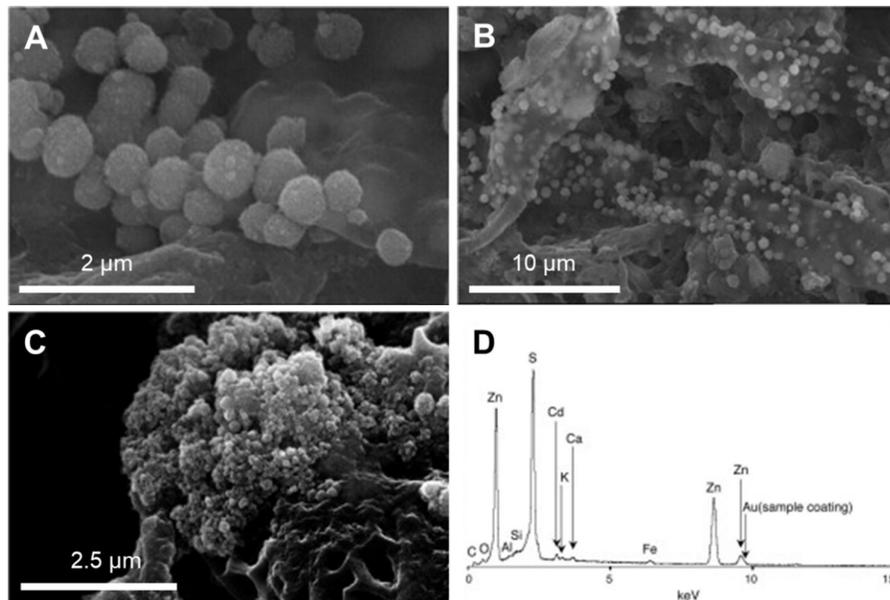
311 Intracellular biomineralization of copper sulfide, in turn, has been recently reported in the culture of the
312 metal-reducing bacterium *Geobacter sulfurreducens*.^[102] This microorganism is a sulfur-reducing
313 organism, and does not have genes to exert dissimilatory sulfate reduction for metal sulfide production.
314 Accordingly, this biomineralization points towards a unique mechanism for the sulfur resources used
315 for this biomineral production. This is magnified by the fact that the bacterium also forms epicellular
316 and extracellular biominerals on top of the intracellular ones.

317 The biological control of copper sulfide biomineralization, therefore, appears at different degrees. Each
318 biomineralization case reflects a high biological influence, which possibly includes biomolecules that
319 control the mineralization process. Although the involvement of an organic matrix in the
320 biomineralization processes is unclear, the reported cases cannot be described simply based on BIM.

321

322 3.5. Zinc sulfides

323 Microbial zinc sulfide biomineralization has been widely reported, not only in SRB cultures but also in
324 the culture of a purple bacterium, a thermophilic anaerobic bacterium, and different fungi (Table 1). In
325 general, zinc sulfide biomineralization is influenced by the activities of biogenic organic molecules. In
326 environmental samples collected from a peatland, zinc sulfide biominerals are associated with organic
327 matters that become the carbon source for bacteria (Figure 6). The organic matter found in the samples
328 is suggested to be a main player of the observed framboidal morphology in aggregates.^[103]



329

330 **Figure 6. SEM images and EDX spectrum of ZnS framboidal aggregates discovered in anoxic peat samples from the Big**
331 **Muck.** (A) Typical morphology of zinc sulfide particles obtained from peats. (B) ZnS particles embedded in unidentified organic
332 residues. (C) Particles found in humidified peat samples. (D) Energy-dispersive X-ray spectrum of one of ZnS framboidal
333 aggregates in (C). (Figure adapted from ^[103] with permission)

334

335 A few zinc sulfide biomineralization cases associated with biofilms also present tightly regulated
336 particle size (less than 5 nm) and defined crystal structures.^[104,105] The bacterial biofilm involved in such
337 highly-controlled biomineralization could be regarded as a frame that controls particle morphology, as
338 well as an efficient means to transport the organic molecules, metal ions, and sulfide sources required
339 to produce the nanoparticles. Microbial extracellular biomineralization within biofilms possibly
340 functions in a similar way to what is observed in eukaryotic biomineralization where an extracellular
341 frame is involved in the control of the biomineral properties, in particular the morphology.^[106-108]

342 Extracellular zinc sulfide are produced by the anaerobic bacterium *Serratia nematodiphila*. They are
343 composed of fine nanocrystals with an average size of 7 nm that become the building blocks of larger
344 aggregates. The particles were suggested to bond with proteins through amide or aliphatic residues.^[109]
345 The yeast strain *Aspergillus flavus* also uses capping agents for extracellular biomineralization.^[110] In
346 this case, the zinc sulfide nanoparticles are coated with the capping agents via amine groups and cysteine
347 residues.

348 In summary, zinc sulfide biominerals commonly show many features attributed to strict biological
349 control based on the role played by capping agents or biomolecules embedded in EPS. This is
350 remarkably not limited to the formation of intracellular particles, but also observed in the case of simple
351 extracellular biominerals.^[104] Accordingly, biomineralization is more than a simple reaction between
352 metabolites and the environment, and microorganisms seem to exert biological control over many
353 reactions related to biomineralization.

354

355 **3.6. Arsenic sulfides**

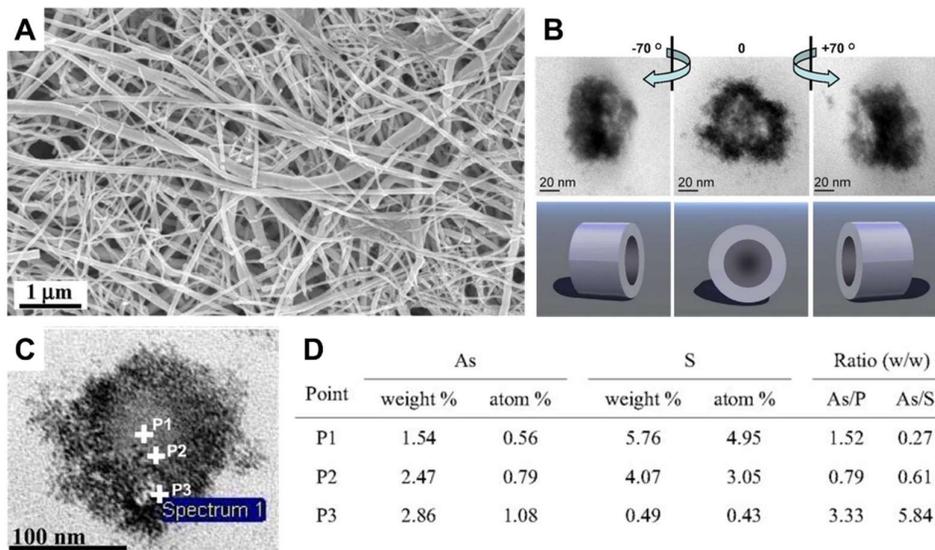
356 The phases discovered in arsenic sulfide biomineralization include AsS (realgar), As₂S₃ (amorphous,
357 orpiment), As₄S (duranusite). The type of arsenic sulfide biominerals depends on the culture conditions,
358 including pH and redox potential. For example, the pH value affects the cellular activities and
359 metabolism, such as efficiency of sulfate reduction and arsenic reduction from As^V to As^{III} in the
360 bacterial culture. A mixed culture of anaerobic bacteria showed 8 times higher efficiency in sulfate
361 reduction at pH 7.1 than at pH 6.1.^[111] The decrease in the sulfate reduction rate leads to more reduction
362 of arsenic ions and the rate of formation between As^{III} and H₂S in turn influences the biomineral
363 formation.

364 An example is found in the sulfate-reducing *Desulfotomaculum Auripigmentum*. Intracellular
365 biomineralization of arsenic sulfide was observed as the encrust in the cell and appeared together with
366 epicellular and extracellular biomineralization.^[112] The intracellular precipitation seems associated with
367 a cytoplasmic membrane and located within the periplasmic space. However, the particles generally do
368 not show a specific control in their morphology or distribution within the cell. This biomineralization
369 is not solely biologically-induced but involves cellular control on a few points such as the particle
370 composition and crystal phase. Epicellular precipitates confined within a membrane-like compartment
371 show a potential involvement of EPS for biological control over biomineralization at the cell surface.

372 Another interesting case is arsenic sulfide precipitates with the morphology of filamentous nanotubes
373 that were observed in the culture of the metal-reducing bacterium *Shewanella* sp. HN-41 (Figure 7).
374 The biomineral has a diameter ranging between 20 and 100 nm and the average length of 30 μm. A
375 phase change occurs in this biomineral with time: amorphous As₂S₃ is first formed and then transformed
376 to realgar and to duranusite.^[113,114] Exopolysaccharides-based substrates are associated with the
377 production of the filaments. The EPS is suggested to serve as the substrate, thereby explaining the

378 morphology.^[113,115] The nanotubes show metallic conductivity after several days of aging because of
 379 deposition of elemental As on them and also photoconductivity at the exposure of UV. Other *Shewanella*
 380 strains also produce arsenic sulfide-based filamentous nanotubes but show similar radial structure
 381 functions from the EXAFS spectra of *Shewanella* sp. HN-41, thereby indicating slight differences in
 382 mineral compositions, in turn supposedly related to different reduction rates.^[114] Similar multiphase
 383 biomineralization is often discovered in biominerals produced by eukaryotes, such as a diatom
 384 *Didymosphenia geminata*, which produces a nanofibrous framework based on multiphase calcium
 385 carbonates using a polysaccharide matrix.^[116]

386



387

388 **Figure 7. Electron micrographs and chemical analysis of biogenic As-S nanotubes.** (A) SEM image. (B) Cross-sectioned
 389 TEM tomograms. (C and D) STEM-EDX point spectra from the cross-section of one of the As-S nanotubes. (Figure adapted from
 390 ^[113] with permission, Copyright (2007) National Academy of Sciences, U.S.A.)

391

392 A final notable case observed in the environment is the mineralization on cell substrates by hot flow
 393 enriched with hydrogen sulfide that goes through open cracks of fungal colonies.^[117] This process forms
 394 a specific morphology following the former arrangement of cells. The precipitation of filamentous
 395 clusters shows a similar composition to orpiment at the hydrothermal sites.^[117] This type of
 396 biomineralization has not been defined by conventional classification for biomineralization types but
 397 could be close to BFM as the dead cell frame composed of organic materials affects the morphology of
 398 biominerals.

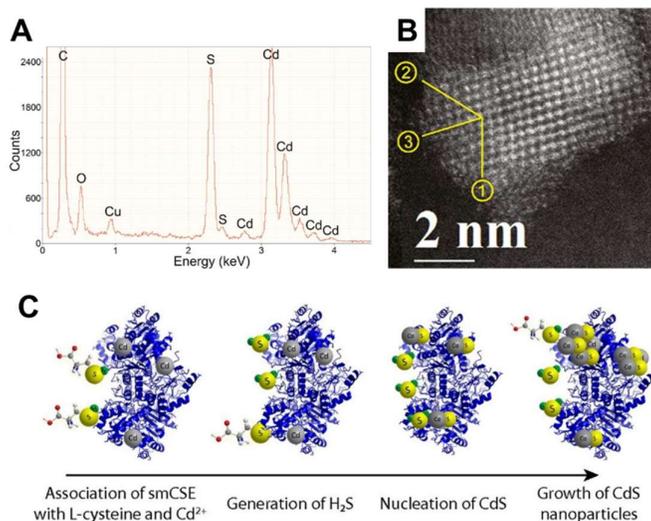
399 In summary, and as in most cases depicted so far, the biomineralization of arsenic sulfides cannot be
 400 simply classified with features distinctive of BFM, BIM, and BCM. In the example of arsenic sulfide
 401 nanotubes produced by *Shewanella* species, the cellular surface and EPS are involved in the
 402 biomineralization as in BFM. The EPS, however, can offer a compartment for controlling the particular
 403 morphology, in a similar way to what is observed in BCM. The biomineralization is also influenced by
 404 metabolic byproducts and environmental factors, as in BIM.

405

406 **3.7. Cadmium sulfides**

407 Crystal phases of cadmium sulfide biominerals that have been reported to include rock-salt, zinc-blende,
408 wurtzite, and amorphous phases (Table 1). In order to produce cadmium sulfide, sulfate reduction and
409 cysteine degradation are used as the main pathways to utilize sulfur sources, while cadmium ions are
410 supplied in excess to the culture. For example, supplementing the culture of the deep-sea bacterium
411 *Idiomarina* sp. OT37-5b with cysteine results in cysteine degradation, thereby producing H₂S in the
412 bacteria, and in turn CdS production on the cell surface.^[118] CdS biomineralization on the surface of
413 cells could also promote energy production as well as reduce the Cd stress. It implies that cadmium
414 sulfide biominerals potentially perform other functions than the protection from heavy metal stress in
415 the environment.

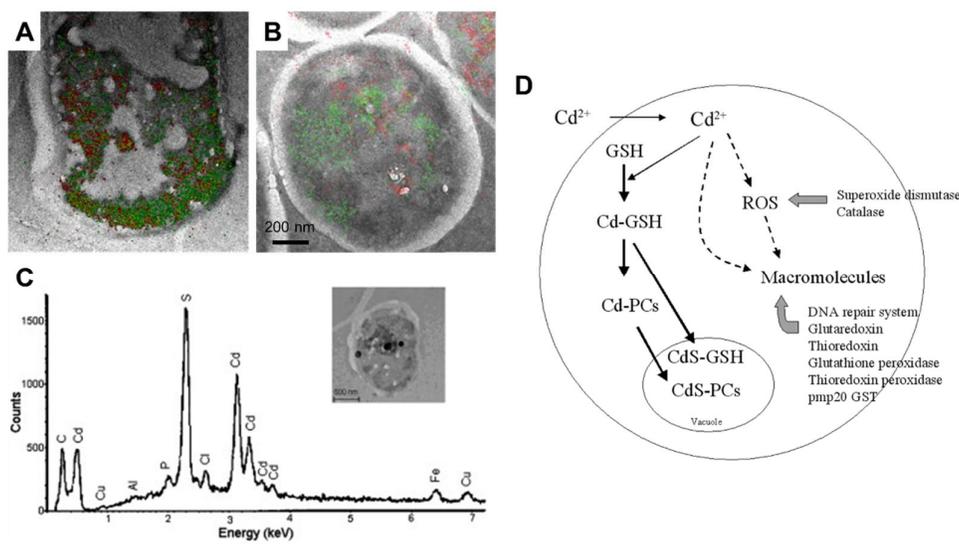
416 In order to produce CdS nanoparticles, some microorganisms use proteins that not only reduce sulfate
417 or cysteine but also work as capping agents. For example, a putative cystathionine γ -lyase (smCSE)
418 produced by the aerobic gram-negative bacillus *Stenotrophomonas maltophilia* strain SMCD1 mediates
419 a reaction between cadmium acetate and L-cysteine to direct the synthesis of nanocrystals of 2 to 4 nm
420 (Figure 8).^[119] As a control, bulk CdS precipitates without size regulation when the enzyme is absent.
421 Similarly, a deep-sea bacterium *Pseudomonas stutzeri* 273 uses an enzyme called threonine dehydratase
422 (psTD) that can control the size and structure, as well as to produce H₂S from L-cysteine.^[120] This
423 enzymatic activity ends up producing wurtzite precipitates composed of nanocrystallites of about 4 nm
424 in size. A fungus *Fusarium oxysporum* can also secrete sulfate reductases into the environment in order
425 to produce stable extracellular cadmium sulfide particles in the size range between 5 and 20 nm.^[121]



426 **Figure 8. Features of extracellular cadmium sulfide biominerals produced by the single enzyme smCSE and the**
427 **schematic biomineralization process.** (A) XEDS spectrum confirming the coexistence of Cd and S in the nanocrystals. (B) A
428 HRTEM image of wurtzite CdS nanocrystal viewed along [211] projections. (C) Schematic of proposed CdS quantum dot
429 synthesis by smCSE. smCSE associates with cadmium acetate and L-cysteine present in solution, smCSE degrades L-cysteine
430 to produce H₂S, H₂S produced by smCSE nucleates CdS nanoparticles, and CdS nanoparticles continue to grow upon the
431 continuous generation of H₂S. (Figure adapted from ^[119] with permission)
432

433
434 Yeasts also use peptide-based capping agents, such as phytochelatins (PC_n), to precipitate cadmium
435 sulfides, both inside and outside the cells.^[122] Phytochelatins have been found in plants, fungi, algae
436 and cyanobacteria and is typically produced by the catalytic activity of an enzyme called PC

437 synthase.^[123] The length of the peptide is determined by the concentration of heavy metals. The
 438 production of peptides is especially activated by cadmium, compared to other heavy metals.^[124] The
 439 complex PC-Cd(II) can also further integrate sulfide ions to form intracellular cadmium sulfide
 440 nanoparticles and be stored in cytoplasmic vacuoles by the activity of HMT1 (Figure 9D).^[125,126]
 441 *Saccharomyces cerevisiae* and *Schizosaccharomyces pombe* showed similar diameters in their PC-CdS
 442 complexes (about 2 nm), but different crystal diffraction patterns.^[122] Figure 9 shows the distribution of
 443 cadmium and sulfur elements, as well as cadmium sulfide biominerals within vacuoles of two yeast
 444 species *S. pombe* and *Candida glabrata*.^[127] The process of biomineralization occurs within the
 445 cytoplasm and vacuoles of the yeast. This biomineralization process involving the activity of capping
 446 agents to control the biomineralization was classified as a type of matrix-mediated biomineralization.^[128]
 447



448
 449 **Figure 9. Features of intracellular (cytoplasmic) cadmium sulfide biominerals produced by yeast species and the**
 450 **schematic biomineralization process.** (A, B) EFTEM-ESI images of *S. pombe* (A) and *C. glabrata* (B) (Cd : red, S : green). (C)
 451 EDX spectrum of the element composition of a selected area in a *C. glabrata* cell presented in the inset. (D) A model for the
 452 cadmium (Cd²⁺) detoxification in *S. pombe*. Free cellular Cd²⁺ ions are scavenged initially by GSH, later by PCs, and eventually
 453 sequestered into the vacuoles as a form of nanocrystalline CdS capped with either GSH or PCs. Cd²⁺ ions escaped from the
 454 complexation damage from the cellular macromolecules either directly or via the production of ROS. The cells overexpress
 455 superoxide dismutases and catalase to remove the ROS and other detoxification proteins to restore the damaged
 456 macromolecules. (Figure adapted from ^[126] and ^[127] with permission)

457
 458 As such, biomineralization of cadmium sulfide depends on several mechanisms and appears in various
 459 microorganisms. As presented in Table 1, the size of nanocrystals of cadmium sulfide generally shows
 460 a narrow size distribution and dimensions below 20 nm, regardless of the localization of precipitation.
 461 For the control over particle properties, one single protein or a set of proteins can be associated or
 462 involved in the compartmentalization of the particles. The particle properties cannot be obtained by
 463 simple inorganic reactions with metabolites and metal ions in the environments. Rather, microorganisms
 464 need to produce adequate biomolecules to capture certain metal ions, and further treat them to react
 465 with reductive sulfur species. The nanoscopic capping agents composed of cellular organic matrix lead
 466 to the regulation of particle properties by creating conditions to supersaturate nanoparticles within the
 467 nanoscopic compartment. As mentioned also in other metal sulfide cases, the production of the capping
 468 agents can be regarded as an active cellular control over metal ions in their environments, and the type

469 and size of capping agents also depend on the environmental conditions. Especially for cadmium sulfide,
470 the capping agent complex is further transported into a cellular organelle, which facilitates the
471 biomineral sequestration and storage. Although biominerals created in such a manner lack particular
472 crystal habits and organization, the cellular activities for this biomineralization and associated biological
473 control are relatively closer to BCM than BIM.

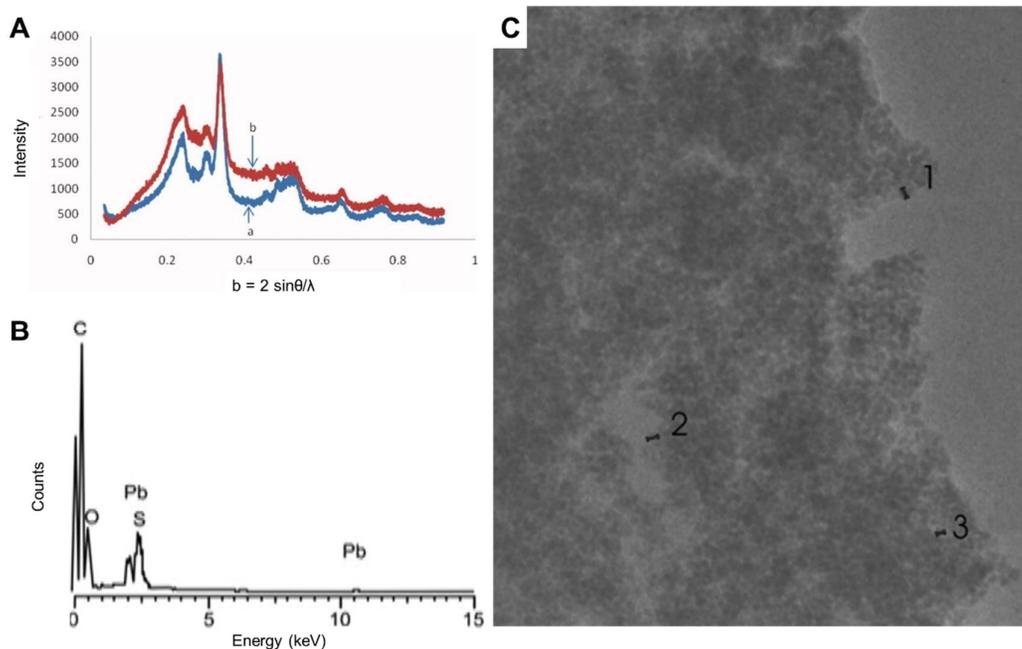
474

475 3.8. Lead sulfides

476 Lead sulfide biominerals are typically associated with a cubic PbS structure and small particle size. The
477 bacterium *Lysinibacillus sphaericus* SH72 produces extracellular particles of 4 to 10 nm in size.^[129] In
478 this case, L-cysteine is not only used as a sulfur source by the bacteria but also as a stabilizing agent of
479 PbS nanocrystals. According to the S-H vibration bond and the EDX spectrum, the presence of organic
480 molecules surrounding particles was proposed.^[129]

481 Yeast species, such as *S. pombe* or *Torulopsis*, are also known to biomineralize CdS but
482 intracellularly.^[130] The particle size ranges from 2 to 5 nm. Capping agents composed of biopolymers
483 are associated with the biomineralization. Intracellular biominerals with similar size distributions are
484 also reported in the marine metal-tolerant yeast *Rhodospiridium diobovatum* (Figure 10).^[131] PbS
485 biomineralization is a widespread phenomenon that also occurs within the periplasmic space in other
486 *Candida* species, but as opposed to CdS or HgS biomineralization, it does not appear within vacuoles
487 in the cytoplasm.^[132] Intracellular biomineralization of lead sulfide has been also reported in a marine
488 bacterium *Idiomarina* sp. strain PR58-8 that synthesizes quantum dots consisting of tetragonal PbS₂
489 with a particle size varying between 2 and 10 nm.^[133]

490



491

492 **Figure 10. Features of intracellular (periplasmic) lead sulfide biominerals produced by *R. diobovatum*.** (A) XRD of PbS
493 nanocrystallites (a) at 96 h and (b) after 6 months of storage. (B) EDX analysis of lyophilized cell pellets containing PbS
494 nanoparticles. (C) TEM micrographs of lyophilized cell pellets containing the PbS nanoparticles. Sizes of bars 1: 6.16 nm, 2: 6.68

495 nm, and 3: 4.81 nm. (Figure adapted from [131] with permission)

496

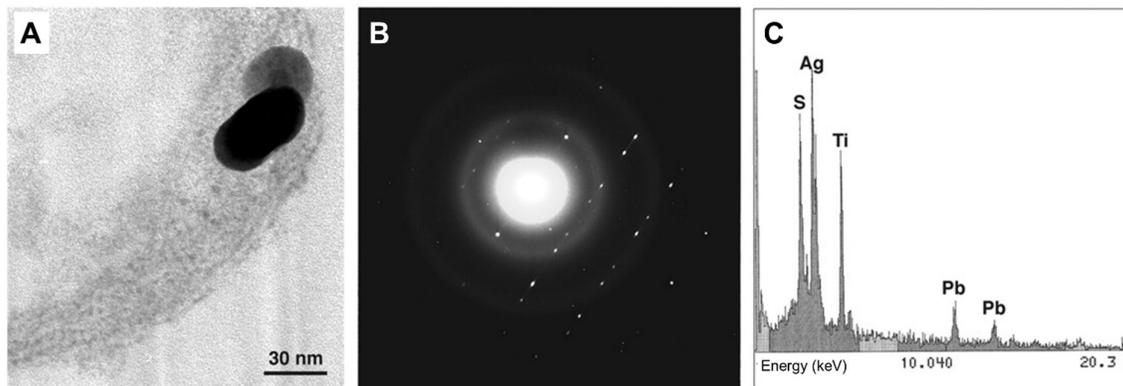
497 Both extracellular and periplasmic lead sulfides commonly show regulation in the size of the biomineral,
498 and in their crystal phase. The lead biomineralization cases occur with active cellular production of
499 biomolecules so that the cells can treat lead ions in their intracellular and extracellular environments.
500 Especially periplasmic biomineralization cases include a surrounding organic matrix composed of
501 chelating molecules along with possible restraints within the periplasmic space. Despite displaying less
502 biological control compared to cytoplasmic biomineralization, the biomineralization of lead sulfides
503 shows some factors matching that of BCM.

504

505 3.9. Other metal sulfides

506 Biomineralization of metal sulfides includes silver sulfide. Silver sulfide nanoparticles composed of
507 Ag_2S are produced using bacteria species such as *Pseudomonas stutzeri* AG259, which deposit Ag_0 and
508 Ag_2S particles sized of up to 200 nm in the periplasmic space (Figure 11).^[134] In the mixed bacterial
509 culture of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, acanthite (Ag_2S) granules are
510 produced on the surface of the bacteria in the presence of sulfide anions and silver cations.^[135] Finally,
511 the yeasts *Candida albicans* and *Candida glabrata* also biomineralize extracellular Ag_2S
512 compounds.^[136]

513



514

515 **Figure 11. Features of intracellular silver sulfide biominerals produced by *P. stutzeri* AG259.** (A) A silver sulfide particle
516 embedded in the periplasmic space of the cell. (B) Crystal diffraction pattern analysis on one of the particles. (C) EDX spectrum
517 and electron diffraction indicating monoclinic Ag_2S . (Figure adapted from [134] with permission, Copyright (1999) National Academy
518 of Sciences, U.S.A.)

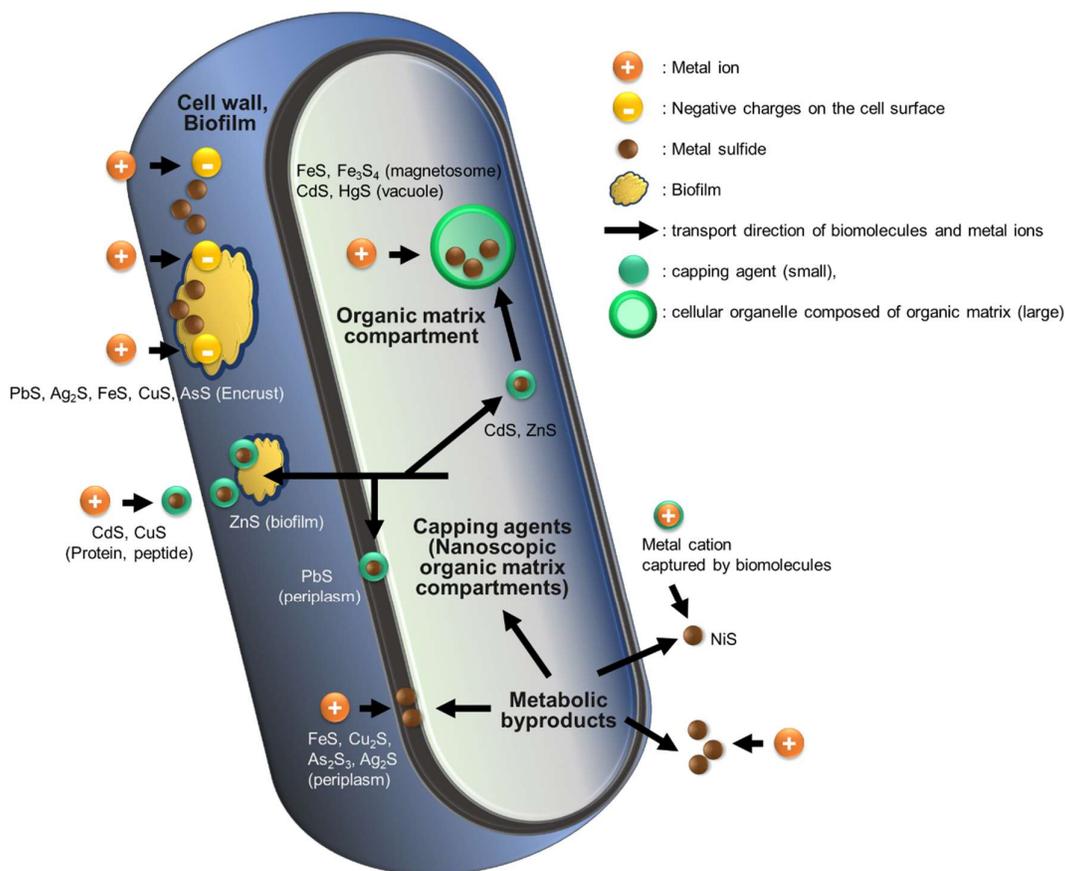
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520 A final example is the biomineralization of mercury sulfide in the yeasts *Candida glabrata*, *Candida*
521 *krusei* and *C. parapsilosis*. These biomineralize extracellular and intracellular mercury sulfide
522 microparticles in acidic conditions.^[132] The intracellular biominerals appear to be stored in a vacuole as
523 in cadmium sulfide biomineralization. As opposed to cadmium sulfide nanoparticles, which are
524 distributed over the cell with controlled size to remain as nanoparticles, mercury sulfide particles mostly
525 stay agglomerated in a few regions within the cell.

526

527 **4. Summary and outlook**

528 Here, we have reviewed the microbial metal sulfide biomineralization providing a comprehensive
 529 overview of the known biomineral diversity. A large variety of biomineralization mechanisms were
 530 identified, depending on both the metal species and the microorganism. The breadth of metal sulfide
 531 microbial biomineralization is summarized in Table 1 and schematically presented in Figure 12. Briefly,
 532 metabolic byproducts obtained from bioreduction of sulfur-containing molecules are first released and
 533 then react with metal ions to produce the biominerals. This process can be mediated by a single or
 534 multiple biogenic macromolecules. For example, biopolymers from EPS, which cover the cell surface,
 535 contribute to biomineralization and thereby further control the properties of biomineralized particles,
 536 such as their size, composition and morphology. Proteins and peptides produced by microorganisms are
 537 released into their intracellular space as well as the extracellular environments to regulate the metal
 538 toxicity by chelating the dissolved metal ion species. A peptide like phytochelatin can chelate heavy
 539 metal ions, sequester metal sulfide particles in and out of the cell, and further store the particles within
 540 a cytoplasmic organelle.



541
 542 **Figure 12. Schematic illustration on types of metal sulfide biomineralization processes in an alive microorganism.** Metal
 543 ions react with metabolic byproducts as well as other types of biogenic organic molecules, such as capping agents or components
 544 from cell substrate or biofilms. Depending on metal species, microorganisms use different strategies of biomineralization for
 545 protection and other life activities.

546

547 For the biomineralization process, microorganisms use various mechanisms to control different metal
548 species in the environment or in the cell as their resources. Microbial cells import or decrease
549 concentration of metal ions by releasing biomolecules in the environment, export metal ions back into
550 the extracellular environments, or even store them in different cellular locations. For sulfur resources,
551 the H₂S production through sulfate reduction or L-cysteine degradation is the main driving force of the
552 process.

553 Extracellular metal sulfide biomineralization results in that the biominerals have distinguishable
554 chemical and/or morphological features from abiotically-produced precipitates obtained under the same
555 condition. E. Peltier *et al.* suggested that the properties of these biogenic metal sulfide particles originate
556 from a slower release rate of H₂S into the environment than what typically occurs with abiotic
557 syntheses.^[39] Molecular crowding effect and surface charges from the cells could also contribute to
558 general properties of biominerals. Moreover, the properties of many extracellular metal sulfides
559 biominerals are controlled by organic matrices, such as peptides, proteins or biofilm components, which
560 exert a control over the particle composition, crystal structure, shape, size, resistance to dissolution,
561 and/or agglomeration of nanocrystallites.

562 In contrast, the highest control in metal sulfide biominerals is found in the intracellular formation of
563 iron sulfide magnetosome particles, which satisfies all the criteria for BCM. Cadmium sulfide and
564 mercury sulfide biomineralization have also been observed in cellular organelles, within cytoplasmic
565 vacuoles, while some cadmium sulfide particles appear to stay captured in capping agents within the
566 cell. Some intracellular biomineralization cases, such as in iron sulfide cases, were reported in the
567 periplasmic space as well. The latter generally show features obtained in the biologically-induced or
568 less controlled manner, which results in random size distribution or morphology of the particles.
569 Compared to those cases, periplasmic lead sulfide biomineralization shows a higher control over size
570 distribution, composition or morphology, originating from the involvement of biomolecules working as
571 capping agents.

572

573 **4.1. Remark on the classification of biomineralization based on the degree of control**

574 Following environmental changes, microorganisms actively control gene transcription, biomolecule
575 production, and sometimes type and speed of their metabolism. Even slight changes in environmental
576 factors can accordingly lead to distinct particle properties in biomineralization processes. Therefore, the
577 reactions of microorganisms to environmental factors can be regarded as a type of cellular control that
578 microorganisms exert over biomineralization as well. Such biological controls, however, are not
579 adequately presented by the conventional description of BIM. In addition, both BFM and BIM mostly
580 occur together in living organisms, especially in the epicellular biomineralization cases. Therefore, the
581 distinction between BFM and BIM is not clear apart from the BFM case occurring by dead cell debris.

582 The distinction between BIM and BCM is intricate and ambiguous as well. Indeed, nanoscopic capping
583 agents, composed of proteins or peptides, could be regarded as a compartment to generate isolated
584 environments for precipitation of metal sulfides. The polymeric capping agents, that are often found in
585 extracellular biomineralization, lead to unique features in material properties. C. T. Dameron and D. R.
586 Winge previously described the biomineralization involving peptides as organic matrix-mediated
587 biomineralization,^[58,128] which is a former term for BCM.^[137] Other example is EPS-based arsenic
588 sulfide nanotubes that show morphological controls with variable chemical compositions. Such cases

589 show all the aspects of BFM, BIM and BCM. In addition, R. B. Frankel and D. Bazylinski already
590 mentioned that many intracellular cases, such as vacuolar inclusions, which correspond to the cadmium
591 sulfide or mercury sulfide biominerals, are difficult to be classified under one category either BIM or
592 BCM.^[55]

593 Therefore, and as A. Veis suggested, it might not be useful anymore to clearly distinguish among
594 conventional categories of biomineralization based on the degree of control in biomineralization.^[60]
595 Rather it is important to understand the degree and range of the biological control for each type of
596 biomineralization, which could help in the understanding of the biomineralization mechanisms.

597

Table 1. Types and features of metal sulfide biominerals and factors influencing their biomineralization

Metal sulfide	Phase	Organism	Morphology (Size, shape)	Factor for biomineralization or other information	Location	Comparison with abiotic precipitates or pure BFM	Ref
Iron sulfide	FeS ₂ (pyrite), FeS (mackinawite)	Desulfovibrio desulfuricans	Flake-like aggregates, thin biofilm of FeS, hundreds of nm Spherules within the film	The presence of ferric phosphate nanoparticles (for pyrite formation)	Extracellular, Biofilm	Different morphology (framboidal pyrite in the abiotic condition)	[68]
	Fe ₃ S ₄ (greigite), FeS (mackinawite), FeS ₂ (pyrite)	Mixed culture of SRB consortium (Lake Pavin, France)	Rounded beads, spherules, encrust	Aging (the size of spherules and phases)	Extracellular, epicellular	Different phase (Pyrite and greigite only detected in the biological condition)	[69]
	Fe ₃ S ₄ (greigite), FeS (mackinawite), FeS ₂ (pyrite)	Thermococcales	Cuboidal, irregular, 30-70 nm	Biofilm, extracellular vesicle	Extracellular (biofilm)		[138]
	Fe ₃ S ₄ (greigite), FeS (mackinawite)	Desulfovibrio hydrothermalis AM13	Irregular, tissue-like, Encrust	Incubation time (for greigite formation)	Extracellular, epicellular	Larger aggregates than abiotic condition but smaller than dead cell debris, more growth than nucleation of mackinawite, greigite only in the biotic condition	[69]
	Fe-S (amorphous)	Desulfotomaculum nigrificans, Desulfovibrio desulfuricans	Irregular, 10-50 nm	Bacteria type (Not observed in Escherichia coli, apart from when sulfide is treated)	Intracellular, extracellular	Different morphology (more separated than when sulfide is provided)	[73]
	Fe _{1-x} S (pyrrhotite), FeS ₂ (marcasite), FeS (mackinawite)	Desulfovibrio vulgaris	Encrust in periplasm, Spherical, oval, 20-200 nm	Electron uptake and metabolic rate are faster with precipitates	Intracellular, extracellular, epicellular		[139]
	FeS (mackinawite-like)	Desulfotomaculum sp. DF-1	Encrust, hundreds of nm random aggregates		Extracellular, epicellular		[90]
	FeS (amorphous, mackinawite), Fe ₃ S ₄ (greigite)	Desulfovibrio vulgaris	4.4 nm (pH 8.6, 4 days), 12.6 nm to 23.9 nm (pH 6.9, 16 days)	pH value, sulfide accumulation (accelerating transformation)	Extracellular		[140]
	Fe ₃ S ₄ (greigite)	Desulfamplus Magnetovallmortis strain BW-1	Pleomorphic, lacking well-defined crystal habit	Magnetosome proteins	Intracellular		[78]
	Fe ₃ S ₄ (greigite)	Uncultured MTB (Single cell MTB, Morro Bay, CA, USA)	~ 60 nm, Width/length ratio 0.2-0.4 in elongated particles, axis of elongation parallel to the magnetosome chain, Fe oxide shell	Magnetosome membrane and proteins	Intracellular		[20]
	Fe ₃ S ₄ (greigite), FeS (mackinawite), Cubic FeS (tentative presence)	Uncultured MTB (single cell MTB and MMP, Morro Bay, CA, USA)	Equidimensional or slightly elongated, 30-120 nm	Magnetosome membrane	Intracellular		[66]
	Fe ₃ S ₄ (greigite)	Uncultured Candidatus Magnetomorum litorale (MMP, Wadden Sea, Germany)	Bullet-shaped, a few arrowhead-shaped, 91 ± 21 nm (length) and 40 ± 6 nm (width)	Magnetosome proteins	Intracellular		[79]
	Fe ₃ S ₄ (greigite)	Uncultured Candidatus Magnetoglobus multicellularis (Araruama Lagoon, Brazil)	Pleomorphic, average 88 nm (length), 71 nm (width)	Magnetosome membrane and proteins	Intracellular		[141]
	Fe ₃ S ₄ (greigite)	Uncultured MTB (MMP, Lake Yuehu, China)	Rectangular, 102 ± 14 nm (length) and 78 ± 13 nm (width)	Magnetosome membrane and proteins	Intracellular		[142]
	Fe ₃ S ₄ (greigite), FeS ₂ (pyrite - later disputed)	Uncultured MTB (MMP, Salt Pond, MA, USA)	Roughly cuboidal, parallelepipedal, flake-shaped, irregular, average 75 nm		Intracellular		[143]
Mixed metal sulfide containing iron	NiS, Fe/NiS, FeS	Desulfotomaculum sp. DF-1	Encrust, random aggregates	Ni-binding polypeptides, Bacterial surface	Extracellular, epicellular	Ni inhibits FeS production	[90]
	Polyphasic (millerite, polydymite, violarite, mackinawite, pentlandite dependent on Ni/Fe ratio)	Desulfovibrio vulgaris DSM 644	Spheroidal, 100-200 nm	Aging (better crystallinity), pH value (more Fe ratio in the particle), Fe concentration (smaller particle, less crystallinity)	Extracellular	Different phase, more crystallinity, larger size, crystal structure distortion by substitution	[91]
	Fe-rich covellite, nukundamite (Cu ₅ FeS ₈), chalcopyrite (CuFeS ₂), Cu-rich mackinawite	Desulfovibrio vulgaris DSM 644	Nanocrystals, nanorods, nanoplates, a few large aggregates (100-200 nm) of fine crystals	Cu/Fe ratio (larger particle in higher Fe concentration), pH value, Chalcopyrite is formed through incorporation of Fe into covellite	Extracellular	Similar morphology, larger size, lower crystallinity	[10]
	Cu-containing magnetosome of Fe ₃ S ₄ (greigite), FeS ₂ (pyrite - later disputed)	Uncultured MMPs (Morro Bay, CA, USA)	Pleomorphic	Cu/Fe ratio differs in particles from the same organism (0.1 to 10 at%)	Intracellular		[94]
	Cu-containing magnetosome of Fe ₃ S ₄ (greigite), FeS (mackinawite), Cubic FeS (tentative presence)	Uncultured MMPs and single cell MTBs (Different places)	Equidimensional or slightly elongated, 30-120 nm	Cu content (slower transformation)	Intracellular		[66]
Nickel sulfide	Ni-S, Co-S	Mixed culture of SRB		Ni-binding protein, concentration of other metal	Extracellular	Higher solubility of Ni	[144]
	α-NiS, NiS (amorphous)	Mixed culture of Desulfosporosinus auripigmenti and Citrobacter freundii	Aggregates and encrust of fine particles (< 5 nm)		Extracellular, epicellular	Better crystallinity (amorphous in the abiotic condition)	[95]
	Ni ₃ S ₂ (heazlewoodite), NiS ₂ (vaesite at 60°C)	Mixed culture of SRB	Disordered, tissue-like	Incubation time (thinner morphology), higher temperature (better crystallinity)	Extracellular	Different phases (mix of heazlewoodite and vaesite in the abiotic condition), Better crystallinity	[96]
	α-NiS, NiS ₂ (vaesite), Ni ₃ S ₄ (polydymite)	Desulfovibrio vulgaris DSM 644	Spheroidal vaesite (< 20 nm), euhedral (100-300 nm), irregular polydymite (10-20 nm)	Presence of other metal	Extracellular	More crystallinity, different morphology	[91]
Copper sulfide	CuS (covellite)	Desulfovibrio vulgaris DSM 644	Nanocrystals (<10 nm), nanorods (20-40 x 6-9 nm), nanoplates (~30 nm)		Extracellular	Smaller size, less crystalline	[10]
	CuS (covellite)	Mixed culture of SRB	Tissue-like	Higher temperature (better crystallinity)	Extracellular	Different morphology, smaller size, less resistance, less crystallinity (related to slower precipitation rate)	[92]
	Cubic Cu ₂ S	Fusarium oxysporum	Spherical, 2-5 nm, surrounded by spherical peptide shells (20 nm)	Potential peptide (20 nm shell)	Extracellular		[101]
	CuS, Cu ₂ S	Mixed culture of SRB		Extracellular polysaccharide (enhancing Cu concentration)	Extracellular (biofilm)		[145]

	Cu ₂ S (chalcocite)	Geobacter sulfurreducens	Spherical, 10-90 nm	Anoxic condition	Intracellular, extracellular, epicellular	Smaller size (100-200 nm in BFM by dead cell debris)	[102]
Zinc sulfide	ZnS (similar to sphalerite, amorphous)	Desulfovibrio sulfuricans		Production speed	Extracellular	More crystalline, more resistance to oxidation	[39]
	ZnS (wurtzite, sphalerite)	Uncultured SRB (peatland near Manning, NY, USA)	Framboidal aggregates, 12-14 nm (wurtzite), ~ 48 nm (sphalerite)	Seasonal change (organism types), other metal impurity (stacking fault), organic matter debris (morphology)	Extracellular		[103]
	Cubic ZnS	Rhodobacter sphaeroides	4 nm (25 h), 12 nm (35 h)	Culture time	Extracellular (Intracellular nucleation and discharged)		[146]
	ZnS (sphalerite)	Uncultured SRB of the family Desulfobacteriaceae (Piquette Pb-Zn mine, WI, USA)	Spherical aggregates (< 10 µm) of fine particles (2-5 nm)	Biofilm	Extracellular (biofilm)		[147]
	ZnS (mainly sphalerite, wurtzite)	Uncultured SRB (Piquette mine, WI, USA)	Spheroidal aggregates (1-5 µm) of fine particles (1-5 nm)	Polymeric coating	Extracellular (biofilm)		[105]
	Hexagonal zinc sulfide	Aspergillus flavus	Spherical, 18-60 nm (DLS), 12-24 nm (TEM) (due to the presence of ionic layer)	Capping agent (protein)	Extracellular, epicellular		[110]
	Cubic ZnS	Serratia nematodiphila	Spherical aggregates (80 nm) of fine spherical particles (average size 7 nm)	Nucleation effect, presence of proteins binding with the particles	Extracellular		[109]
	ZnS (sphalerite)	Thermoanaerobacter	Aggregates (21.5 ± 6.0 nm, 11.8 ± 2.7 nm) of fine particles (2-10 nm, depending on thiosulfate concentrations)	pH value, aging, concentration of salts (sulfur source)	Extracellular		[148]
Cubic ZnS	Saccharomyces cerevisiae MTCC 2918	30-40 nm		Intracellular, extracellular		[149]	
Arsenic sulfide	As ₂ S ₃ , As ₂ S ₅	Mixed culture of As ^v -reducing and SO ₄ ²⁻ reducing bacteria	Aggregates of fine particles, encrust	pH value	Extracellular, epicellular		[111]
	As ₄ S ₄ (β-realgar)	Clostridiaceae strain YeAs	Encrust, dendritic, tissue-like	Anaerobic condition	Extracellular, epicellular		[150]
	As ₂ S ₃ (orpiment)	Uncultured fungal colonies from seafloor (several locations)	Filamentous nanotube	Hot flow enriched with H ₂ S	Entire cells of fungal colony killed by hydrothermal fluid	Different phase and morphology	[117]
	As ₂ S ₃ (amorphous), realgar (AsS), duranusite (As ₄ S)	Shewanella sp. HN-41	Filamentous nanotube, 20-100 nm (diameter), ~ 30 µm (length)		Extracellular		[113]
	As ₄ S ₄ , As ₂ S ₃ , and As ₄ S ₃	Shewanella sp. strain HN-41, S. alga BrY, S. oneidensis MR-1, S. putrefaciens CN-32	Filamentous nanotube, 10-100 nm (diameter, depending on species)		Extracellular		[114]
	As ₂ S ₃	Desulfotomaculum auripigmentum	Irregular, encrust		Intracellular, extracellular, epicellular	Less sensitive to sulfide or pH value	[112]
Cadmium sulfide	CdS	Pseudoalteromonas sp. MT33b	Cuboidal	Promoted by cysteine	Epicellular		[151]
	CdS	Idiomarina sp. OT37-5b	Cuboidal, irregular	Promoted by cysteine. Potential association of particles with harvesting energy through light energy	Epicellular		[118]
	CdS (amorphous)	Clostridium thermoaceticum	Starved cells : amorphous with small electron-dense granules	Promoted by cysteine	Extracellular, epicellular		[152]
	CdS (wurtzite)	Escherichia coli	2-5 nm	Capping agent	Intracellular, extracellular		[153]
	CdS (six-coordinate rock-salt structure)	Schizosaccharomyces pombe	Aggregates of fine particles (1.8 nm)	Capping agent (phytochelatin)	Intracellular, extracellular		[128]
	CdS (intermediate between rock-salt and the naturally occurring zinc-blende four-coordinate structure)	Candida glabrata	Aggregates of fine particles (2 ± 0.3 nm)	Capping agent (phytochelatin)	Intracellular, extracellular		[128]
	CdS (Zinc-blende structure)	Stenotrophomonas maltophilia strain SMCD1	2-4 nm	Capping agent (smCSE)	Extracellular		[119]
	CdS (wurtzite)	Pseudomonas stutzeri 273	84.53 nm, crystallite size of 3.7 ± 0.4 nm	Capping agent (psTD also as a catalytic enzyme, L-cysteine also as a substrate)	Epicellular		[120]
	Hexagonal CdS	Fusarium oxysporum	5-20 nm	Secretion of sulfate reducing enzymes	Extracellular		[121]
	Cubic CdS	Rhodospseudomonas palustris	8.01 ± 0.25 nm	Intracellular enzymes	Extracellular (Intracellular nucleation and discharged)		[154]
Cubic CdS	Rhodobacter sphaeroides	Spherical, 2.3 ± 0.15 (36 h), 6.8 ± 0.22 (42 h), and 36.8 ± 0.25 nm (48 h)	Culture time, C-S-lyase	Intracellular, extracellular		[146]	
Lead sulfide	PbS (galena)	Bacillus cereus sp. Abq	4-10 nm	Anaerobic condition, Promoted by cysteine	Extracellular, epicellular	Different phase (no PbS formation in abiotic condition)	[155]
	Cubic PbS	Lysinibacillus sphaericus SH72	Spheroidal aggregates (~ 105 nm) of fine particles (5-10 nm)	The band gap shift (quantum size effect), Capping agent (L-cysteine)	Extracellular		[129]
	Cubic and hexagonal PbS	Torulopsis	Spherical, 2-5 nm	Small bandgap	Intracellular		[130]
	Cubic PbS	Rhodospiridium diobovatum	Spherical, well-dispersed, 2-5 nm	Capping agent coating with protein-bound thiols	Intracellular		[131]
	Tetragonal PbS ₂ (β-PbS ₂)	Idiomarina sp. strain PR58-8	Spherical, 2-10 nm		Intracellular		[133]
	CdS, PbS	Bacillus megaterium	10-20 nm	pH value (yield), no H ₂ S production	Extracellular		[156]
Other metal sulfide	MnS (rambergite)	Shewanella oneidensis MR-1	Aggregates (50-200 nm) of fine particles	EPS	Epicellular, extracellular		[157]
	Monoclinic Ag ₂ S	Pseudomonas stutzeri AG259	Equilateral triangles and hexagons, up to 200 nm		Extracellular, epicellular, intracellular(periplasm)		[134]

Ag ₂ S (acanthite)	Mixed culture of Thiobadillus ferrooxidans and Thiobacillus thiooxidans	Spherical, tens of nm		Epicellular	[135]
Ag ₂ S	Candida albicans, Candida glabrata			Extracellular	[136]
HgS (cinnabar), Cubic PbS (galena), cubic CdS (hawleyite)	Candida species (C. albicans, C. glabrata, C. krusei, C. Parapsilosis)	Bunch-like clusters (CdS)		Intracellular(HgS, CdS), epicellular(PbS)	[158]

599

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606

607 Conflict of interest

608 The authors declare no conflict of interest.

609

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613 biomineralization • extracellular biomineralization • intracellular biomineralization • metal sulfide •
614 metal sulfide nanoparticles • organic matrix

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828

829 **Biographies**

830 Yeseul Park

831 Yeseul Park obtained her BSc in chemistry and nanoscience in 2013 from the Ewha Womans University

832 (SIP). She completed a material science MSc program organized by the Technical university of Munich,

833 the University of Augsburg and the University of Munich. She worked at BASF and at Max Planck

834 Institute for Polymer research as a research intern and later at LG electronics. Currently, she is pursuing

835 her Ph.D. at Aix-Marseille University in France, working at CEA Cadarache under the supervision of

836 Dr. Damien Faivre with focus on biomineralization of magnetic materials and metal sulfides.

837 Dr. Damien Faivre

838 I am broadly interested by the interactions between life and inanimate. I looked for traces of Life on

839 rocks during my PhD (Institute of Earth Physics, Paris, France; and Caltech, Pasadena, USA). I tried

840 forming nanoparticles with controlled properties using biomacromolecules during my post doc (Max

841 Planck Institute of Marine Microbiology, Bremen, Germany). My group (Max Planck Institute of

842 Colloids and Interfaces, Potsdam, Germany) studied calcite biomineralization, the effect of

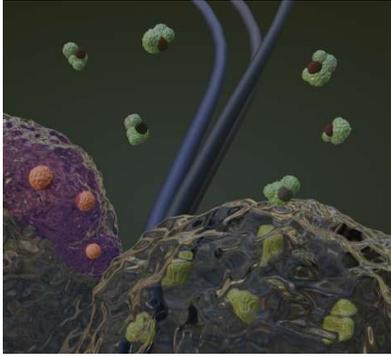
843 nanoparticles on eukaryotic cells, microswimmers or how magnetic nanoparticles can be used in a

844 medical context. I finally joined the Bioscience and Biotechnology Institute of Aix Marseille in 2018

845 (CEA Cadarache, France) where I continue this diverse research.

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866 In this review paper, types of general interactions among microorganisms with metal species are first
867 discussed, which is followed by general classification of microbial biomineralization. In this context,
868 distinctive features and mechanisms found in biomineralization of metal sulfides are introduced with
869 several examples by the atomic order. Some environmental factors are presented, together with biogenic
870 molecules that are used to regulate biomineral properties. Finally, common factors for unique features
871 in each biomineral are summarized with authors' general remarks on biological control in
872 biomineralization.