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Mineral Formation by Microorganisms

Concepts and Applications

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Preface

Biomineralization is recognized as a multifactorial and complex phenomenon that results in the formation of various mineral crystals. In this regard, studies have shown that microorganisms play a key role in the formation of some types of minerals. These minerals can be formed either intracellularly or extracellularly in order to sustain microbial life. Some of these biominerals are produced in an active form while the others are induced in a passive form. This *Microbiology Monographs* volume examines various forms of microbial mineral formation and their role in microbial domains. Furthermore, common techniques for studying biomineral-producing microorganisms, factors affecting biomineralization, and the use of this process in real-life applications are demonstrated. All chapters of this book are written by world-renowned scientists who are regarded as leaders in their areas of expertise. First chapter of this book, by Abdullah and others, considers the microbial domains and their role in the formation of minerals. Intracellular and extracellular bacterial biomineralization is written by Jroundi and others in second chapter. Geophysical monitoring and characterization of biomineralization processes are discussed by Ntarlagiannis and others in third chapter. In fourth chapter, Skeffington and others discuss the molecular genetics of microbial biomineralization, while fifth chapter covers silicate minerals induced by microorganisms that is written by Brindavathy and others. Sixth chapter by Jantschke covers non-silicate minerals (carbonates, oxides, phosphates, sulfur-containing compounds, oxalates, and other organic crystals) induced by microorganisms. In seventh chapter, magnetosome biomineralization by magnetotactic bacteria is discussed by Cypriano and others. In eighth chapter, Joshi and others discuss the factors affecting biomineralization, while in ninth chapter, Lamérand and others deal with the experimental modeling of carbonate mineral precipitation in the presence of cyanobacteria. Finally, Akyel and others cover the key applications of biomineralization in tenth chapter. This book could serve as a unique reference book for the emerging topic of microbial mineral formation. Professionals, researchers, academic staff, and students across science and engineering would benefit from this book. We truly hope the approach and

methods adopted throughout this book will give the reader an understanding of the principles of biomineralization process.

Enjoy the book.

Hamilton, New Zealand

Aydin Berenjian
Mostafa Seifan

Contents

Microbial Domains and Their Role in the Formation of Minerals

Shorish M. Abdullah, Kamal Kolo, Kurt O. Konhauser, and Mohammad Pirouei

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Abstract Bioformation of minerals is found in almost all living organisms. It is one of the important biochemical processes shared by organisms from all three domain systems (eukaryotes, archaea, and bacteria) but with different structural and functional aspects. Biominerals play diverse roles and functions in the life cycle of living organisms, and, many of which are yet to be explored. These roles involve providing mechanical strength and support, protection, gravity sensor, storage, magnetotaxis and magnetic navigation, homeostasis, and a sink of toxic metals through metal complexation. In some organisms, there can exist a combination of more than one function. Similarly, one biomineral may have a different function among organisms that belong to the same domain system. For example, in eukaryotes, calcium carbonate biominerals in the form of calcite have the role of mechanical strength in the cuticle of crustacean, while the same biomineral plays a gravity sensor role in the inner ear of mammalian. Among all living organisms, microorganisms, especially bacteria, fungi, and algae, are among the most active microorganisms in the production of biominerals, playing an essential role in the biogeochemical cycle of elements since the emergence of life on Earth due to its ability to grow under different habitat and environmental conditions. In this chapter, the types of biomineralization by microorganisms and the processes of interaction of microorganisms with mineral surfaces are reviewed altogether as well as their role in recycling of elements, environmental impact, and how they reshaped the Earth's surface.

1 Microbial Biomineralization

Biomineralization is the formation and deposition of minerals and processes contributing to the creation of these organic-inorganic composites (Weiner and Dove 2005; Estroff 2008). This process holds a special position in life sciences because, unlike other biological transformations, which at best leave no lasting signature on the environment or a tenuous scribble, the formation of hard bioinorganic materials such as bones and shells is recorded in fossil records (Mann 2001). Minerals formed by living organisms have investigated. Lowenstam (1981) reported 31 biominerals distributed in the organisms belonging to all three domain systems. In the past four decades, expanding knowledge about the processes of biomineral production and understanding Earth's past and future evolution, biological mineralization has advanced to the forefront of various science fields. As a result, the amount of identified biomineralization products formed from different phyla is more than 86 different minerals, and this number continues to increase (Table 1).

The most comprehensive reason for producing new biogenic minerals is due to the fact that the original precipitates of minerals may vary from the form in which they are eventually stabilized, or one mineral may substitute for another during organism development (Lowenstam 1981). This fact imparts to biominerals two specific characteristics that can be distinguished from non-biogenic minerals, and these characteristics are as follows: (1) they have specific morphologies and

Table 1 Overview of biominerals formed by direct and induced metabolisms and the organism(s) involved

Mineral	Name	Chemical formula	Example of involved organism	References
Oxide	1. Magnetite	Fe_3O_4	Chiton's teeth, tuna/salmon (head) Bacteria (controlled): magnetotactic bacteria, Fe(III)-reducing bacteria, sulfate-reducing bacteria, thermophilic iron-reducing bacteria Bacteria (induced): *Geobacter metallireducens* and *Shewanella putrefaciens*	Frankel et al. (1983), Lovley (1991), Zhang et al. (1997), Mann (2001), Bazylinski and Frankel (2003), Bazylinski and Williams (2007), Konhauser (2007)
	2. Hematite	Fe_2O_3	Fe-oxidizing chemolithotrophic bacterium (*Gallionella ferruginea*)	Hallberg and Ferris (2004)
	3. Maghemite	γ-Fe_2O_3	Thermophilic iron-reducing bacteria, *Actinobacteria* sp.	Zhang et al. (1997), Bharde et al. (2008)
	4. Manganese oxides	Mn_3O_4	Bacteria (*Pseudomonas putida*, *Leptothrix discophora*, *Bacillus* sp.)	Brouwers et al. (2000), Villalobos et al. (2003), Tebo et al. (2004)
	5. Ilmenite	$Fe^{+2}TiO_3$	Fe-oxidizing bacteria: *Acidithiobacillus ferrooxidans*	Navarrete et al. (2013)
Hydroxides and hydrous oxides	6. Goethite	α-FeOOH	Fe-oxidizing chemolithotrophic bacterium (*Gallionella ferruginea*) Lichen on metamorphic rocks, feldspars, granite, and gneiss (*Parmelia conspersa*, *Parmelia tiliacea*, *Xanthoparmelia conspersa*) Limpet's teeth	Galvan et al. (1981), Mann (2001), Hallberg and Ferris (2004)
	7. Akaganeite	β-FeOOH	Bacteria	Gebeshuber (2016)
	8. Lepidocrocite	γ-FeOOH	Marine bacteriophage, *Bacillus subtilis* Sponges (filaments), chiton (teeth)	Châtellier et al. (2001), Mann (2001), Daughney et al. (2004)
	9. Ferrihydrite	$5Fe_2O_3 \bullet 9H_2O$ or Fe_5HO_8. H20	Fe-oxidizing chemolithotrophic bacterium (*Gallionella ferruginea*),	Hallberg and Ferris (2004)

(continued)

Table 1 (continued)

Mineral	Name	Chemical formula	Example of involved organism	References
			Leptothrix ochracea, *Bacillus subtilis* Animal/plant (ferritin), chiton (teeth), beaver/rat/fish (tooth surface) Lichen action on augite and olivine of basalt (*Pertusaria corallina*), lichen on recent lava flow (*Stereocaulon vulcani*)	
	10. Ferric/iron oxyhydroxide	$Fe(OH)_3$ (approx.)	Iron-oxidizing bacteria	Jackson and Keller (1970), Jones et al. (1981), Mann (2001), Hallberg and Ferris (2004)
	11. Green rust	$2Fe(OH)_3 \bullet Fe(OH)_2$ (approx.)	Bacteria (*Shewanella putrefaciens*)	Chan et al. (2009)
	12. Humboldtine	$FeC_2O_4 \bullet 2H_2O$	Lichens: *Acarospora smargdula*, *Aspicila alpina*, *Lecidea lacteal* on iron-rich crystalline limestone and cupriferous rocks	Gadd (2007)
	13. Birnessite	$Na_4Mn_{14}O_{27} \bullet 9H_2O$	Bacteria (*Pseudomonas putida*) Fungi (*Cladosporium* sp., *Alternaria* sp.), siderite boulder, and Typic Natraqualf soil	Golden et al. (1992), Villalobos et al. (2003), Kukkadapu et al. (2004)
	14. Todorokite	$(Mn^{+2}\ CaMg)\ Mn_3{}^{+4}$ $O_7 \bullet H_2O$ $Mn_4\ O_7 \bullet H_2O$	Fungi: *Penicillium* sp., *Mucor* sp., *Rhizopus* sp. in cave deposits and waters	Cunningham et al. (1995)
Carbonates	15. Calcite	$CaCO_3$	Bacteria: sulfate-reducing bacteria, cyanobacteria, soil bacteria (*Bacillus megaterium*) Fungi: Myxomycetes (stalactite), Hyphomycetes, *Fungi imperfecti* (quaternary eolianites and calcretes),	Went (1969), Kahle (1977), Thompson and Ferris (1990), Verrecchia et al. (1990), Boetius et al. (2000), Mann (2001), Reitner et al. (2005), Lian et al. (2006), Gadd (2007), Sherman et al. (2015)

			Cephalotrichum sp., *Penicillium corylophilum*, *Penicillium simplicissimum* Lichens: *Caloplaca aurantia*, *Verrucaria* spp. Algae, archaea, coccolithophores (cell wall scales), foraminifera (shell), trilobites (eye lens), molluscs (shell), crustaceans (crab cuticle), birds (eggshells)	
	16. Aragonite	$CaCO_3$	Cyanobacteria (*Synechococcus leopoliensis)*, *Nesterenkonia halobia*, *Halomonas eurihalina* Scleractinian corals (cell wall), molluscs (shell), gastropods (love dart), fish (head)	Rivadeneyra et al. (1998, 2000), Mann (2001), Obst et al. (2009)
	17. Vaterite	$CaCO_3$	Bacteria (*Kocuria*, *Myxococcus xanthus*, *Bacillus sphaericus*) Gastropods (shell), ascidians (spicule)	Mann (2001), Rodriguez-Navarro et al. (2007), Zamarreño et al. (2009)
	18. Monohydrocalcite	$CaCO_3{\bullet}H_2O$	Crustaceans (crab cuticle), plants (leaves)	Mann (2001)
	19. Dolomite	$CaMg(CO_3)_2$	Bacteria (*Nesterenkonia halobia*)	Rivadeneyra et al. (2000)
	20. Mg calcite	$(Mg_x\ Ca_{1-x})\ CO_3$	Octocoral (spicule), echinoderms (shell/spines)	Mann (2001)
	21. Siderite	$FeCO_3$	Thermophilic iron-reducing bacteria, bacteria (*Shewanella alga*)	Zhang et al. (1997), Parmar et al. (2000)
	22. Rhodochrosite	$MnCO_3$	Bacteria (*Leptothrix discophora*)	Zhang et al. (2002)
	23. Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Lichen: *Sterocaulon vesuvianum* (mycobiont of lichen in ruins of a lead-smelting mill)	Jones et al. (1982)
	24. Hydromagnesite	$Mg_5(CO_3)_4(OH)_{2\cdot4}{\bullet}H_2O$	Fungi: *Penicillium simplicissimum* cultured with hydromagnesite	Gadd (2007)

(continued)

Table 1 (continued)

Mineral	Name	Chemical formula	Example of involved organism	References
	25. Magnesite	$MgCO_3$	Bacteria: *Bacillus subtilis* *Algae*	Stanley et al. (2002), Han et al. (2019)
	26. Strontianite	$SrCO_3$	Snails, microbes, cyanobacteria	Gebeshuber (2016)
Sulfides	27. Sphalerite (ZnS)	ZnS	Bacteria: *Thiobacillus ferrooxidans*	Fowler and Crundwell (1999)
	28. Wurtzite	ZnS	Sulfate-reducing bacteria	Pósfai and Buseck (1997)
	29. Cubic FeS (sphalerite type)	FeS	Magnetotactic bacteria	Pósfai et al. (1998)
	30. Mackinawite (tetragonal FeS)	FeS	Magnetotactic bacteria, sulfate-reducing bacteria	Ivarson and Hallberg (1976), Pósfai et al. (1998)
	31. Pyrite, marcasite	FeS_2	Magnetotactic bacteria, sulfate-reducing bacteria	Mann et al. (1990)
	32. Pyrrhotite	$Fe_{1-x}S$	Magnetotactic bacteria	Farina et al. (1990)
	33. Greigite	Fe_3S_4	Magnetotactic bacteria, sulfate-reducing bacteria	Farina et al. (1990), Mann et al. (1990), Reitner et al. (2005), Bharde et al. (2008)
	34. Galena	PbS	*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*	Weiner and Dove (2005), Mejía et al. (2012)
	35. Hydrotroilite	FeS·nH2 O	Sulfate-reducing bacteria	Ferronsky et al. (2014)
	36. Acanthite	Ag_2S	Sulfate-reducing bacteria	North and MacLeod (1986)
Arsenates	37. Orpiment	As_2S_3	*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Sulfobacillus sibiricus*	Skinner (2005), Yuan et al. (2010)
Phosphates	38. Hydrous ferric phosphate	$FePO_4•nH_2O$	Bacteria (*Acidovorax* sp.)	Miot et al. (2009)
	39. Vivianite	$Fe_3(PO_4)_2•2H_2O$	Sulfate-reducing bacteria and *Shewanella putrefaciens*, *Alkaliphilus metalliredigens*	Kukkadapu et al. (2004), Zegeye et al. (2007), Roh et al. (2007)

	40. Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Vertebrates (bone), mammals (teeth), fish (scales)	Mann (2001)
	41. Hydroxyapatite/calcium phosphate	$Ca_5(PO_4)_3(OH)$	Bacteria (*Ramlibacter tataouinensis*, *Corynebacterium matruchotii*, *Streptococcus mutans*, *Streptococcus sanguis*)	Streckfuss et al. (1974), Van Dijk et al. (1998), Benzerara et al. (2004)
	42. Dahllite (carbonated hydroxylapatite)	$Ca_5(PO_4,CO_3)_3(OH)$	Fungi: *Candida albicans*	Ennever and Summers (1975)
	43. Octacalcium phosphate	$Ca_8H_2(PO_4)_6$	Vertebrate (bone/teeth)	Mann (2001)
	44. Struvite	$MgNH_4PO_4•6H_2O$	Bacteria (*Myxococcus xanthus*, *Pseudomonas*, *Flavobacterium*, *Acinetobacter*, *Yersinia*, *Corynebacterium, Azotobacter*)	Rivadeneyra et al. (1983), Da Silva et al. (2000)
	45. Brushite	$CaHPO_4•2H2O$	Bacteria: *Burkholderia caribiensis*, *Burkholderia* sp.	Delvasto et al. (2006)
	46. Whitlockite	$Ca_{18}H_2(Mg,Fe)_2^{+2}(PO_4)_{14}$	Vertebrate (bone, teeth)	Thackray et al. (2004), Skinner (2005)
	47. Francolite	$Ca_{10}(PO_4)6F_2$	Sulfate-reducing bacteria	Tribovillard et al. (2010)
	48. Amorphous calcium pyrophosphate	$Ca_2P_2O_7•2H_2O$	Mammalian: (bone/teeth)	Dorozhkin (2010)
	49. Amorphous calcium phosphate (at least six forms)	Variable	Chitons (teeth), gastropods (gizzard plate), bivalves (gills), mammals (mitochondrial and milk)	Mann (2001), Weiner and Dove (2005)
Sulfates	50. Jarosite	$KFe_3(SO_4)_2(OH)_6$	Bacteria (*Sulfobacillus thermosulfidooxidans*, *Acidithiobacillus ferrooxidans, Thiobacillus ferrooxidans*)	Ivarson and Hallberg (1976), Daoud and Karamanev (2006), Ding et al. (2007)
	51. Schwertmannite	$Fe_8O_8SO_4(OH)_6$	Bacteria (*Acidithiobacillus ferrooxidans*)	Egal et al. (2009)
	52. Gypsum	$CaSO_4•2H_2O$	Jellyfish larva (statoconia)	Mann (2001)

(continued)

Table 1 (continued)

Mineral	Name	Chemical formula	Example of involved organism	References
	53. Barite	$BaSO_4$	Algae, loxedes (intracellular), xenophyophores (intracellular)	Mann (2001), Meldrum and Cölfen (2008)
	54. Celestite	$SrSO_4$	Acantharia (cellular)	Mann (2001)
	55. Melanterite	$FeSO_4•7H_2O$	Sulfate-reducing bacteria	Fortin et al. (1996)
Silica	56. Silica	SiO_2	Diatoms, radiolarians, bacteria (*Thiobacillus*, *Bacillus subtilis*)	Urrutia and Beveridge (1993), Fortin et al. (1997)
	57. Amorphous Silica	$SiO_2•nH_2O$	Cyanobacteria (*Calothrix*, *Fischerella* sp.) and *Shewanella oneidensis* Sponges, diatoms (cell wall), choanoflagellates (cellular), radiolarians (cellular), chrysophytes (cell wall scale), limpets (teeth), plants (leaves)	Mann (2001), Konhauser et al. (2001), Benning et al. (2004), Furukawa and O'Reilly (2007), Meldrum and Cölfen (2008)
Halides (halogenides)	58. Atacamite	$Cu_2Cl(OH)_3$	Bloodworm	Weiner and Addadi (2002), Gebeshuber (2016)
	59. Fluorite	CaF2	Skeleton, fish skin, mollusk shells	Wright and Davison (1975), Gebeshuber (2016)
	60. Hieratite	K_2SiF_6	Mammalian gravity receptors	Gebeshuber (2016)
Organic crystals	61. Earlandite	$Ca_3(C_6H_5O_2)_2•4H_2O$	Vertebrate	Barskov et al. (1998), Weiner and Dove (2005)
	62. Whewellite	$CaC_2O_4•H_2O$	Fungi: *Penicillium corylophilum*, *P. simplicissimum*, *Pseudallescheria boydii* cultured in calcium-containing compounds and minerals growth media and naturally on limestone cement microcosms Lichens: *Acarospora rugulosa*, *A. smargdula*, *Aspicila alpine*, *Caloplaca flavescens*, *Cephalotrichum sp.*, *Hypogymnia physodes*, *Lecanora atra*, *Lecanora rupicola*, *Lecidea inops*, *L. lacteal*, *Lobothallia calcarea*	Graustein et al. (1977), Verrecchia et al. (1993), Kolo and Claeys (2005), Gadd (2007), Kolo et al. (2007)

			on basalt, serpentinite, cupriferous rocks, gabbro, dolerite, andesite, and volcaniclastite	
	63. Weddellite	$CaC_2O_4 \bullet nH_2O(2<n<2.5)$	Fungi: *Hysterangium crassum*, *Penicillium corylophilum*, *Penicillium simplicissimum*, *Pseudallescheria boydii.* Cultured in calcium-containing compounds and minerals growth media and naturally on limestone cement microcosms Lichens: *Acarospora rugulosa*, *Aphyllophorales* spp., *Aspicilia calcarea*, *Caloplaca aurantia*, *C. flavescens*, *Geastrum* spp., *Hypogymnia physodes*, *Lecanora atra*, *L. rupicola*, *Lecidea inops*, *L. lacteal*, *Ochrolechia parella* on serpentinite, cupriferous rocks, andesite, and volcaniclastite	Graustein et al. (1977), Kolo and Claeys (2005), Gadd (2007), Kolo et al. (2007)
	64. Glushinskite	$MgC_2O_4 \bullet 2H_2O$	Fungi: *Penicillium simplicissimum* cultured with hydromagnesite Lichen: *Lecanora atra* on serpentinite	Wilson et al. (1980); Kolo and Claeys (2005); Gadd (2007)
	65. Mn oxalate	$MnC_2O_4 \bullet 2H_2O$	Lichen on Mn ore; *Pertusaria corallina*	Wilson and Jones (1984)
	66. Guanine	$C_5H_3(NH_2)N_4O$	Fish, spiders	Gebeshuber (2016)
	67. Sodium urate	$C_5H_3N_4NaO_3$	Human body	Hyndman et al. (2016)
	68. Uric acid	$C_5H_4N_4O_3$	Fungi: *Ustilago maydis*, *Chaetomium trialterale*, *Candida utilis*, *Claviceps purpurea* *Bacteria*: *Bacillus pasteurii*, *Escherichia coli*, *Proteus mirabilis* Plant	Eichhorn et al. (1912), Christians and Kaltwasser (1986), Rando et al. (1990), Costantini (1992), Hafez et al. (2017)
	69. Ca tartrate	$C_4H_4CaO_6$	Plant	Hawthorne et al. (1982)

(continued)

Table 1 (continued)

Mineral	Name	Chemical formula	Example of involved organism	References
	70. Ca malate	$C_4H_4CaO_6$	Plant	Pantoja and Smith (2002)
	71. Ca-oxalate	$CaC_2O_4.xH_2O$ (x unknown)	Lichen: *Verrucaria* sp.	Klappa (1979a, b)
	72. Fe-oxalate	$Fe_2(3C_2O_4)$	Lichen; on Fe-rich crystalline limestone (*Caloplaca callopisma*)	Ascaso et al. (1982)
	73. Cu-oxalate (moolooite)	$CuC_2O_4.nH_2O$ (n~0.1)	Lichen: *Acarospora rugulosa*, *Lecideainops, Lecidea lactea*, *Rhizopogon rubescens*, *Serpula himantioides* on copper-bearing rocks Fungi: *Aspergillus niger*, *Beauveria caledonica cultured with copper-containing compounds and minerals, e.g., copper phosphate*	Purvis (1984), Gadd (2007)
	74. Cd-oxalate	CdC_2O_4	Fungi: *Beauveria caledonica* cultured with cadmium compounds and minerals, e.g., cadmium phosphate	Gadd (2007)
	75. Co-oxalate	CoC_2O_4	Fungi: *Aspergillus niger* cultured with cobalt compounds	Gadd (2007)
	76. Pb-oxalate, Pb-oxalate dihydrate	PbC_2O_4, $PbC_2O_4•2H_2O$	Fungi: *Aspergillus niger*, *Beauveria caledonica* cultured with pyromorphite, or in growth media containing lead compounds	Gadd (2007)
	77. Mn-oxalate	$MnC_2O_4•2H_2O$	Fungi: *Aspergillus niger* cultured in growth media containing manganese compounds Lichens: *Pertusaria corallina* on manganese ore	Gadd (2007)
	78. Mg-P oxalate (struvite)	$NH_4MgPO_4.6H_2O$	Fungi: *Mucor*; *Rhizopus oryzae*	Kolo and Claeys (2005), Kolo et al. (2007)

	79. Sr-oxalate hydrate	$SrC_2O_4•H_2O$; $SrC_2O_4•2.5H_2O$	Fungi: *Penicillium simplicissimum*, *Pseudallescheria boydii*, *Serpula himantioides* cultured with strontium containing compounds and minerals such as strontianite ($SrCO_3$)	Gadd (2007)
	80. Zn-oxalate	$ZnC_2O_4•2H_2O$	Fungi: *Aspergillus niger*, *Beauveria caledonica*, *Rhizopogon rubescens*, *Suillus collinitus* when exposed to zinc oxide, zinc phosphate	Gadd (2007)
	81. Montmorillonite (R=Na+, K+, Ca_2+, Mg_2+) and/or halloysite	$R_{o.33}Al_2Si_4O_{10}(OH)_2•nH_2O$ $Al_2Si_2O_5(OH)_4•2H_2O$	Lichen; action of lichens on rocks (*Parmelia*, *Rhizocarpon, Lasallia* sp.) Fungi; cave deposits and waters (*Penicillium* sp., *Mucor* sp., *Rhizopus* sp.)	Ascaso et al. (1976), Cunningham et al. (1995)
	82. Micas	Biotite => vermiculite	Experimental; Basidiomycetes	Weed et al. (1969)
Native elements	83. Elemental sulfur	S	Bacteria (*Chromatiaceae*, *Beggiatoa* spp., *Thiothrix*, *Thiovulum*, *Thioploca*)	Strohl et al. (1981), Brune (1995)
	84. Elemental gold	Au	Sulfate-reducing bacteria and *Bacillus* sp., *Rhodopseudomonas capsulate*, *Shewanella algae Yeast*, *sponge*	Cunningham et al. (1995), Lengke and Southam (2006), Konishi et al. (2007), Gebeshuber (2016)
	85. Silver	Ag nanoparticles	Fungi	Gebeshuber (2016)
	86. Uranium Uramphite Chernikovite	U nanoparticles $NH_4(UO_2)(PO_4)•3H_2O$ $(H_3O)_2(UO_2)_2(PO_4)$ $•26H_2O$	Bacteria Fungi: *Beauveria caledonica*, *Hymenoscyphus ericae*, *Rhizopogon rubescens*, *Serpula himantioides cultured with uranium-containing compounds and minerals such as uranium oxides and metallic depleted uranium*	Gadd (2007), Gebeshuber (2016)

References Lowenstam and Weiner (1989), Verrecchia (2000), Mann (2001), Weiner and Dove (2005), Heim (2011), Gebeshuber (2016)

chemistry including isotopic signatures, and (2) many of them are composites of minerals and organic matter (Weiner and Dove 2005).

Most of these biologically produced minerals within the biological system are either amorphous, monocrystalline, or polycrystalline. Besides the different functional value of each structure to the organism, the biological system has a unique control mechanism for crystal nucleation, growth, and spatial organization (Mann 1983; De Yoreo and Vekilov 2003). Organisms form their mineralized tissues in a wide variety of different ways and from different minerals (Albeck et al. 1996), but the process to generate biominerals is restricted to two separate pathways. The first process is part of and totally regulated by the cell metabolism process, which enables the organism to precipitate minerals that serve physiologically specific purposes (Konhauser 2007) and is a "biologically controlled mineralization" process that previously was also defined as "organic matrix-mediated mineralization" (Lowenstam 1981) or "boundary-organized biomineralization" (Mann 1986). In the second process, the cells have limited or no control over the production of biomineral, and the precipitation of minerals takes place outside the cell in the open environment, through metabolic activity of the cell or cell interaction with the surrounding aqueous environment (Konhauser 2007). Lowenstam (1981) defined this process as "biologically induced mineralization." By studying both mineralization processes, we can explain how and where the biominerals can accumulate as ions or solid phases, translocation types that can occur, resting places, and end-product transformations (Weiner and Dove 2005).

1.1 Microbial Biomineralization as a Metabolic Process

During the direct metabolism of producing biominerals, microorganisms control the composition, growth, crystal morphology, and final location of minerals through their cellular metabolism activity (Sherman et al. 2015). This control refers to the genetic and biochemical influence over certain minerals' nucleation and growth. Therefore, the formed biominerals have well-ordered crystals with distributions of narrow sizes and species-specific and consistent particle morphologies (Bazylinski and Frankel 2003). Most of the biominerals produced under biologically controlled processes are classified as either intracellular/intercellular or extracellular biomineralization based on the site of the mineralization within a specific cell. But in some instances, minerals do not belong to this classification as minerals initially begin to form within the cell and later proceed outside the cell (Weiner and Dove 2005).

Biominerals produced by the process of direct metabolic actions are required for microbial cells, some of which are important to support their physiological functions and are essential requirements for living in such microorganisms in a specific environment, such as magnetite (Fe_3O_4) and greigite (Fe_3S_4) in magnetotactic bacteria. Magnetotactic bacteria are chemoheterotrophic; they can use nitrate, ferric iron, nitrous oxide, and sulfate as terminal electron acceptors (depending on the type

of strain); but they still use oxygen at a very low rate for magnetite synthesis (Bazylinski and Blakemore 1983; Sakaguchi et al. 1993; Konhauser 2007).

Therefore, magnetotactic bacteria are generally present in the highest numbers at the sediment-water interface or just below it since almost all of them are microaerophiles or anaerobes. These are generally found at the oxic-anoxic interface (magnetite) and the anoxic areas of the habitat (greigite) or both (Bazylinski and Williams 2007; Konhauser 2007).

Spormann and Wolfe (1984) reported that magnetotactic bacteria are oriented within the Earth's geomagnetic field and then use their flagellum to migrate to oxygen-poor sediments, where the desired oxygen and redox levels are located. They named this process "magnetotaxis." Magnetotactic bacteria use magnetotaxis as a navigational tool, increasing the cell's efficiency to find and retain optimum location in vertical chemical and/or redox gradients characteristic of sediments and stratified water bodies (Konhauser 2007). To maintain cell survival, magnetotactic bacteria try to move in an oxic-anoxic interface area. If a cell moves too far up inadvertently and the concentration of oxygen becomes inhibitory, it reverses direction. Likewise, the cell once again reverses the direction and moves back upward once it moves too far down into the soil where the hydrogen sulfide concentrations are prohibitively high (Frankel et al. 1997; Konhauser 2007).

Silicification is another example of the direct metabolic process by some eukaryotes, such as radiolarians and diatoms. Siliceous shells, perhaps the most notable being an armor against zooplankton predation, are the cause of silica used by these eukaryotes. Due to this intracellular content, diatoms generally show lower mortality rates compared to other smaller algae with comparable growth levels (Hamm et al. 2003). Silica may play a role in the pH buffering, which allows bicarbonate to be converted enzymatically into CO_2 in waters in which its concentration is lower than the photosynthesis requirement (Milligan and Morel 2002). Similar to silica-secreting eukaryotes, the formation of shells from calcium carbonate (in the form of calcite $CaCO_3$) by carbonate-secreting organisms such as coccolithophores and foraminifera is another example of direct metabolic processes used by microorganisms (Konhauser 2007).

1.2 Microbial Biomineralization as Induced (Secondary) Processes

As the microbial metabolism activity interacts with the surrounding environment by altering the local pH, removing certain inhibitors, and the saturation state of elements, secondary mineral precipitation happens; this process is termed "biologically induced" mineralization (Frankel and Bazylinski 2003; Dong 2010). In the secondary mineralization process, the surface of the cell wall is important in the induction stage because it often acts as a causative agent for nucleation and subsequent growth of minerals, and the remaining biominerals on the cell surface are evidence of this

phenomenon (Bazylinski and Frankel 2003; Knoll 2003; Van Cappellen 2003). The two main factors involved in mineral nucleation and precipitation on the cell surface are known groups of carboxyl (COOH), hydroxy (-OH), amino (NH_3), and phosphate (PO_4^{3-}) as functional groups that are negatively charged and thus attract positively charged metal cations from natural environments (Beveridge and Murray 1976, 1980; Beveridge et al. 1983; Ferris et al. 1986, 1987). Additional appendages on the cell surfaces, such as lipopolysaccharide (LPS) and extracellular polymeric substances (EPS), help bind metal ions and serve as nucleation sites (Fein et al. 1997; Daughney et al. 2001; Borrok et al. 2005).

Characterization of the formed biominerals by induced mineralization process often shows low crystallinity and heterogeneous chemistry depending on their environment, including variable external morphology, water content, the composition of trace elements, structure, and particle size. Furthermore, the lack of control over mineral formation also contributes to a low mineral specificity and/or to impurities being introduced into the mineral system (Frankel and Bazylinski 2003; Weiner and Dove 2005).

Fortin and Beveridge (2000) and Southam (2000) distinguished the induced biomineralization process on the surface of the organism's cells into two processes and termed active and passive mineralization. Passive mineralization is used when nonspecific cation binding and the presence of the anions that accompany it induce nucleation and mineral production. Nonliving cells can form mineralization in addition to living cells through passive mineralization by exposing negatively charged surfaces that serve as nucleation sites where metal cations are exposed (Urrutia and Beveridge 1993). Biominerals believed to be formed through this process include Fe, Mn, and metal sulfides; metal sulfates, phosphates, and carbonates; metal oxides such as ferrihydrite ($5Fe_2O_3•9H_2O$), hematite (α-Fe_2O_3), and goethite (α-FeOOH); and Fe and Fe-Al silicates (Southam 2000). The production of induced biominerals by active mineralization process consists in the direct redox conversion of different metal ions bound to the cell surface or the excretion of metabolically formed ions, thereby creating minerals (Fortin and Beveridge 2000; Southam 2000; Frankel and Bazylinski 2003). Examples of precipitating biominerals through this process are the formation of iron sulfides by sulfate-reducing bacteria; the promotion of the precipitation of Fe and Mn oxides by raising the pH and increasing the concentration of O_2 through oxygenic photosynthesis and the precipitation of certain minerals by the absorption of bicarbonate from solution and the release of hydroxy anions by cyanobacteria; nucleation of gypsum ($CaSO_4•2H_2O$) on the surface layer in some bacteria and archaea species; and precipitation of calcite ($CaCO_3$) as a result of increasing in pH at the surface layer during photosynthesis (Schultze-Lam et al. 1992; Fortin and Beveridge 2000).

Most biologically induced mineralization studies focused on nucleation and precipitation of biominerals outside the cell, i.e., extracellular, while certain studies show that minerals are deposited inside the cell, which tends to blur the line between biologically induced mineralization and biologically controlled mineralization. For example, in the growth medium with high concentrations of iron, deposition of iron-sulfide particles will happen within cells of some sulfate-reducing bacteria including

Desulfovibrio and *Desulfotomaculum* species (Jones et al. 1976) and unidentified, presumably magnetic, electron-dense particles by several photosynthetic bacteria including *Rhodopseudomonas palustris* and *Rhodopseudomonas rutilis* (Bazylinski 1995). Another example is unidentified iron oxide particles within the dissimilarly iron-reducing bacterium *Shewanella putrefaciens* grown as an electron acceptor in an H_2/Ar environment (Glasauer et al. 2002).

2 The Nature of Microbe-Mineral Interactions and Processes

In the biosphere, microbes play important geoactive functions, predominantly with regard to biotransformation and biogeochemical cycling; mineral transformations, decomposition, mineral-microbial weathering; and the formation of soil and sediments (Gadd 2010). All types of microbes, including prokaryotes and eukaryotes, and their symbiotic relationships, as well as higher organisms, may make an essential contribution to geological phenomena (Gleeson et al. 2007; Konhauser 2007; Gadd 2008, 2010). Examples of geochemical transformations by bacteria include iron, manganese, sulfate, sulfur, silicates, carbonates, phosphates, and other minerals (Gadd 2007; Kim and Gadd 2008; Gadd and Raven 2010), phosphate availability as nutrition for the plant by mycorrhizal fungi (Amundson et al. 2007), and rock weathering by lichens (Gadd 2007).

The primary Earth materials with which microbes interact, from macroscopic to microscopic, are minerals (Dong 2010). In many extreme environments on Earth, microorganisms have been recovered, ranging from deep subsurface crystalline rocks to ancient sedimentary rocks, millennium glaciers trapped under Antarctic ice sheets, acid drainage of mines, hot springs, hypersaline lakes, dry deserts, and hydrothermal structures, including deep-sea vents (Reysenbach and Shock 2002; Johnson and Hallberg 2005; Fredrickson and Balkwill 2006; Dong and Yu 2007; Costa et al. 2009; Dong 2010; Priscu and Christner 2014). Microbes are distributed in different geological environments, and various approaches to their analysis have become a common thread, i.e., mineral microbe interactions link all these studies to the same framework (Edwards et al. 2000; Rogers and Bennett 2004).

According to previous studies on microbe-mineral interactions in natural and artificial environments, the causes behind the microorganisms' attachment to minerals were attributed to (1) defensive mechanisms of microorganisms against extreme environmental and physicochemical stress (Decho 2000) or against predators (Wey et al. 2008), (2) availability of nutrients in minerals (Roberts 2004; Carson et al. 2009), (3) electrostatic contact between charged minerals and components of the cell surface (Roberts 2004; Walker et al. 2004), and (4) association of microorganisms with minerals due to entrapment as a result of mineral precipitation (Fortin et al. 1997; Southam 2005). As a result of this interaction between microbes and minerals, through their effect on the solubility and diversification of minerals,

minerals provide the inorganic nutrients and living environments that lead to microbial growth, activity, and survival; also microbes influence mineral weathering and diagenesis of mineral substrates by altering their physical and chemical state (Edwards et al. 2000; Rogers and Bennett 2004; Gadd 2010).

The mechanism of interacting microorganisms with mineral substrates begins with the dissolution of minerals in the contact area and goes through three stages, (1) adhesion to cells, (2) formation of biofilms, and (3) acquisition of energy and nutrients (Burford et al. 2003), then biomineralizes the local environment directly by induced processes, and alters the mineral surface chemistry and reactivity (Hochella 2002; Burford et al. 2006); within this process, microorganisms also influence elemental speciation and mobility by modulating redox reactions, inducing mineral precipitation, releasing organic and inorganic by-products, and altering mineral degradation levels and mechanisms (Gadd 2000, 2004, 2007). However, the mineral types (Boyd et al. 2007; Mauck and Roberts 2007) and their particle sizes (Albrechtsen 1994; Sessitsch et al. 2001) are the two key factors that affect the distribution and abundance of this process.

Nutrients necessary for microbial growth are found in many rocks and minerals, and microbes can actively extract nutrients from solid materials (Uroz et al. 2009a). Such nutrients are classified into two groups, essential elements (e.g., P, K, F, S, Mg, etc.) and nonessential elements (e.g., Al, Pb, etc.) (Burford et al. 2003). Mineral surfaces containing phosphorus (P) such as apatite, olivine, feldspars, glass, and basalt and iron (Fe) such as hornblende are favored for colonizing microbes due to phosphorus and iron deficit in natural environments due to low solubility of mineral-containing phosphorus and insoluble iron oxides under oxic conditions (Liermann et al. 2000; Kalinowski et al. 2000; Roberts 2004; Rogers and Bennett 2004; Roberts et al. 2006; Mauck and Roberts 2007; Mailloux et al. 2009). Enzyme cofactors such as Cr, Cu, Fe, Mg, Mo, Ni, and Zn are provided by the dissolution of sulfide minerals and ferromagnesian silicates (Banfield et al. 1999; Rogers and Bennett 2004).

The main characteristics that help microorganisms recognize mineral surfaces that provide the required nutrients is their strategy to reach specific sites on mineral surfaces and their ability to change the molecular arrangements on their outer cell membrane and respond to molecular configurations on the mineral surfaces (Lower et al. 2001; Dong 2010). Interaction of certain types of bacteria such as *Shewanella oneidensis* MR-1 with goethite and *Shewanella putrefaciens* with hematite and the use of Fe in anaerobic respiration through dissimilatory iron reduction (DIR) are examples of microbe-mineral interaction characteristic (Lower et al. 2001; Rosso et al. 2003). The factor which plays a vital role in the process of microbial attachment to mineral surfaces and subsequent mineral dissolution is the surface appendages, especially extracellular polymeric substances (EPS) (Barker et al. 1998; Welch et al. 1999). With the existence of EPS and due to the adequate supply of nutrients and the protection from environmental stress and predation, each microbe benefits from living on minerals and rock surfaces and tends to produce signal molecules that attract other organisms to build a community called “biofilm” (Harrison et al. 2005). For such a community, symbiotic relationships between fungi and photosynthetic algae or cyanobacteria in the form of lichens are the best example as they work

together to obtain atmospheric nitrogen and inorganic nutrients trapped in minerals and rocks (Banfield et al. 1999).

3 Microbial Structure in Microbe-Mineral Interactions

Common ways to interact microbes with the mineral surface are through the formation of biofilms and symbiotic activity. Here we focused on the role and functions of both structures in the process of microbe-mineral interaction.

3.1 Biofilms

Biofilms are fixed microbial communities that irreversibly adhere to each other and/or to surfaces or interfaces. They are embedded in 3D structures of extracellular polymeric substances (EPS) that contain multispecies colonies, each of which has its metabolic function, including bacteria, archaea, fungi, cyanobacteria, algae, and other microbial eukaryotes (Costerton 1995; Cuadros 2017). Biofilm formation is a means of survival for microorganisms, which is why microbial biofilms are a feature of life forms in extreme environments such as hot springs or deserts (Costerton 1995). Nearly all solid surfaces (substrata) exhibit biofilms and are responsible for interaction between the solid surfaces like minerals and rocks (subaerial rock surfaces, and in endolithic environments), water bodies (solid-water interfaces), and the atmosphere (solid-air interfaces). Biofilm-controlled metabolic exchange processes globally influence biogeochemical cycles (los Rios et al. 2003; Reitner 2011) by increasing the overall chemical reactivity on mineral surfaces as they develop biological interfaces between the mineral surface and bulk solution, with surface area far greater than an abiotic interface (Cunningham et al. 1997; Brown et al. 1999; Lee and Beveridge 2001).

Microbial biofilm development requires five consecutive stages, beginning with reversible attachment, irreversible attachment, microcolony forming, biofilm maturation, and dispersion (Stoodley et al. 2002). Microbial activity to form biofilms at each stage is affected by some physical and chemical conditions present on the surface of the mineral grains. Physical factors include light, temperature, water content, flow rate, pressure, and density. And chemical factors include pH, alkalinity, redox potential, salinity, the concentration of oxygen and other chemical species (e.g., H_2S, NO_3^-, Fe(III)), and organic composition (e.g., dissolved organic carbon) (Stolz 2000). At the same time, the interaction of physical and chemical factors impacts the lateral expansion and thickness of biofilms (Cuadros 2017) and creates gradients and microenvironments that promote the growth and proliferation of certain species, particularly in biofilms where steep and fluctuating gradients occur (Stolz 2000).

The prominent roles of biofilms in the microbial community are controlling their environment, mineral surface attachment, protection against predation, moisture maintenance, and facilitating communication among individual microbes. The structural and functional integrity of biofilms are the main responsibility of EPS and are known to be the main components assessing biofilm's physicochemical and biological properties (Wingender et al. 1999). EPS consists of 50–90% polysaccharides, glycoproteins, exoenzymes, and nucleic acids (Wingender et al. 1999; Billi and Potts 2002; Cuadros 2017). As fundamental components of biofilms, EPS determine the mechanical stability of biofilms (Mayer et al. 1999), improve the ability of the biofilm community to scavenge water and nutrients from the environment when both are restrictive (Billi and Potts 2002), and protect cells from dehydration by providing a matrix of various water stress proteins and polysaccharides. In addition, the formation of a gel-like network that holds the microorganisms in a biofilm together aids in protecting them from noxious environmental influences (Wingender et al. 1999).

EPS production from fungi mainly depends on the type of fungal strain, physical conditions, and type of rock-mineral composition as a nutrient medium such as nitrogen (in the form of ammonium minerals and nitrate minerals), phosphate minerals (KH_2PO_4 and K_2HPO_4), magnesium sulfate ($MgSO_4{\cdot}7H_2O$), calcium chloride ($CaCl_2$), and sodium chloride (NaCl). Many fungi are known for their ability to synthesize EPS, including higher basidiomycetes, lower filamentous fungi, and yeasts from various environmental fields, and their capability to produce EPS is variable depending on the type, species, and growth condition (Mahapatra and Banerjee 2013). The most physical factors on which fungi rely for EPS production are temperature, pH, oxygen supply, and incubation time. The majority of fungal strains generate maximum EPS at 22°C to 30°C (Lim et al. 2004; Kim et al. 2005; Feng et al. 2010; Wu et al. 2012) and a few at 20°C (Hwang et al. 2003; Pokhrel and Ohga 2007). A pH range from 3.0 to 6.5 is favored by most fungi species for maximum EPS production (Lim et al. 2004; Kim et al. 2005; Feng et al. 2010; Wu et al. 2012), while a few fugal strains prefer alkaline pH ranging between 7.5 and 10 (Hwang et al. 2003; Pokhrel and Ohga 2007; Abdel-Aziz et al. 2012). Most of the EPS-producing fungi are aerobic or facultatively anaerobic, and 4–15 days of incubation are needed for optimum production of EPS by different fungal strains (Shu and Lung 2004).

3.2 Symbiosis

Symbiotic activity is the second common way in which microbes interact with minerals. Symbiosis is a term to describe the biological structure that has arisen as a result of the long-term interaction between two or more different organisms with each other physically and/or metabolically (syntrophic interactions). Health and survival are the main reasons behind this form of collaboration between some organisms (Dattagupta and Zielinski 2011). Mutualisms, commensalisms, and

parasitisms are three types of symbiosis phenomenon that exist in nature. Mutualism is a mutually beneficial relationship in which both organisms benefit, each giving an advantage to the other, allowing them to dominate each other and thus improving their survival chances. Commensalism is where one individual profits and the other remains unaffected. Parasitisms occur when one organism profits and the other is impaired (Combes 1995; Parmentier and Das 2004). However, this classification is not suitable in all situations because sometimes the behavior of the interaction changes depending on the environmental conditions. For example, the interaction of symbiotic mycorrhizal fungi with their host plants is mutualistic symbiosis through nutrient uptake, but this interaction changes to parasitic relationships under high nutrient conditions through the metabolic cost of the plant (Johnson et al. 1997; Sachs and Simms 2006). Similarly, temperature and humidity fluctuations and strong solar radiation on rock surfaces make symbiotic life differ between mutualistic and commensalism interactions (Gorbushina 2007). Generally, symbiosis phenomenon plays an important role in eukaryotic life's origin and diversification (evolution of eukaryotes mitochondria and plastids from bacterial endosymbionts (Margulis 1970); biogeochemical cycles such as global carbon and nitrogen cycling by mycorrhizal symbioses (Jackson et al. 2008; Taylor et al. 2009); nitrogen fixation bacteria on legume root (α- and *β-proteobacteria*) (Venn et al. 2008); geological processes such as mineral and rock weathering by lichens (fungi and algae and/or cyanobacteria) physically and/or chemically (Banfield et al. 1999; Chen et al. 2000); and plant root symbiosis by arbuscular mycorrhizal fungi, or ectomycorrhizal fungi, which involve soil mineral weathering and chemical alteration (Taylor et al. 2009).

4 Role of Microbes in The Recycling of Elements

The perception of geochemical cycles is essential to a proper understanding of the status of an element in different states such as solid, liquid, or gas (Garrels et al. 1975). Different chemical, physical, and biological factors might change the state of an element, and the living matter is a crucial stage in the cycle of most elements (Ehrlich et al. 1977).

Geochemical cycles are natural phenomena, but anthropogenic activities might affect the cycling of the elements (Trudinger et al. 1979). All elements tend to be cycled in the biosphere in specific pathways from the environment to organisms and back to the environment. These quasi-circular paths are known as biogeochemical cycles (Odum 1971). According to Odum (1971), there are two basic groups of biogeochemical cycles: (1) gaseous types in which the main element reservoir is the atmosphere and (2) sedimentary types in which the main reservoir is the Earth's crust. Since all the organisms are made up of elements, they are involved in the cycling of the elements. The cycling of elements as nutrients is vital for ecosystem health and also for supporting life, decreasing the toxic accumulation of the elements. The cycling of some elements such as carbon and nitrogen is specifically important because of their role in greenhouse gasses formation (Follett et al. 2011).

Microbes, as the oldest inhabitants of the Earth, had a considerable role in elemental cycling. During billions of years of coevolution with Earth, microbes have contributed to shaping the Earth's surface, creating an ecosystem habitable for higher organisms, including humans. By some estimates, microbes account for up to half of the biomass on the planet today (Whitman et al. 1998). They thrive in different environments on the Earth, including hot springs, hydrothermal vents, salt and soda lakes, acid mine drainage, and deep subsurface, and thus define the boundaries of the biosphere. Certain types of bacteria such as the anaerobic methanotrophic archaea (ANME) involved in the anaerobic oxidation of methane (AOM) play an important role in the oceans for controlling global methane emission (Huang et al. 2019). Microbes can exchange electrons between cells (Summers et al. 2010; Shi et al. 2016). Electron exchanges between the quinol/quinone pools in the microbial cytoplasmic membrane and extracellular substrates are known as microbial extracellular electron transfer. Microbes with extracellular electron transfer abilities are prevalent in the hydrosphere, where they play crucial roles in the cycling of important elements, including C, N, S, Fe, and Mn (Myers and Nealson 1988; Nielsen et al. 2010; Kappler and Bryce 2017).

Microbes, through interaction with minerals, influence the biogeochemical cycling of the elements such as heavy metals radioactive elements in different environments (Dong and Lu 2012). Both microbes and minerals have large surface areas, and they can sorb large quantities of metals on their surface by electrostatic and surface complexation, and also, the elements in the structure of the minerals can be replaced by metals (Cheng et al. 2012; Lu and Wang 2012; Southam 2012). Therefore, microbes can mobilize the elements by dissolution or precipitation of minerals and consequently affect the mobility and recycling of elements in different media (Lovley 2000; Cheng et al. 2012).

Elements can enter into solution or be removed from solution by adsorption, coprecipitation, and redox transformations. Therefore microbes, by using these mechanisms, are causing the mobility of elements or their precipitation. For example, elements such as uranium and chromium are mobile in a neutral environment in the oxidizing state, but microbes, through changing the redox conditions in the environment to reduced ones, cause the precipitation of these elements as minerals (Dong and Lu 2012).

5 Microorganisms and Bioremediation

Microorganisms, bacteria, archaea, and fungi have been at the center of focus since decades for their biochemical interactions and products in various natural environments. A vast literature exists on their role in the element's geochemical cycles through rocks and minerals dissolution and precipitation in complex aerobic or anaerobic environments, whether that be soil, air, or water or within sediments at or below water-sediments interface (e.g. Gadd 1999; Verrecchia 2000). Most of these interactions, apart from biomechanical ones in case of fungi, involve reducing

or oxidizing reactions between the microorganisms and their surrounding environment. These microbial interactions have been the focus of multidisciplinary studies in economic mineral exploration and biogeochemistry (Ehrlich 1999; Krumbein et al. 2003; Dunn 2007), plant symbiosis, and bioremediation of polluted soils and water (e.g., Das and Dash 2014). Recently, microbial geochemical biosignatures or even fossils have been the extensively investigated as possible traces of extraterrestrial life on Mars (Onstott et al. 2019).

It is this natural and ubiquitous high capacity of microorganisms to interact with the environment elements under various conditions that made them excellent driving agents in environmental bioremediation technologies for organic and nonorganic pollutants in soil and water. This process removes the harmful chemicals by mineralization, transformation, or alteration or degradation that eventually leads to the detoxification of the environment (Shannon and Unterman 1993).

Generally, native microorganisms in a specific environment, such as the soil, naturally carry out bioremediation processes by converting complex organic compounds into simple inorganic compounds with lower or non-toxicity (Chen et al. 2015). Natural bioremediation has been used for wastewater treatment for centuries, but the modern application of bioremediation to treat wastewater and other media is only decades old. For instance, George Robinson first used microbes for degradation of oil spill around the Santa Barbara coast in the late 1960s (US Microbics 2003), and since the 1980s, bioremediation techniques were taken into consideration a lot in the treatment of different pollutants (Shannon and Unterman 1993).

During bioremediation, some redox reactions such as respiration and other biological functions inside the microbial cells produce energy. The requirement of the system for the bioremediation process includes nutrients, an electron donor, and an electron acceptor (Omokhagbor Adams et al. 2020). A good example of such an interaction is the role of *Dehalococcoides mccartyi* bacteria in the bioremediation of chlorinated compounds in ground water through reductive dehalogenation (Löffler et al. 2013)

5.1 Bioremediation Technologies

Bioremediation technologies applied to contaminated sites are largely either in situ or ex situ operations mostly selected upon the type of contaminants, their spatial distribution, accessibility, and cost economics. Of specific importance are two techniques that employ either native bacteria in contaminated sites or injected slurries enriched with contaminant-specific bacteria, techniques known as biostimulation and bioaugmentation, respectively. Biostimulation is referring to stimulating the indigenous microbial communities by injecting electron acceptors (i.e., phosphorus, nitrogen, oxygen, or carbon) and donors (e.g., molasses, vegetable oil) (Elektorowicz 1994; Omokhagbor Adams et al. 2020). The addition of the electron donors and acceptors can increase the activity and population of indigenous microbes, and consequently, the rate of bioremediation will increase (Perfumo et al.

2007). The advantage of biostimulation is that the microbes are native and well suited in the place of contamination. The disadvantages include the following: (a) local geology of the contamination place (such as permeability of the lithology, presence of fractures) will control the pathway of the additive to reach the microbes; and (b) heterotrophic microbes (which are not degraders of contaminants) might compete with the resident microflora for inserted nutrient (Adams et al. 2014).

Bioaugmentation is the introduction of contaminant-specific microbes to the polluted site to remediate contamination by the degradation of the pollutants such as chlorinated solvents and petroleum products. By 1992, there were at least 75 bioaugmentation cultures available commercially for in situ bioremediation (Major and Cox 1992). This method is used when the indigenous microbial communities within the impacted site cannot decompose the wide range of potential substrates present in complex mixtures, such as petroleum (Leahy and Colwell 1990), or they may be in a stressed state due to the recent introduction to the spill. Moreover, the population of the native microbes might not be high enough to degrade all the pollutants, and the speed of decontamination is crucial (Forsyth et al. 1995). In order to have successful bioaugmentation in the field, the inserted microbes should have the ability to decompose most of the pollutants and compete with native microbes. They should also have the ability to move through the fractures of the rock or pores of the sediment to the pollutants (Goldstein et al. 1985). Different factors such as the concentration and chemical structure of the contaminants, the availability of the pollutants to the microbes, the size and nature of the microbial population, and the physical condition of the environment should be considered for choosing and screening the type of microorganisms for bioaugmentation.

5.2 *Bioremediation of Pollutant Environments Affected by Heavy Metals and Radionuclides*

Heavy metals and radioactive elements can enter the environments in different ways, such as waste products of mining (e.g., chromium) or nuclear enrichment (e.g., uranium). The other source of heavy metals and radionuclides is nuclear power plant operations that release contaminants either by accident (such as Chernobyl in 1986 and the Fukushima Daiichi nuclear disaster in Japan in 2011) or due to improper long-term storage of radioactive materials (Dong and Lu 2012). The addition of these elements in high concentrations can result in the pollution of the environment and consequently lead to carcinogenic diseases in human.

Minerals and microbes, through interaction with heavy metals and radionuclides, control their mobility in a different environment (Lovley 2000; Cheng et al. 2012). Both microbes and minerals have large surface areas, and a range of metals and radionuclides can sorb onto their surfaces via electrostatic attraction and surface complexation (Cheng et al. 2012). Thus, any microbial activity that either dissolves

or precipitates minerals would have significant implications for the mobility of these metals. A good way of removing these elements in the contaminated area is to manipulate redox conditions to reduce the metals either chemically or biologically (Cheng et al. 2012). The biological reduction can be promoted by adding nutrients to stimulate native microbial activity (biostimulation) or by injecting certain bacteria (bioaugmentation). Several metal-reducing and sulfate-reducing bacteria can reduce these metals enzymatically. When locally enriched, these reduced metals can form economically valuable deposits (Dong and Lu 2012).

5.3 Bioremediation of Environments Polluted by Hydrocarbons

Hydrocarbons are still among the most common environmental pollutants (Heider et al. 1998). The main source of anthropogenic hydrocarbon contamination is due to its production, transport, chemical processing, and distribution (Farhadian et al. 2008). According to Chen et al. (2015), hydrocarbons are considered toxic materials in the environment and can have a negative impact on it. The ability of the microorganism to degradation of hydrocarbons as an energy source makes them a strong tool for remediation and treatment of the polluted environment by hydrocarbons (Ławniczak et al. 2020).

The study of microbes and determining the type of hydrocarbons that they can metabolize are important since remediation of the sites polluted by hydrocarbons requires a mixture of different microorganisms; this is because the hydrocarbons are composed of different compounds with different chemical structures and each microbial species might metabolize limited range of compounds (Bordenave et al. 2007; Esmaeil et al. 2009).

The bioremediation process depends on nutrient availability and the optimum presence of other factors that support biological functions. These factors include the following:

- Contaminant concentrations: The high concentration of the contaminants may have toxic effects on the present bacteria. In contrast, low contaminant concentration may prevent the induction of bacterial degradation enzymes.
- Contaminant bioavailability: The contaminants that are strongly attracted by sediments or enclosed in the grains of polluted media or diffuse in micropores and microfractures of the sediments can decrease the bioavailability for microbial reactions (ICSS 2006).
- Site characteristics: The environmental conditions of the site, such as pH (optimum range 6–8), temperature (rate of microbial activity increases with increasing of temperature to some extent), water content (the optimum amount of water is 12–25%), nutrient availability (as an electron donor that can be added in a useable form or via an organic substrate amendment), and redox potential (can be affected

by electron acceptors), are crucial for remediation of the contaminated sites (Leeson et al. 2004; Mukherjee and Das 2005; ICSS 2006).

6 Microbial Role in the Formation of Mineral Ores

In the deep biosphere, microbial communities coexist in complex and poorly known ecosystems where microorganisms play a significant role in the solubility and precipitation of minerals (e.g., Fyfe 1996). Of special scientific and economic interest is the role of these microbial communities in the formation of ore deposits. Since microbes are the main controllers of sulfate reduction, iron-redox reactions, and the oxidation of organic matter, they can impart a significant impact on the formation of different kinds of mineralization, such as banded iron formation (BIF), exhalative massive sulfides (VMS), and secondary metal ores (e.g., Fallick 2001; Konhauser et al. 2002; Nordstrom and Southam 1997). Deposition of the minerals (and ore deposits) occurs by microbes in two different ways and includes intracellularly at the cell surface, for example, on the cell envelope or walls, and as a bulk phase external to the cells. Formation of the minerals in the bulk phase can occur as authigenic or diagenetic. The first condition expels a mineral in a soluble form (i.e., sulfidic mineral) that later at sufficient concentration precipitates. Moreover, in some conditions, the sulfide might reduce soluble ions to insoluble ions and lead to precipitation of the ions. In diagenetic conditions, bacteria can reduce a species and cause its precipitation (i.e., reducing MnO_2 to form $MnCO_3$).

The main physical and chemical condition for the formation of minerals include (a) excess concentration of at least one dissolved component, (b) very low solubility of produced mineral in the environment, (c) appropriate pH in the environment, and (d) stability of the product and redox condition of the environment (Ehrlich 1999).

In recent years, research has focused on the role of microbes in the formation of ore deposits, and here some main important cases will be mentioned. Banded iron formations (BIFs) are the famous ore deposits in the world that were discussed for decades for the microbe's roles in their formation (e.g., Chan et al. 2016; Posth et al. 2013). BIFs are layered ore deposits which contain alternative layers of iron oxides and silica. Mineralogy of the BIFs includes ferric hydroxide ($Fe(OH)_3$), siderite (FeII (CO_3)) (partially secondary), greenalite ($(Fe)3Si_2O_5(OH)_4$), and amorphous silica (Klein 2005). The thickness of the layers varies from micrometer to several meters (Klein 1992, 2005). According to Posth et al. (2013), the formation of BIF is linked to temperature-induced bacterial Fe(II) oxidation to abiotic silicification; this model also can explain the banding of the BIFs.

The role of microbes was studied in the formation of other deposits, such as the formation of sphalerite in carbonate-hosted Zn-Pb ores (Kucha et al. 2010), giant copper deposits (Tornos et al. 2019), and manganese ore deposits (Fan et al. 1999; Yu et al. 2019), and also Dexter-Dyer et al. (1984) studied in detail the microbial roles in the formation of Precambrian ore deposits including gold, uranium, and iron.

7 Reshaping of the Earth's Surface

The Earth's surface serves as a boundary between the atmosphere and lithosphere, and the interaction of tectonic and climatic processes results in a global topography (Sinclair 2014). Two main forces include endogenic and exogenic forces, affecting the Earth's surface, and consequently, they reshape the Earth's surface. Endogenic forces are internal forces powered by the Earth's interior heat engines such as faulting, plate tectonics, earthquakes, and volcanoes. Exogenic are exterior processes that occur on or above the Earth's surface, such as weathering and erosion (Spellman 2020).

Volcanism, as an example of an endogenic force, brings magma from the mantle to the surface or near to the surface of the Earth, causing a reshaping of the Earth's crust. The tectonic setting, as another endogenic force, defines the gross morphology of the oceans.

Weathering and erosion are the main exogenic forces that reshape the crust. During geological time, the Earth's crust has always changed by weathering and erosion continuously. According to Anderson (2019), weathering is the process of rock decomposition occurring in the Earth's critical zone (the permeable layer of Earth) interact. The key point in weathering is that when the rocks formed under certain conditions deep within the Earth are uplifted onto the surface, they change to the new conditions which include temperature, pressure, etc. Many factors affect the rate of weathering, including parent rock, the structure of the area, climate, slope, biological activities, and time. Weathering is categorized into three types: physical, chemical, and biological. Physical weathering is the degradation of the rock by physical processes. In contrast, chemical weathering is the degradation of the rocks by chemical processes. Water and weak acids (i.e., carbonic acid) formed in water are the most critical factor for chemical weathering.

Bioweathering is a process caused by biota activity. During bioweathering, microorganisms, plants, and animals create mechanical forces and metabolic compounds, causing the alteration of the rocks (Uroz et al. 2009b; Brantley et al. 2012). Usually, the bioweathering commences by the activity of chemolithoautotrophic bacteria, which cause the weathering of rocks by using their minerals contents as electron donors (Lopez and Bacilio 2020).

Plants, as another agent of bioweathering, play an important role in the weathering and erosion and, consequently, the reshaping of the Earth's crust. The association of plants and microorganisms is beneficial for both of them (Porder 2019). In rocky substrates, plants supply carbon compounds for microorganisms, which, in return, microorganisms provide nutrients dissolved from primary minerals for plants. This cooperation affects the increase in the rate of rock and mineral weathering (Christophe et al. 2006).

Glaciation is another exogenic force that affects the reshaping of the Earth by the action of glaciers. Earth has experienced several glaciations and interglacial periods. For example, the Earth's crust has been changed severely by glacial erosion in the areas that have been buried by ice.

In desert regions, wind erosion acts as a significant agent in the reshaping of the Earth's surface by transporting and depositing sediment and forming dunes. Moreover, in this area, the communities of cyanobacteria, chlorophytes, fungi, heterotrophic bacteria, lichens, and mosses can enhance the weathering of rocks and contribute to the shaping of the desert landscapes (Thomas 2011). In this environment, the microorganisms use substances such as EPS for absorbing and retaining water, as well as assisting in the adherence of weathering-facilitating organisms to rock surfaces (Mazor et al. 2006).

In the geologic past, colonization of land by early plants and fungi had resulted in major changes on Earth both climatic and bio-morphological. Heckman et al. (2001) in their study on early colonization of Earth by plants and fungi suggested that colonization event produced two major global events: global glaciations so known as Snowball Earth that occurred from 750 to 580 Ma and the "Cambrian life explosion" caused by the Neoproterozoic rise in oxygen. The complex effects of fungal bioweathering leading to lowering of CO_2 and global temperatures (Hoffman et al. 1998), geochemical cycling of elements, and redisposition of new minerals changed the Earth landscape early in its history.

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Intracellular and Extracellular Bacterial Biomineralization

Fadwa Jroundi, Mohamed L. Merroun, Francisca Martínez-Ruiz, and María Teresa González-Muñoz

Contents

Abstract Biomineralization mediated by microorganisms is ubiquitous in nature. This process mostly encompasses phosphate, carbonate, silica and sulphate precipitation as well as iron mineralization. The mechanisms by which microbial biominerals are formed include intracellular and extracellular biomineralization. Minerals produced by microorganisms are often related to environmentally friendly synthesis of metal nanoparticles, which are chiefly more stable than those synthetized through chemical and physical methodologies. Important applications are known for this microbe-mediated mineralization including cultural heritage conservation, pollutant removal, industrial and biomedical applications. This chapter reviews extracellular and intracellular biomineralization that occur in nature mediated by microorganisms as well as their mechanisms. A discussion on the advantages

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of these processes is provided to create a background for future research.

1 Introduction

Microbial biomineralization is the process mediated or indirectly influenced by diverse microorganisms that produce a broad range of mineralized structures (biominerals) (Ehrlich 1999; Mann 2001; Weiner and Dove 2003). Such biominerals are normally localized within some unicellular organisms including different taxonomic groups such as bacteria, fungi and algae (Simkiss and Wilbur 1989).

Concerning the way in which these biominerals are produced, a large difference exists among the different taxonomic groups. After animals, bacteria are the foremost group able to induce the precipitation of minerals, followed by vascular plants and finally fungi and protozoa (Lowenstam and Weiner 1989). To date, more than 60 different biominerals have been identified, being phosphates the most numerous known biominerals followed by oxides, carbonates and sulphates (Crichton and Louro 2019). However, the most commonly found biominerals based on taxonomic distribution are often the carbonate and phosphate salts of calcium that associate with organic polymers such as collagen and chitin to offer mechanical support in bones and shells. These biominerals are strictly controlled from nanoscopic to macroscopic levels, producing complex structures with multifunctional properties. Such a high control over mineral growth is beyond contemporary engineering achievements and is greatly desirable for material design as well as biotechnological applications.

Microbe-mediated mineralization is one of the most studied processes since it can be relatively easily mimicked and is proposed to be a promising biotechnology in medicine, consolidation and restoration of construction materials, metal and radionuclide remediation, enhanced oil recovery and carbon sequestration (Rodriguez-Navarro et al. 2003; Achal et al. 2012; Zhu and Dittrich 2016; Jroundi et al. 2017; Martinez-Ruiz et al. 2018).

In the microbe-mediated mineralization, the so-called biogenic mineralization, microorganisms are able to induce the precipitation of different type of minerals, among which the most widespread are calcium phosphates and calcium carbonates (Fig. 1).

Typically, this process can occur either (1) by highly controlled biomineralization process—"biologically controlled biomineralization"—where highly ordered precipitates are stringently controlled and produced in isolated biological compartments within a living organism or (2) by inducing the precipitation of minerals through processes that involve little or no control over the biomineralization, "biologically induced biomineralization", where the cells do not directly control where or how the precipitates are produced (e.g. Ehrlich 1999; Mann 2001; Weiner and Dove 2003; Seifan and Berenjian 2019).

A broader classification of microbe-mediated mineral production may refer to intracellular and extracellular mineralization. The biologically induced

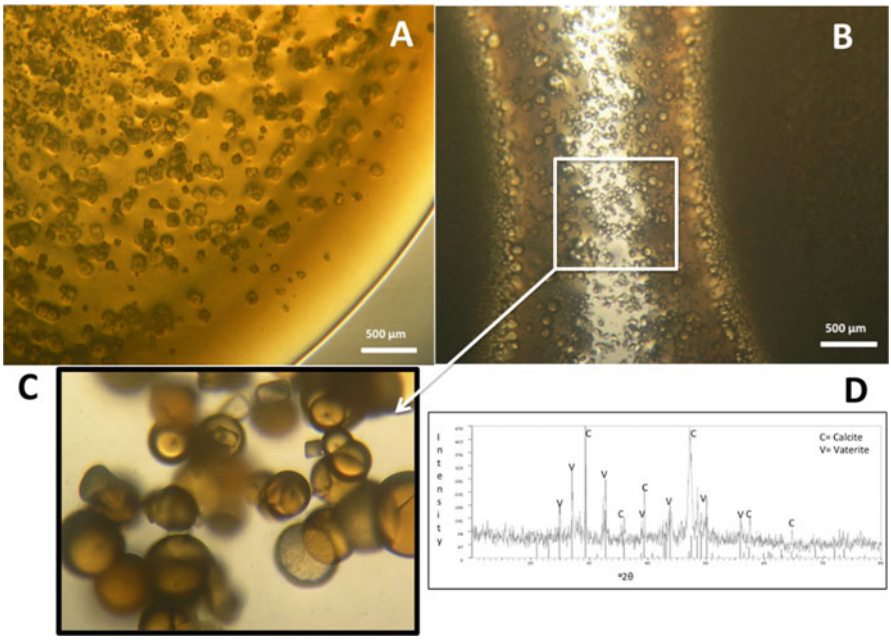

Fig. 1 Biomineralization and precipitation of different crystals mediated by bacteria. (**a**) bacterial colony with precipitated crystals, (**b**) crystal precipitation in the bulk medium, (**c**) details of crystal morphology and (**d**) X-ray diffraction showing calcite and vaterite as the main mineralogical phases

mineralization is typically a result of an extracellular mineralization that originates from a passive cellular mechanism. This type of mineralization is often observed at the surface of the cells, which acts as a heterogeneous nucleation site for the mineral production. In addition, in this case, the organism cannot extensively control the mineral properties because of the widely open system where the mineralization happens. As a result, the particles may appear with various size distributions, and no typical particle morphology is distinguished (Frankel and Bazylinski 2003). In contrast, in the intracellular biomineralization, where the highest degree of control is obtained, the cells form the mineral intracellularly inside dedicated organelles, and the mineral may be then transported extracellularly at a final stage, for example, to the cell surface. In this chapter, we provide an elucidation on the mechanisms by which microbes mediate the mineralization that occurs in nature as extracellular and intracellular biomineralization.

2 Intracellular Biomineralization

Intracellular biomineralization in microorganisms commonly happens in dedicated compartments, where the organism is able to exactly regulate the chemical composition, morphological structure and particle size of the mineral (Bazylinski and Frankel 2003; Lin et al. 2014). For this to occur, elements may enter the cell directly at the site where they will be mineralized, or alternatively, they may be transported to the exact site where mineralization will occur after cell entry. Ions are then concentrated in vacuoles or vesicles—bound intracellularly to the membrane—in an amorphous or highly disordered solid phase that is afterwards transported to the final mineralization site (Weiner and Addadi 2011). Specialized organelles with their own protein systems, such as ion transporters, ion pumps and some ion channels, which may enable the cellular uptake and facilitate the passive diffusion of ions through biological barriers, are often involved in this process. Some chemical or structural modifications of the ion species of interest may occur inside the cell for the temporary storage of the imported elements (Faivre and Godec 2015). Once transported to their deposition site, the elements need to be transformed into the biomineral of interest. For this to happen, the physico-chemical parameters required for nucleation and growth, such as pH or redox potential, may be adjusted by systems for proton translocation or redox-active proteins, such as cytochrome, respectively (Van Driessche et al. 2017).

2.1 The Example of Magnetotactic Bacteria

An excellent example of microbe-mediated intracellular mineralization, and the most studied, is that of magnetotactic bacteria, which use the biologically controlled mineralization (BCM) through a vacuole-based system for the crystallization of magnetic biominerals (Faivre and Godec 2015; Jacob and Suthindhiran 2016; McCausland and Komeili 2020). Magnetotactic bacteria are a diverse group of prokaryotes with the ability to orient and migrate along the magnetic field lines in search for a preferred oxygen concentration in chemically stratified water column and sediments (Lefèvre et al. 2014; Faivre and Godec 2015). Magnetotactic bacteria have high biomineralization ability and can adjust themselves to variety of new environmental conditions (Jajan et al. 2019). They generally biomineralize either iron oxide or iron sulphide in magnetosomes containing crystals of magnetite (Fe_3O_4) or crystals of greigite (Fe_3S_4), respectively.

2.2 Mechanisms of Biomineralization in Magnetotactic Bacteria

The mechanism of controlled magnetite or greigite mineralization in these magnetotactic bacteria is related to a complex system involving several steps that occur inside magnetosomes—membrane-bound organelles. These steps include (1) magnetosome vesicle formation, (2) iron uptake by the cell, (3) iron transport into the magnetosome vesicle and (4) controlled crystal mineralization within the magnetosome vesicle (Bazylinski and Frankel 2003; Yan et al. 2017).

Iron Uptake by Magnetotactic Bacteria Iron can be taken up as Fe^{3+} or Fe^{2+}, under a strict control by the bacteria (Bazylinski et al. 2014). This iron uptake is generally thought to occur by non-specific means since these bacteria possess no unique uptake systems for Fe^{2+}, which is soluble up to 100 mM at neutral pH. The uptake of insoluble Fe^{3+} instead is achieved in most of these microbes by the production of iron chelators called siderophores, which bind and solubilize Fe^{3+} for uptake into the cells (Prozorov 2015). However, some magnetotactic bacteria such as *Magnetospirillum gryphiswaldense* seem to display two iron uptake systems including an energy-dependent process for the uptake of Fe^{3+} and a slow diffusion-like process for the Fe^{2+} uptake, when no evidence for the production of siderophores is found (Schüler and Baeuerlein 1998).

Magnetosome Vesicle Formation It is a complex system involving the invagination and pinching off of the inner cell membrane, as confirmed by electron chromatography on *Magnetospirillum* species. It consists of a lipid bilayer containing a set of phospholipids, fatty acids, some unique proteins and some typical of cytoplasmic membrane but distinct from the outer membrane. The magnetosome membrane has a specific and unique set of proteins very distinct from that of other subcellular compartments (Grünberg et al. 2001; Tanaka et al. 2006). This may be the reason that magnetosomes in almost all magnetotactic bacteria appear to be anchored to the cytoplasmic membrane. However, it is still not clear if the magnetosome vesicle formation occurs prior to magnetite nucleation and precipitation or whether this precipitation is produced in the periplasm and then the invagination of the cytoplasmic membrane occurs around the precipitates (Bazylinski et al. 2014).

Iron Transport into the Magnetosome Vesicle Additional iron must be transported for the crystal growth in the magnetosome vesicle. There is some evidence that MagA, a magnetosome transmembrane protein, is the one responsible for such a transport of ferrous ions into the vesicle, which are eventually oxidized to ferric ions in the presence of aldehyde ferredoxin oxidoreductase (AOR). This protein has significant homology with the cation efflux proteins including KefC (a K^+ translocating protein in *Escherichia coli*) and NapA (a putative Na^+/H^+ antiporter in *Enterococcus hirae*) (Nakamura et al. 1995). However, this protein alone is not responsible for the magnetosome synthesis, but it functions in concert with genes and proteins that are clustered within the so-called magnetosome island,

Table 1 Summary of different magnetosome protein groups (Adapted from Lefèvre and Bazylinski (2013))

Name of cluster	Origin of the name (abbreviation)	Name of protein	Function of protein
Mam	Magnetosome membrane	MamB, MamI, MamL, MamQ, MamY	Membrane formation
Mme	Magnetosome membrane	MamA, MamM, MamN, MamO, MamP	Magnetite crystallization
Mms	Magnetosome membrane specific	MamC, MamD, MamE, MamF, MamG, MamR, MamS, MamT, MmsF, Mms6	Control of particle size
Mtx	Magnetotaxis	MamJ, MamK	Chain assembly
Mad	Magneto-deltaproteobacteria specific		

basically organized around four gene clusters (mms6, mamAB, mamGFDC and mamXY operons) that encode all known magnetosome membrane proteins (Table 1), necessary for biomineralization (Lefèvre and Bazylinski 2013).

Controlled Crystal Mineralization within the Magnetosome Vesicle Fe^{2+} is the precursor of the bacterial magnetite particle. Then, proteins attached to these particles initiate the nucleation and regulate the morphology of the magnetite crystals, while other proteins (e.g. mms6, mamGFDC, msmS, mamT, mamR, mmsF and mamP) promote and regulate the growth of the crystals to their correct shape and size. The crystal growth may be regulated in several steps including the formation of the initial cubo-octahedral particles, followed by anisotropic growth and elongation along the correct direction (Weiner and Addadi 2011; Li et al. 2015). Some external factors such as temperature may also somehow influence the biosynthesis of the magnetite nanoparticles (Mata-Perez et al. 2015). The crystals in the magnetosomes are finally arranged as a chain within the cell, maximizing thus the magnetic dipole moment of the cell and resulting in its passively alignment along magnetic field lines as it swims.

The magnetic nanoparticles produced by these magnetotactic bacteria exhibit peculiar characteristics which include a uniform morphology, thin size distribution, low toxicity and the presence of a biological membrane preventing agglomeration of the particles. All these characteristics make the application of such bacteria an interesting topic in material and medicine science research.

2.3 Other Bacteria Inducing Intracellular Biomineralization

Some other bacteria can also produce tight regulation over the mineralization process, producing uniform crystalline minerals. For example, *Rhodopseudomonas palustris* or *Escherichia coli* can form uniform cubic or hexagonal crystals of CdS nanoparticles, respectively (Sweeney et al. 2004; Bai et al. 2009). However, no clear

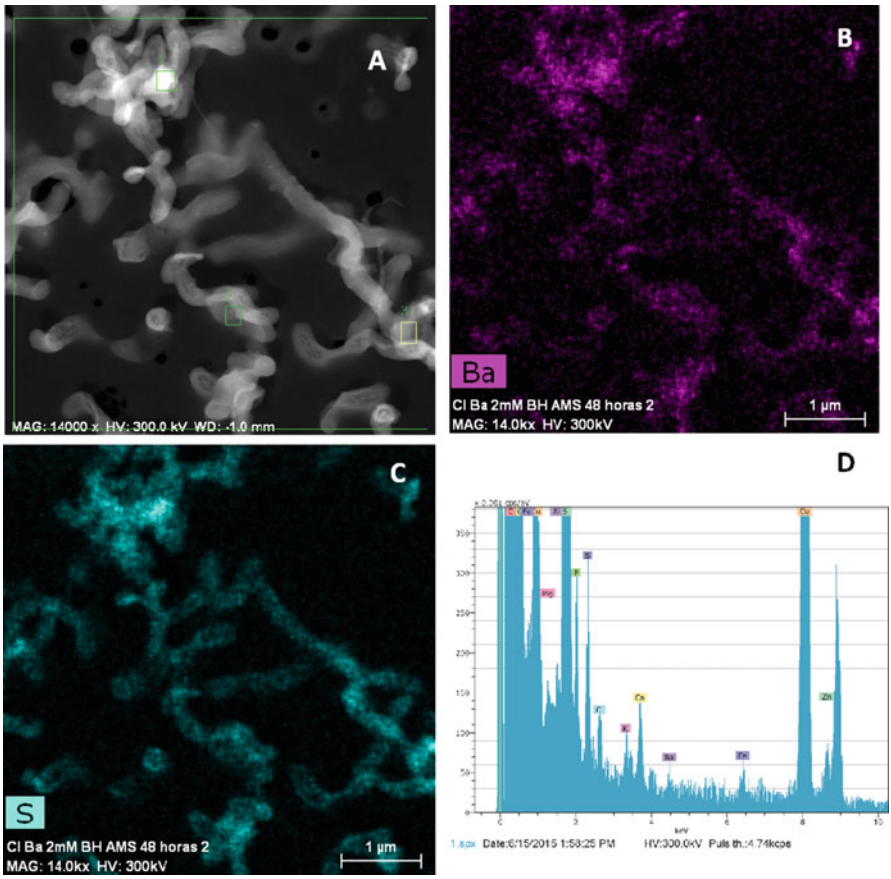

Fig. 2 High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs of thin sections of cells and EPS from marine bacteria showing the intracellular precipitated barite. (**a**) Cells, EPS and Ba precipitates after 48 h of incubation, (**b**) the corresponding EDX map with the distribution of Ba and (**c**) distribution of S, (**d**) EDX spectrum of precipitate 1 in image **a**

mechanisms are known that regulate the biomineralization process in these cases. The intracellular bacterial mineralization is, however in some cases, not subjected to a strict control like that of the above-mentioned bacteria. For instance, *Cyanobacteria* are able to precipitate carbonate deposits inside the cells that have unusual stoichiometry and are amorphous (Couradeau et al. 2012), while *Pseudomonas stutzeri* and *Rhodanobacter* A2-61 can each precipitate three types of crystalline silver or uranium phosphate minerals, respectively (Klaus et al. 1999; Sousa et al. 2013). Also, certain marine bacteria (e.g. *Idiomarina loihiensis*) can precipitate intracellular barium through an amorphous phosphate precursor that evolves to barite crystals (Fig. 2) (Martinez-Ruiz et al. 2018). Other examples of microbial metabolic activities that may result in intracellular mineralization, and where the

biominerals once formed may be exported outside the cell or remain within the cell, include (1) ureolysis (e.g. *Bacillus* sp., which utilizes urea as nitrogen source); (2) nitrate reduction by denitrifying bacteria; (3) ammonia oxidation by nitrifying bacteria; (4) ammonification of amino acids (e.g. the soil bacterium *Myxococcus xanthus*); (5) iron oxidation by iron-oxidizing bacteria; (6) sulphur reduction by sulphate-reducing bacteria; (7) sulphur oxidation by sulphur-oxidizing bacteria; and (8) methane oxidation to bicarbonate under anoxic conditions by methanotrophic bacteria or archaea (Chen et al. 2014; Ehrlich et al. 2015; Zhu and Dittrich 2016).

3 Extracellular Biomineralization

Extracellular biomineralization is a widespread phenomenon that results from the modification of the microenvironment chemistry through microbial metabolic activity and has important implications to natural biogeochemical cycling, industrial applications and environmental remediation (Qin et al. 2020). Many examples of extracellular biomineralization can be evolved such as Fe-oxide formation by Fe(II)-oxidizing microorganisms (Bryce et al. 2018), manganese-oxide formation by Mn (II)-oxidizing microorganisms (Wright et al. 2016), induced calcite formation through alkalinity generated by oxygenic photosynthesis (Dupraz et al. 2009), gypsum formation by sulphur-oxidizing bacteria (Harouaka et al. 2016), metal sulphide formation by sulphate-reducing bacteria (Thiel et al. 2019) or barite precipitation in the ocean water column (Gonzalez-Muñoz et al. 2012; Martinez-Ruiz et al. 2018). In the extracellular mineralization, an active and a passive mineralization process can be established. Active mineralization refers to mineralization by direct redox conversion of specific ions bound to the bacterial surface or by the production of metabolically excreted ions and subsequent formation of the minerals. The passive mineralization, instead, refers to a non-specific binding of cations and the involvement of surrounding anions causing nucleation and growth of minerals (Fig. 3) (Frankel and Bazylinski 2003). The latter can be even mediated by dead cells and their debris, due to the presence of negatively charged surfaces acting as nucleation sites for metal cations. Especially, extracellular polymeric substances (EPS) (Decho and Gutierrez 2017) may be involved in this passive mineralization process. EPS contain negatively charged functional groups whose capacity to bind metal ions has been widely demonstrated (e.g. Braissant et al. 2007; Tourney and Ngwenya 2014; Martinez-Ruiz et al. 2018). Hence, EPS provide nucleation sites to locally enhance ion concentration leading to precipitation. It has been also proved that some microbial minerals as dolomite can precipitate in the absence of living cells through passive mineralization of EPS (Bontognali et al. 2014).

For the extracellular mineralization to occur, there are several requirements that have to be available including (1) sufficient raw materials such as the concentration of dissolved inorganic carbon, (2) pH (often alkaline conditions), provided by the microbial metabolic activities (e.g. sulphate reduction, amino acid degradation and urea hydrolysis), and (3) the availability of nucleation sites.

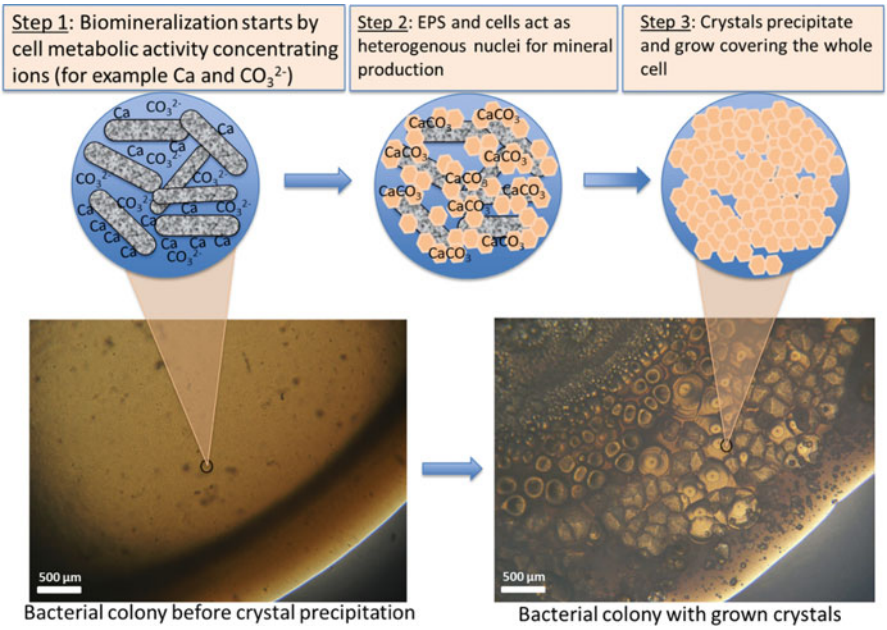

Fig. 3 Overview of passive mineralization steps mediated by bacteria: the case of calcium carbonate precipitation

3.1 Raw Material

Microorganisms that perform extracellular mineralization are firstly in the need to attain sufficient soluble materials, for example, soluble phosphorus for the saprophyte bacteria and fungi, which can lower the pH of their environment to dissolve inorganic phosphate by secreting organic (carboxylic acid) and inorganic acids (e.g. hydrochloric acid) (Wei et al. 2018). Also, microbes can accelerate the release of C and N sources from soil organic matter by increasing their activity and biomass (Alori et al. 2017). The catalysis by enzymes such as alkaline phosphatase is another mechanism for the solubilization and concentration increase of soluble ions (Cosmidis et al. 2015).

3.2 pH

The microbial metabolic activities induce the conditions for the precipitation of the minerals. Microbial metabolism can be described by a series of chemical reactions in which reactants are removed and metabolic by-products are added to the environment. This alters the geochemical environment, including the pH, and finally impacts the precipitation of the mineral. For example, calcium carbonate

precipitation by *Cyanobacteria* is triggered by high rates of oxygenic photosynthesis resulting in the production of large amounts of metabolic products, notably oxygen and organic carbon, and induces bicarbonate dissociation into CO_2 and OH^- increasing the pH of the environment to alkalinity and favouring $CaCO_3$ precipitation (Arp et al. 2001; Altermann et al. 2006). In general, pH can strongly influence the ionic binding since not all ions bind equally and certain functional groups bind ions more efficiently at a given pH. Particularly, acidic pH tends to inhibit ion binding, while neutral or basic pH tends to promote ion binding.

3.3 Nucleation Sites

Bacterial cell surfaces and the surfaces of their extracellular polymeric substances (EPS) likely serve as physical substrate for mineral precipitation, since they provide the ultimate location for the mineral nucleation influencing the crystal morphology and composition. Negative charges on these surfaces can result in cations binding by non-specific electrostatic interactions, effectively inducing local supersaturation. By extension, these nucleation sites are also in most cases passively or actively incorporated within the mineral product. EPS consists of conformations and physical/chemical properties in a range of molecular sizes and has a strong correlation with nucleation because of the presence of polysaccharides, proteins, lipids and even nucleic acids that are actively secreted components (Decho and Gutierrez 2017). The binding capacity of the EPS is supplied by the abundance of functional groups including carboxylic acids, hydroxyl groups, amino groups and phosphate groups, all of which are capable of complexing strongly with metal ions (Decho and Gutierrez 2017). In addition, binding facilitates the stabilization of the surfaces of nascent mineral particles by decreasing the free energy barrier for the critical crystal nucleus formation (Frankel and Bazylinski 2003).

Nucleation on cell surfaces has been also well reported (Picard et al. 2018), for example, formation of palladium or platinum nanoparticles (NPs) on the cell surface of *Desulfovibrio vulgaris* (Martins et al. 2017), production of SeNPs at the extracellular space of *Stenotrophomonas bentonitica* under aerobic and anaerobic conditions (Ruiz-Fresneda et al. 2018, 2019, 2020), the precipitation of calcite and other biomineral crystals exhibited on filamentous fungi (Duane 2016; Menon et al. 2019), the precipitation of meta-autunite (uranyl phosphate) on the cell walls and EPS of *M. xanthus* (Fig. 4) and precipitation of U-P deposits on *Amycolatopsis ruanii* cells (Fig. 5), as well as ion reduction through surface enzymes or proteins present on cell wall or cell membranes for the mineralization of different metallic nanoparticles (Selvakannan et al. 2013; Gauthier et al. 2014; Han et al. 2015; Jäger et al. 2018).

Precipitation within EPS is a common process, particularly in the case of carbonates and also for marine barite (Fig. 6). Thus, the rate of mineralization of amorphous to crystalline mineral particles would become several orders of magnitude faster than with inorganic mineralization, which occurs without surface binding and nucleation.

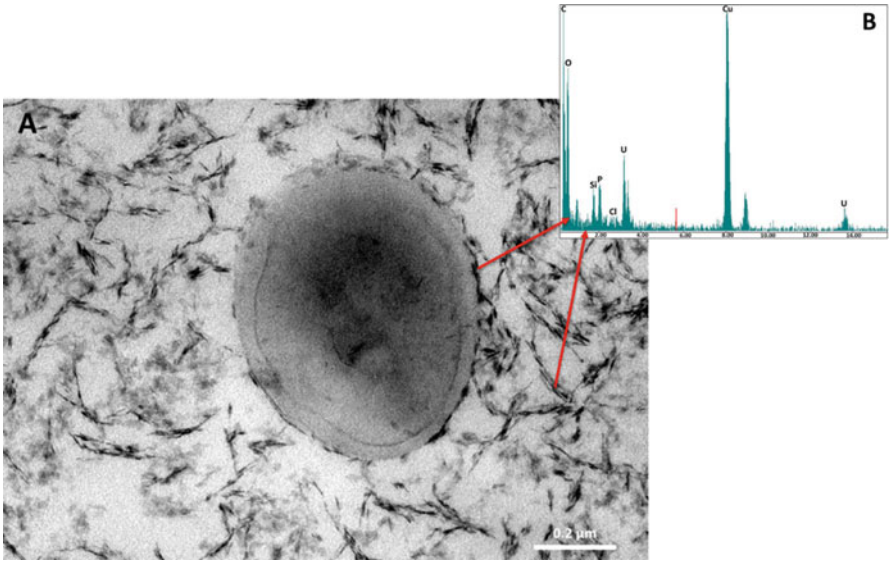

Fig. 4 Biomineralization of uranium by *Myxococcus xanthus*. (**a**) High-resolution transmission electron microscopy micrograph of *M. xanthus* showing the precipitation of uranyl phosphate on cell wall and EPS and (**b**) EDX microanalysis showing the elemental composition of the precipitates

3.4 Crystal Growth

After the nucleation, the subsequent crystal growth is an important process that ultimately determines the morphology and the final size of the crystals. This process may occur layer by layer, by adding single atoms or molecules to the nucleation site. Here, different parameters may induce different growth rate of every single crystal facet, determining thus the crystal morphology (Bahrig et al. 2014). Nevertheless, in some cases, the mineral may entomb the bacterial cells. Microbes in these cases need to balance potential benefits versus the risk of cell encrustation and death. Preventing cell entombment may be achieved by affecting crystal growth, dissolution and absorption reactions with the combined action of modifying the cell surfaces, the secreted organic molecules and the chemistry of the cell microenvironments (Lazo et al. 2017; Mansor et al. 2020).

3.5 Examples of Extracellular Mineralization

3.5.1 Microbial Mats

Microbial mats are attributed to microbial precipitation of carbonate minerals, commonly termed microbialites, and are commonly present in the geologic past

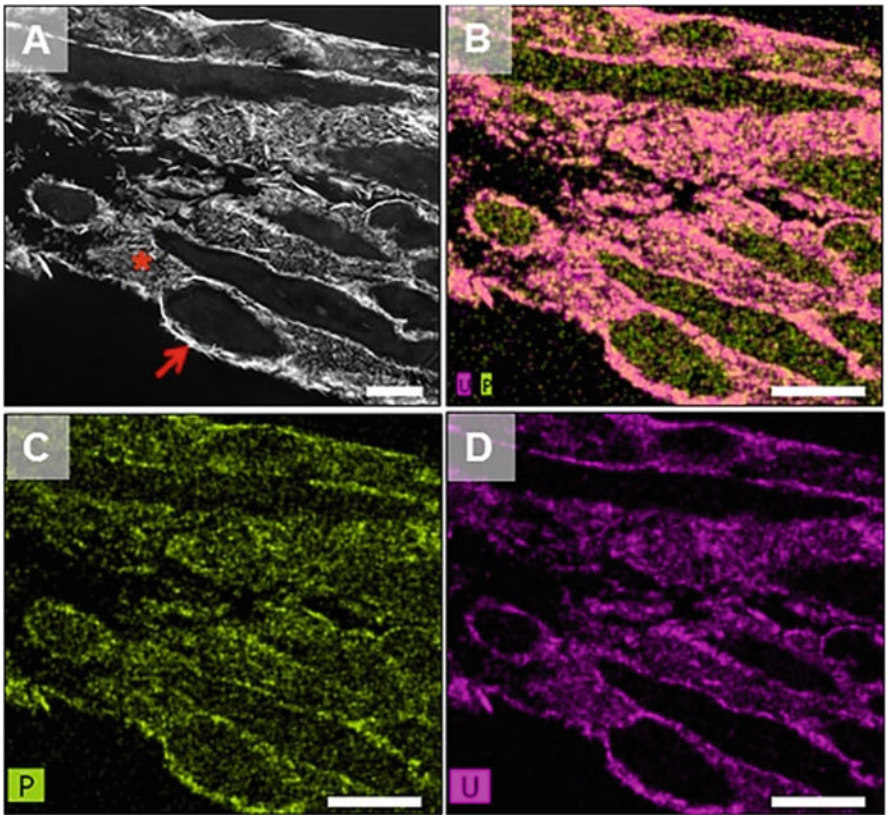

Fig. 5 High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs of thin sections of *Amycolatopsis ruanii*/bacterial consortium (*Bradyrhizobium-Rhizobium* and *Pseudomonas*, BRP) cells treated with uranium and glycerol-2-phosphate (G2P) showing U-P deposits at cell wall level (arrow) and extracellular (asterisk) uranium phosphates precipitates (**a**) and their corresponding EDX maps with the distribution of P (**c**), U (**d**) and P + U (**b**). Bar scale: 500 nm (**a**); 800 nm (**b**, **c** and **d**) (Povedano-Priego et al. 2019)

(Bosak et al. 2013). They are highly organized, laminated communities able to undergo complex interactions with and influence the geochemical environment, impacting the precipitation of minerals, especially calcium carbonate, through extracellular microbially induced mineralization. Microbial mats function as a consortium where particularly high metabolic activity is displayed that continuously changes the geochemical environment, favouring carbonate mineral precipitation (Wilmeth et al. 2018), for example, by changing oxygen profile within the microbial mats, being supersaturated during the afternoon in the mat layers and turning anoxic after the end of the light period (Wieland and Kühl 2006). Microbial mats had a major impact on the development of early atmosphere, through photosynthetic consumption of the greenhouse gas CO_2, and the production of CH_4 and free oxygen (Altermann et al. 2006). Their role in such processes has been crucial throughout the history of the

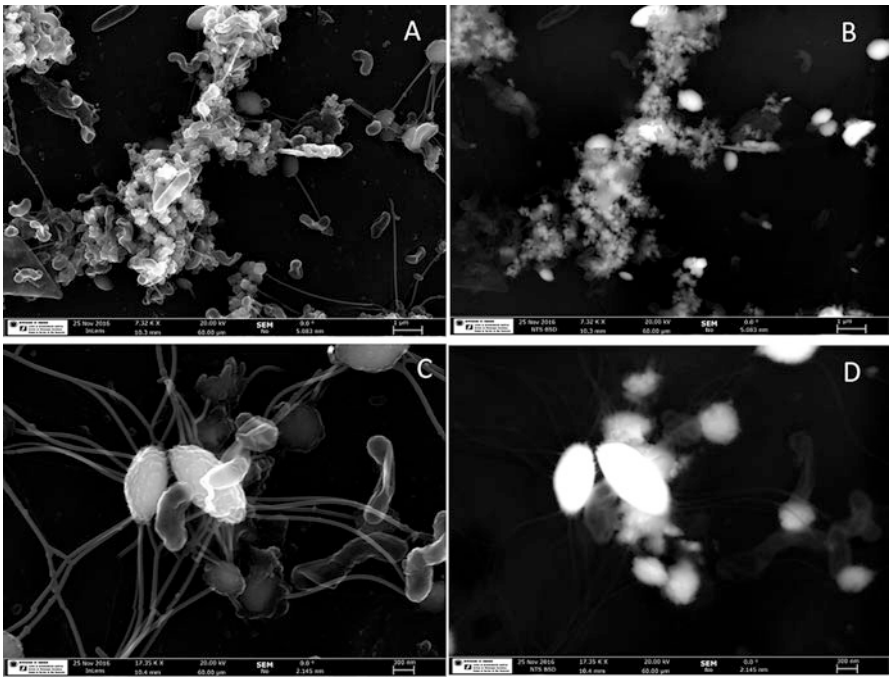

Fig. 6 SEM images of cells and EPS from marine bacteria showing the precipitated barite. (**a**) Cells, EPS and Ba precipitates after 48 h of incubation, (**b**) same image shown in **a** in backscattered electron (BSE) mode, (**c**) details of the bacterial cells and barite precipitates, (**d**) same image shown in **c** in backscattered electron (BSE) mode

Earth, representing the first ecosystems together with stromatolites. They can be found in diverse environmental conditions that are extreme and challenging for many organisms such as high saline concentrations, radiation, low pH and high pressure (Charlesworth and Burns 2016). Undoubtedly, microbial mats can be considered a natural laboratory where microbial diversity (community composition and structure), evolution and adaptation to adverse environments could be vastly studied (Ward et al. 1998; Villanueva et al. 2007; Inskeep et al. 2013). Mineralization within mats that is independent of living microbial activity can be influenced by three factors including concentrations of CO_3^{2-} ions and Ca^{2+} ions and surface chemistry or nucleation centres. The first two factors relate to the saturation state of the calcium carbonate and the third one to the potential for locations to serve as nuclei for carbonate minerals to form (Dupraz et al. 2009), for example, the known role of photosynthetic cyanobacteria in promoting calcium carbonate precipitation (Arp et al. 2001; Altermann et al. 2006; Ehrlich et al. 2015). Yet, specific details on microbes-environment interactions and the potential role of microbial metabolism on mineral products are still not fully understood. It seems, however, that environmental conditions influence the type of precipitation within the mats, specially by controlling the potential impact of microbial metabolism on mineral products. Recently,

Roche et al. (2019) reported the impact of the substrate physical and chemical composition on the development of microbial communities and mineralization potential of tufa microbialite. The authors concluded that suitable substrate physical and chemical conditions were necessary for the potential of lithification and mineral precipitation in microbial mats.

3.5.2 Biomineralization for Remediating Decayed Construction Materials

Microbially induced extracellular biomineralization has been proposed in the recent years as emerging discipline for the protection and restoration of decayed building structures and materials. The method makes use of carbonatogenic bacteria able to biomineralize calcium carbonate for the conservation and restoration of built cultural heritage mimicking what occurs in the nature, as many carbonate rocks have been cemented by the calcium carbonate induced by microorganisms. This technology, considered as a novel environmentally friendly strategy, has been successfully used for solving problems of durability issues in this field. A lot of work have been performed since the affirmation of Boquet et al. in 1973 that the precipitation of calcium carbonate is a matter of several soil bacteria. Other researchers showed the precipitation of carbonates by marine bacteria (Drew 1911; Shinano 1972). Several bacteria were then tested for their ability to precipitate and form crystals including *Pseudomonas* and *Bacillus* species. Afterwards, the microbial origin of limestone and the great resistance of the calcite crusts to erosion were demonstrated resulting in the application for a patent for the treatment of artificial surfaces by a cement produced by microorganisms and the consequent establishment of the company "Calcite Bioconcept" (Adolphe et al. 1989; Orial et al. 1993). Promising results by this company encourage many researchers to look for different approaches and test different bacteria for their ability in biomineralization. Up until now, a variety of technologies were tested from the application of macromolecules to the usage of different microbes (highly carbonatogenic microbes) and their metabolic activities along with carbonate precipitation by microbiota inhabiting the stone by providing a suitable nutritional solution (Price et al. 1988; Rodriguez-Navarro et al. 2003; Tiano et al. 2006; Barabesi et al. 2007; González-Muñoz 2008; Jroundi et al. 2012, 2015, 2017; De Muynck et al. 2013; Dhami et al. 2014; Yoosathaporn et al. 2016). In all of these strategies, biomineralization mediated by microorganisms was the principal agent for the consolidation and restoration of decayed built material. Regarding the in situ application of this biomineralization process, very few attempts have been performed at a larger scale, for example, a company, namely, KBYO Biological (Spain), scaling up a nutritional solution stimulating stone microbiota that promotes $CaCO_3$ mineralization on stone, which took as a basis the in situ small-scale tests adopting treatment conditions that mimic those to be followed in larger-scale applications (e.g. González-Muñoz et al. 2008; Rodriguez-Navarro et al. 2003, 2012; Jimenez-Lopez et al. 2008; Jroundi et al. 2010, 2012, 2015, 2017; Ettenauer et al. 2011).

Nevertheless, little is known about the molecular aspects of the biomineralization process. Few studies have highlighted the role of cellular fractions, genes and molecules in inducing the precipitation of calcium carbonate in *Bacillus subtilis* and suggested a link between biomineralization, redox reactions of fatty acid metabolism, changes in phospholipids membrane composition and surface characteristics (Barabesi et al. 2007; Marvasi et al. 2017). Further studies in this sense are needed in order to help in the search of molecules enhancing precipitation and, at the same time, improving the biomineralization performance by bacteria.

3.5.3 Other Examples

Extracellular biomineralization can also be a result of biologically controlled mineralization implying the production of macromolecular matrix outside the cell. Such a matrix forms a three-dimensional framework, typically composed of proteins, polysaccharides or glycoproteins, where the cell actively supplies cations to the matrix for nucleation and growth of the biomineral. For example, *Geobacter metallireducens* and *Shewanella putrefaciens* are both the most well-studied species defined as Fe biomineral producers through the extracellular biologically controlled mineralization (Lovley and Phillips 1986; Skinner and Ehrlich 2014). They are able to gain nutrients, including Fe, through the utilization of organic compounds or CO_2, for energy and carbon sources. Eventually, they also use inorganically generated hydrogen gas for energy, and an electron transfer system coupled with Fe(III) reduction to its advantage (Bazylinski and Frankel 2003). Also, some sulphur-reducing bacteria can use iron as the sole electron acceptor from an iron-rich environment for the extracellular nucleation and production of greigite, pyrrhotite or nonmagnetic sulphides such as pyrite and marcasite (the two polymorphs of FeS_2). Studies reported on the detection of temperature-dependent fractionation of oxygen in the formation of Fe_3O_4 and water, typical of extracellular magnetite produced by thermophilic Fe_3-reducing bacteria (Mandernack et al. 1999). In this case, minerals were dependent on the temperature, pH, Eh and the source and availability of sulphur, iron and oxygen (Skinner and Ehrlich 2014).

4 Conclusions

In the chapter above, we intend to summarize the state of knowledge about the mechanisms of biomineralization. In particular, we have devoted most of our attention to the broader classification of mineral precipitation mediated by microbes as extracellular and intracellular mineralization. Although, as described, significant progress has been achieved towards understanding mineralization mechanisms, still more investigations are needed to elucidate the applicability of biomineralization in several exciting research biotechnologies, for example, medicine, cultural heritage or industry. Also, one underestimated concept is the potential role of cell surface

structures and chemistry in the crystal nucleation, aggregation and growth. Very little is still known on the molecular aspects of biomineralization, and further research on this field should be performed, including the exploitation of bacterial pathways, cell components and macromolecules, in order to improve the applicability of such process in a broader scale. Regarding global change research, the precipitation of barite in the ocean water column by bacteria and EPS has opened an exciting field of research to explore the microbial role in biogeochemical cycles.

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Geophysical Monitoring and Characterization of Biomineralization Processes

Dimitrios Ntarlagiannis, Yuxin Wu, and Adrian Mellage

Contents

Abstract Quantitative monitoring and characterization of biomineralization processes in environmental science and engineering applications remains challenging, in particular, during field investigations, where in situ measurements are limited. Current, traditional, methodologies can provide very detailed information but are restricted in their spatial and temporal extents. Furthermore, common subsurface processes (e.g., water saturation changes, weathering) could mask the impact of biomineralization at scales of interest. Recently, geophysical methods have gained traction as potential candidates for monitoring biomineralization in real time, and at field-relevant spatial and temporal scales. In the emerging field of biogeophysics, geophysical methods, which have traditionally been utilized to study purely abiotic

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targets, have been shown to be sensitive to specific biomineralization processes, thus offering a powerful tool for monitoring and characterization. This chapter presents the state of the art of biogeophysical methods relevant to the detection of subsurface biomineralization, highlights current applications, and discusses future opportunities for continued method development.

1 Introduction

In geology a mineral is typically defined as a naturally occurring, inorganic, solid, crystalline substance with a defined structure and fixed chemical composition, or one that varies within certain limits. When the mineral-forming process is dictated and controlled by living organisms, it is termed biomineralization (Weiner and Dove 2003; Dhami et al. 2013). Biominerals, the end products of biomineralization, refer to the formed mineral and to composite materials made up of both mineral and organic components (Weiner and Dove 2003; Ntarlagiannis et al. 2005; Williams et al. 2005). In the relatively young discipline of biogeophysics (Atekwana and Slater 2009), for example, the term biomineral was used to describe otherwise healthy and motile microbial cells that were covered with a metal sulfide coating on the outer cell wall (Fig. 1) (Ntarlagiannis et al. 2005; Williams et al. 2005).

The study of biominerals in the natural environment has gained traction since the growth of biogeochemistry as a discipline (Weiner and Dove 2003). From a purely mineralogical standpoint, biominerals can provide important clues on the conditions in ancient environments that resulted in their formation and deposition. More recently, attention has focused on the detection of biominerals with respect to processes relevant for biogeochemical cycling, soil structure and composition, and

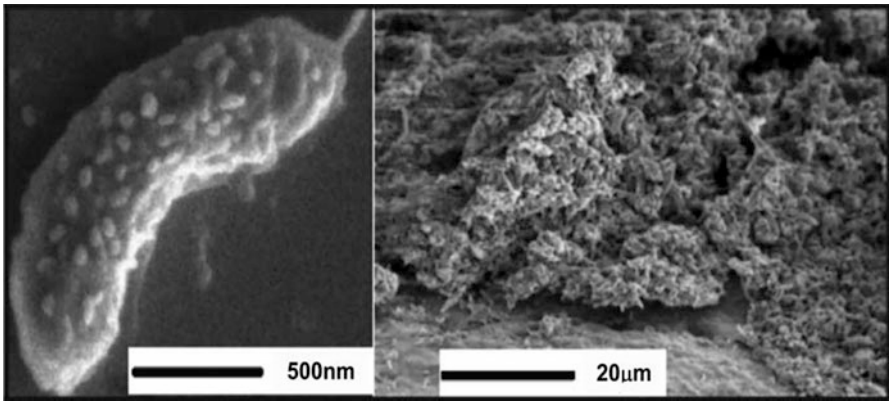

Fig. 1 An SEM image of a biomineral (left) and mineralized biofilm (right) covering a quartz grain (from (Ntarlagiannis et al. 2005))

contaminant remediation. The ability, whether intended or not, of microbes to manipulate the chemical composition of their immediate environment yields dynamic precipitation and dissolution of environmentally relevant biominerals, such as carbonates, phosphates, metal oxides, and sulfides. In fact, the biogeochemical cycling, mobility, and speciation of metals, metalloids, radionuclides, and those elements commonly associated with metallic minerals are determined by geo-microbiological metal and mineral transformations (Gadd and Pan 2016).

Biomineralization can sequester heavy metals or radioactive metals rapidly and efficiently and is beneficial for the remediation of metals, such as Pb^{2+}, via aqueous removal (Zhang et al. 2019). In addition, biomineralization of iron oxides can result in indirect remediation of contaminants such as Cd and As, where oxidized aqueous species are assimilated into the mineral structure via chemisorption (Byrne and Kappler 2017). Biogenic pyrite can sequester As from contaminated groundwater, and sorption can lead to arsenian-pyrite formation, effectively modifying mineral composition (Langmuir et al. 2006; Saunders et al. 2018). In addition to their importance for remediation, biogenic iron minerals, such as magnetite, can act as both a sink and source of energy (in the form of electrons) for microbial metabolism (Weiner and Dove 2003), thereby fueling reversible redox reactions. The presence of magnetite and microbes that couple hydrocarbon degradation with iron reduction has been reported at legacy contaminated sites (Beaver et al. 2016). Hence, tracking biomineral formation (and dissolution) can provide targeted information on the (bio)geochemical conditions and dynamics in specific systems. However, quantifying the rates and mechanisms of metal transformation and biomineral formation by organisms, especially in a field setting, is hampered by parallel processes that may act to mask biomineralization carried out by bacteria (Atekwana and Slater 2009; Posth et al. 2014). Moreover, sample collection and characterization for mineral detection and identification limits the kinetic information that can be retrieved when monitoring biomineralization and related processes.

Geophysical methods have long been used to study the subsurface of the Earth, focusing on inorganic targets and processes. In the last two decades, research showed that biological processes could contribute to observable geophysical anomalies, even in cases where the causes and triggers were thought to be purely abiotic (Atekwana and Slater 2009; Liu et al. 2012). The field of geophysics rapidly adapted, and the novel research area, now termed biogeophysics, aimed to study microbial processes and interactions in the subsurface utilizing geophysical methods, emerged (Atekwana et al. 2006; Atekwana and Slater 2009).

Owing to their unique properties (e.g., magnetism, surface chemistry), biominerals are well poised for non-invasive detection using geophysical techniques, that is, reducing the need for sample destruction or manipulation. Specifically, carbonates, iron oxides, and sulfides have been successfully detected and their occurrence and temporal dynamics monitored using electrical and magnetic techniques (e.g., Ntarlagiannis et al. 2005; Saneiyan et al. 2019). Research focus areas rapidly evolved in response to increasingly growing interest and the overwhelming potential of non-invasive sensing technologies. The interdisciplinary nature of biogeophysical investigations and their relevance for non-geophysical fields have

led to a shift toward innovative and smaller-scale measurement targets. For example, microbially mediated iron mineral transformations are of particular interest because they comprise approximately 40% of all minerals formed by microorganisms and are commonly affected by hydrocarbon degradation processes (Ameen et al. 2014; Abdel Aal et al. 2014; Lund et al. 2017). In addition, such mineral changes can be sensed with a multitude of geophysical methods such as induced polarization (IP), magnetic susceptibility (MS), and self-potential (SP) (Atekwana et al. 2014; Abdel Aal et al. 2014; Heenan et al. 2017; Lund et al. 2017). Another emerging area of biogeophysical research is the mineralization of calcium carbonates, directly linked to environmental engineering applications (Ntarlagiannis et al. 2005; Dhami et al. 2013). Microbial induced carbonate precipitation (MICP) is a natural process that can be easily enhanced and/or induced, with minimal environmental side effects, for improving the geotechnical properties of a soil, and as a remediation and CO_2 sequestration tool. Specifically, carbonates, iron oxides, and sulfides have been successfully detected and their occurrence and temporal dynamics monitored using electrical and magnetic techniques (e.g., Ntarlagiannis et al. 2005; Saneiyan et al. 2019).

In this chapter we highlight the unique physicochemical properties that enable the detection of biominerals (including amorphous phases) using geophysical tools and review experimental studies that have successfully applied geophysical approaches to monitor biomineralization processes.

1.1 Why Geophysics?

Unlike their abiogenic counterparts, biominerals are often a composite of minerals and organic components, with roughly a quarter of all known biominerals being amorphous, that is, they do not diffract X-rays (Weiner and Dove 2003). Their hybrid organic and mineral structure stems from their genesis. Bacterial exopolymers provide a template for mineral nucleation sites (Ferris 2005; Posth et al. 2014), and precipitates can remain firmly attached to the outer cell structure (Weiner and Dove 2003). Biogenic precipitation can be induced by unintended changes in chemistry in the direct vicinity of cells, or it can be controlled. Controlled mineralization can occur within or outside of the bacterial cell structure. Bacteria produce macromolecular matrices (comprised of proteins, polysaccharides, or glycoproteins) to act as a template for mineralization; these matrices are genetically programmed to regulate the formation of biomineral composites (Weiner and Dove 2003). Communities of single-celled organisms may also form intracellular biominerals, effectively binding them together (Weiner and Dove 2003). Mineral precipitation can also be induced internally, where controlled nucleation and mineral growth occurs inside the cell followed by a secretion step (Weiner and Dove 2003). While the mechanisms of biomineralization are not the focus of this chapter, they shed light on the inextricable link between organic macromolecules, microbes, and mineral precipitates. Not all biominerals exhibit strong crystallinity; however, they

do possess similar electrical (i.e., charge), (semi-)conductive, and magnetic properties as abiogenic minerals. These properties are the focal point of the discussion below in relation to their in situ detection using geophysical methods. Moreover, the concurrent presence of organic molecules as well as microbes cannot be neglected, and must be considered as they act to mask or enhance specific properties that could either hinder or magnify biomineral detectability.

Typical geophysical investigations designed to target the detection and monitoring of biomineralization processes (and biogeochemically driven signals, in general) are conducted at both the field and laboratory scales. A schematic representation of a generalized surface-based imaging approach, borehole measurements, and bench-scale setups, along with an illustration of the processes that control measured geophysical signals, at the pore scale, is shown in Fig. 3. The depicted measurement approaches are for electrical methods (e.g., resistivity and induced polarization). Electrical methods, as with most geophysical methods, rely on sensors (various types of electrodes, from metal stakes to metal porous pots (Clerc et al. 1998; LaBrecque and Daily 2008)) that come into contact with the medium of interest. The simplest approach is at the bench scale where four-electrode (or more) configurations can be installed into traditional batch reactor and flow-through columns to enable non-invasive geophysical characterization and monitoring. Multielectrode configurations are typically used for geophysical imaging, allowing the 2-dimensional (2D), and even 3D, reconstruction of the subsurface through processing, inversion and interpretation (Binley and Kemna 2005; Rubin and Hubbard 2005). In cases where the survey resolution cannot be resolved with depth, the electrodes can also be installed depth-wise in boreholes. Regardless of the measurement target scale, the underlying processes that govern geophysical signals are at the pore scale. Dynamic changes in IP signals, for example, arise due to increasing or decreasing biomineral-driven surface charge properties. The latter, coupled to the existing charge contribution of the subsurface itself (for simplicity, shown as quartz sand in Fig. 3), generate an integrated polarization and conduction signal stemming from the electrical conductivity of the pore water and the surface charge and conduction related to the electrical double layer (EDL) of mineral grains and colloids. Although the discussion is focused on electrical methods, similar sensor configurations can be used for seismic methods (Saneiyan et al. 2018). In contrast, magnetic susceptibility measurements can offer only point measurements (no imaging) in either field or laboratory implementation (Lund et al. 2017).

The surface chemistry of (biogenic and abiogenic) metal (hydr)oxides and oxide minerals controls their surface charge. When in contact with water, the surfaces of oxides and oxide minerals are covered by surface hydroxyl groups (S-OH), whose charge, positive, negative, or neutral, is governed by protonation and deprotonation (Schindler and Stumm 1987). Thus, depending on the environmental pH, biominerals may exhibit varying charge characteristics, which are also subject to change. In the context of electrochemical polarization as a detectable charge storage mechanism (e.g., via induced polarization—IP), to be detectable, a biogenic mineral must exhibit a strong negative charge (or positive charge—however, this is typically only relevant under acidic conditions). A high, negative surface charge would yield

an electrical double layer, polarizable under an external electrical current. A mineral's point of zero charge, that is, the pH at which the majority of charged sites are neutrally charged, provides insight into the potential for charge storage of specific minerals under ambient pH conditions.

In addition to the polarization of loosely bound counterions in the EDL, the pH-dependent charge characteristics of metal (hydr)oxides and oxide minerals result in counterion surface complex formation. Adsorption alters the surface electrical properties of oxides. Metal ion adsorption above critical surface concentration can lead to hydroxide clusters of the adsorbed metal on the adsorbing surface (Bleam and McBride 1985). The process, also known as surface precipitation (Farley et al. 1985), may yield complete coating of the initial surface (Schindler and Stumm 1987). Changes in surface chemistry by either adsorption or surface precipitation can provide an additional, indirect characteristic that can be harnessed for the detection of biogenic minerals. Previously, IP signals have been shown to be sensitive to the adsorption of charged species (Vaudelet et al. 2011).

Analogous to the properties of (hydr)oxides and oxides, magnetite (also an oxide) and pyrite exhibit variable surface charge characteristics that are a function of electrolyte biogeochemistry (Weerasooriya and Tobschall 2005; Hubbard et al. 2013). In addition, both pyrite and magnetite are semiconductors. Their semiconductivity reflects the presence of charge carriers that arise from deviations in stoichiometry, impurities in the solid solution, and thermal excitation (Pridmore and Shuey 1976). Under an applied electrical field, (semi)conductors act as a barrier for charge transfer, and charged ions at the mineral-electrolyte interface are forced to migrate tangentially around the metal surface, accumulating at dipoles (Wong 1979). The impedance of metallic particles is determined by the diffusion of active ionic species and the degree to which active ions can engage in charge transfer reactions enabling charge transfer (or leakage) through the mineral particle (Wong 1979). The diffusion impedance (also termed Warburg impedance) of metallic minerals yields frequency-dependent polarization responses detectable using IP. Abdel Aal et al. (2014) suggest that the development of an EDL and the accumulation of charge (ions) at conductive mineral-fluid interfaces are influenced by the number of mobile charge carriers (electrons and hole polarons) within the semiconductive iron minerals, thereby controlling the magnitude of the polarization response. Charge transfer across the mineral itself depends on the presence of redox-active ions (Hubbard et al. 2013). Conductivity is thought to yield stronger polarization responses than purely electrochemical signals arising from a high mobility of charge within (semi)-conductive minerals and redox reactions that transfer charge from and to the electrolyte (Hubbard et al. 2013; Abdel Aal et al. 2014).

Rock and mineral magnetic properties offer a unique opportunity to "remotely" study biomineralization processes. Magnetic sensing is an efficient, non-invasive, and highly sensitive approach to understanding the concentration, domain state, grain size, and mineralogy of magnetic particles (Liu et al. 2012). Magnetic measurements can be directly linked to the original and/or subsequent mineral-forming processes, ultimately revealing the geological and environmental history of soils and rock (Thomson and Oldfield 1986; Liu et al. 2012).

Paleomagnetism enables the study of mineral/rock evolution, providing insight into biomineralization processes over geologically relevant scales (Liu et al. 2012). Environmental magnetism, on the other hand, is a valuable tool to study present/ongoing biomineralization processes (Liu et al. 2012). For example, it is now known that hydrocarbon biodegradation is directly linked to magnetic signals through microbial iron cycling, and the subsequent formation of magnetite (Lund et al. 2017). Furthermore, measurements based on environmental magnetism can be used as an efficient tool to interrogate Fe^{2+}-Fe^{3+} deposition and/or transformations in common iron oxides with many of these processes being microbially driven. It is well known that Fe exerts a dominant role on redox activity in near-surface soils, and even in benthic environments (Berg et al. 2016). Fe cycling is incompletely understood, with many steps, including biomineral intermediates poorly described (Liu et al. 2012; Melton et al. 2014). Current Fe biogeochemistry typically relies on actual soil sampling and subsequent analysis which inevitably misses dynamic changes in soils in between sampling events (Barcellos et al. 2018). Geophysical magnetic methods could offer the resolution needed to study Fe biomineralization processes at varying temporal scales. Indeed, environmental magnetism techniques are increasingly applied in the field and the laboratory to characterize Fe-related processes (Liu et al. 2012; Atekwana et al. 2014; Kappler and Bryce 2017).

2 Geophysical Methods

Geophysical methods collectively describe a series of techniques that measure the physical properties (e.g., electrical conductivity) of Earth media. They are inherently indirect, as they only link parameters of interest such as subsurface geology, hydrogeology, and the presence of contaminants to measured signals either through qualitative relationships (e.g., property contrast) or increasingly by petrophysical relationships (Rubin and Hubbard 2005; Slater 2007; Reynolds 2011; Weller et al. 2013). In contrast, direct methods typically involve invasive sampling and direct analysis of the medium of interest. While geophysical methods cannot offer the high accuracy and detailed information that can be obtained via direct sampling and analysis, they do offer a wealth of advantages that make them attractive for subsurface studies. Geophysical methods offer high temporal and spatial resolution, are suited for real-time and long-term monitoring, and are noninvasive and cost-efficient. It should be noted that geophysical methods cannot completely replace direct sampling methods, but can immensely complement them to enhance monitoring and characterization applications.

There are a variety of geophysical methods based on the physical properties they target. The most relevant to biomineralization are electrical, seismic, and magnetic methods. All these methods have been described in great detail elsewhere and thus are only briefly introduced in this chapter.

2.1 Electrical Methods

Electrical geophysical methods probe subsurface properties and processes by measuring and imaging subsurface electrical charge conduction and storage. The specific technologies most commonly used include direct current (DC) resistivity (or conductivity), time domain induced polarization (TDIP), and spectral induced polarization (SIP). These methods can be used as surface-based measurements or in borehole logging (see Fig. 3) and are discussed briefly below.

2.1.1 Direct Current (DC) Resistivity

The DC resistivity method is based on the principle that the electrical potential distribution in the subsurface is controlled by its electrical resistivity distribution. By injecting electrical currents into the subsurface via typically metallic electrodes and measuring the resulting voltage at predefined locations, the electrical resistivity of the subsurface can be inferred via the utilization of numerical inversion (Reynolds 2011). A large number of electrodes can be multiplexed for current injection and potential measurement to provide a tomographic view of the electrical resistivity distribution in the surface in both 2D and 3D. This method is termed electrical resistivity imaging (ERI) (Kemna et al. 2002; Binley and Kemna 2005, p. 20; Binley 2015, p. 05; Falzone et al. 2019). With a large number of electrodes, multiple types of geometrical arrangements e.g., Schlumberger, Wenner, and dipole-dipole arrays, can be used for data acquisition, each providing different sensitivities for specific applications (Furman et al. 2003; Reynolds 2011; Binley 2015).

The applicability of the DC resistivity method for biomineralization depends on whether a discriminatory resistivity signal exists during, or after, the biomineralization process of interest (Atekwana and Slater 2009). This often relates to changes in pore fluid electrical conductivity, size/density/interconnectedness of pores, and the electrical properties of mineral constituents involved (Fig. 2). Changes in pore fluid electrical conductivity are typically related to the microbial metabolic processes that consume organic nutrients and produce by-products, altering pore fluid properties (Atekwana and Slater 2009). The precipitation or dissolution of new minerals is a process that can produce a detectable DC resistivity signal due both to the production of conductive minerals and modification of the pore structure (Fig. 2). Because of the complexity of the biomineralization processes, where multiple compounding factors can influence DC resistivity, it is typically too difficult to quantitatively understand the causal correlations driving DC resistivity changes. As a result, the application of DC resistivity alone for biomineralization is limited.

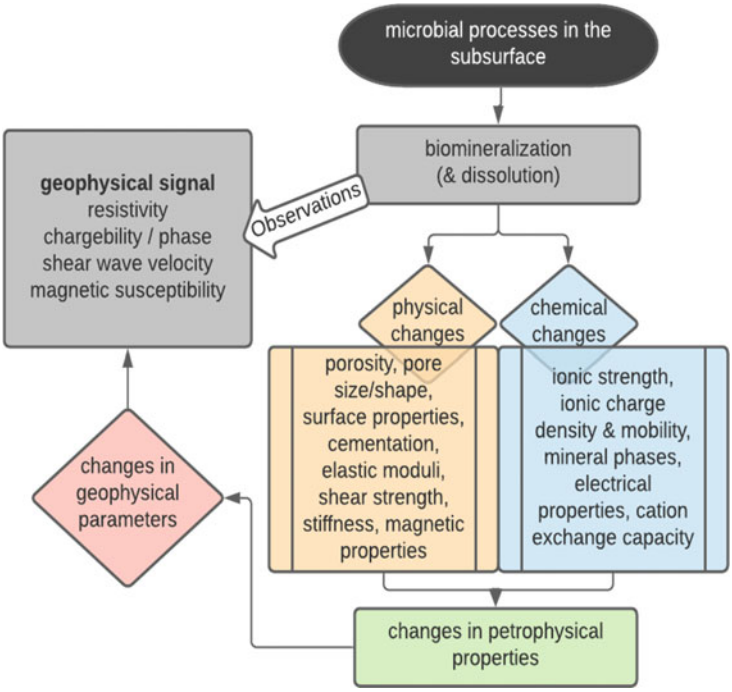

Fig. 2 Flowchart showing the impact on biomineralization on geophysical signals (modified from Ntarlagiannis et al. 2005)

2.1.2 Time Domain Induced Polarization

The time domain induced polarization (TDIP) method can be considered an extension of the resistivity method. During a TDIP measurement, current is shut off, leading to a quick drop in measured voltage to a nonzero value, followed by an approximately exponential decay of a secondary voltage (Revil et al. 2012). The slow decay is directly controlled by the ability of a medium to store charge, that is, to polarize, and is known as the induced polarization or IP effect. The TDIP method (commonly referred to as IP) is thus uniquely suited for the characterization and monitoring of biomineralization processes (Atekwana and Slater 2009).

The IP effect stems from the charge storage behavior at mineral-fluid interfaces in the EDL in both metallic and nonmetallic minerals (Marshall and Madden 1959). Detectable IP effects are associated with a diverse range of charge storing processes, such as mineral surface charge, charge accumulation at interfaces of contrasting electrical properties, and accumulation via pore throat blockage (Vinegar and Waxman 1984). The IP method can be applied in both borehole logging and surface-based tomography modes by multiplexing multiple electrodes (Fig. 3). High sensitivity IP measurements typically utilize non-polarizing retracted

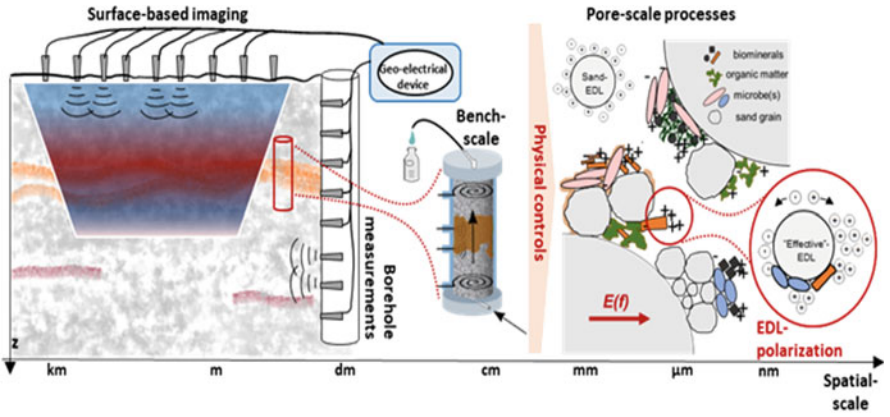

Fig. 3 Schematic illustration of surface-based, borehole, and bench-scale geophysical measurement approaches along with a depiction of pore-scale processes that control measured signals

electrodes, made from Ag/AgCl or $Cu/CuSO_4$ (Clerc et al. 1998). To minimize electrode-originated polarization noise, electrodes are placed outside the current pathway, in an electrolyte solution of their own metal, to minimize any geochemical reactions, and are only in ionic contact with the medium under investigation (Vanhala and Soininen 1995; Ulrich and Slater 2004).

Large IP effects in natural systems are typically associated with minerals with significant surface charge following the application of an external electrical field. These could be metallic minerals, such as sulfides, or nonmetallic, or high surface area minerals, such as clays. The magnitude of IP signals associated with biomineralization is dictated by the type of mineral formed. The microbial production of metal sulfides or oxides, e.g., pyrite or magnetite, has been repeatedly demonstrated to have large IP effects (Ntarlagiannis et al. 2005; Williams et al. 2005; Personna et al. 2008). In addition to enhancing IP effects, biomineralization could generate detectable signals by masking existing polarization signals, by, for example, coating a charged surface with a mineral of a different composition, structure, surface area, and/or surface charge.

2.1.3 Spectral Induced Polarization (SIP)

SIP, also known as the complex conductivity method, is a frequency-resolved variant of the IP method. During an SIP measurement, current is typically injected over a broad range of frequencies, and the ratio between current and voltage amplitude and the phase shift are recorded across two potential electrodes. Conduction through pore-filling electrolyte, a real term, and conduction along EDL on mineral surface, a complex term, contribute to the overall recorded signal (Kemna et al. 2012). The SIP method spans a wide range of frequencies with predetermined intervals, typically from millihertz to tens of kilohertz. Thus, temporal signal monitoring over time and space could yield data of three dimensions: space, time, and

frequency. One of the strengths of SIP is that it offers highly resolved frequency information (Kemna et al. 2012) and thus can shed light on specific polarization mechanisms associated with different processes and biomineralization products.

While frequency domain SIP measurements are typically used, time domain measurements can also be processed to extract SIP-relevant information (Fiandaca et al. 2012). SIP measurements are typically conducted in the laboratory where dimensions and geometric setup of the systems can be well controlled for aquiring high-quality data. Field SIP data acquisition often faces data quality challenges, but a handful of applications have demonstrated the potential for SIP to provide valuable insights beyond what ERT and single-frequency IP can offer (Flores Orozco et al. 2011; Saneiyan et al. 2020).

The applications of electrical geophysical methods to study biomineralization processes have largely focused on the SIP method (Atekwana and Slater 2009). This is largely attributed to the rich information contained in the frequency spectrum responses that are often correlated with dynamic reactive processes. Specifically, the changes of the overall signal magnitude and shifts in peak signal frequency are often characteristic of, and quantitatively correlated with, the volume of the mineral products and their size/geometry, thus providing a noninvasive method for tracking reaction progress in real time (Ntarlagiannis et al. 2005; Personna et al. 2008; Saneiyan et al. 2018).

2.2 Seismic Methods

Seismic methods study the behavior of seismic waves of known origin when traveling through the subsurface, through the media of interest. Reflected and refracted seismic waves provide information on the materials they travel through, such as their elastic properties. Biomineralization processes typically lead to the formation of new mineral phases, or the modification of existing ones, that would impact soil properties affecting the propagation of seismic waves. Shear wave velocity (S-wave) measurements are sensitive to new formed minerals, and to change in the shear modulus (G_{max}) of the media, while with the addition of compression wave velocity (P-wave) measurements estimates of the Poisson's ratio can be made (Flores Orozco et al. 2011; Saneiyan et al. 2018).

2.3 Magnetic Susceptibility

Low-field magnetic susceptibility (MS) (χ, mass specific, or k, volume specific) is the one most relevant magnetic method for biomineralization applications (Liu et al. 2012; Atekwana et al. 2014; Abdel Aal et al. 2014). The MS method describes the ease with which a material can be magnetized when placed under a magnetic field and is defined as the ratio between the magnetic response (M) of the material to the

applied magnetic field (Liu et al. 2012). MS is widely used for environmental magnetism studies due to its relatively simple application, both in the laboratory and the field, and the proven sensitivity to magnetic particles associated with anthropogenic activities (Liu et al. 2012, 2016; Magiera et al. 2018). We should highlight that MS signals are strongly influenced by ferromagnetic materials (e.g., magnetite), although antiferromagnetic materials, e.g., hematite, and even minerals that are considered "nonmagnetic," such as paramagnetic (e.g., clays) and diamagnetic (e.g., carbonate) minerals, can generate small, but detectable, signals. The quantitative interpretation of MS data should thus be performed cautiously, taking into consideration the local environmental conditions, such as soil and host rock types, and potential sources of contaminants (Liu et al. 2012; Magiera et al. 2018).

2.4 Modeling

In general, two schools of models have been developed and applied to improve the quantitative interpretation of electrical geophysical signals in an effort to link to the fundamental processes driving these signals, namely, petrophysics-based and process-based models. Petrophysics-based models serve the primary function of fitting observational data. In terms of SIP modeling, the Cole-Cole and Debye decomposition models are good examples that are widely used (Cole and Cole 1941; Nordsiek and Weller 2008; Ustra et al. 2016). The benefits of the petrophysical models are that they are fairly straightforward to apply and often work well in a wide range of systems. Petrophysical methods, also known as phenomenological models, are particularly useful in extracting global parameters, e.g., relaxation time and chargeability, across multiple datasets helping to extract characteristic parameters from frequency-resolved data, thereby allowing for an improved cross-comparison of multiple datasets. While widely applicable across both lab and field datasets, petrophysical models often do not offer much insight into the mechanistic processes driving the observed signals.

In contrast, mechanistic models derived based on the kinetic and thermodynamic processes at the microscopic scales are often very useful in understanding the fundamental processes driving the observed geophysical signals. A significant amount of such effort has been devoted to modeling the SIP response of various model systems, such as phyllosilicate or clay minerals (Leroy and Revil 2009; Jougnot et al. 2010; Revil 2012; Leroy et al. 2017). Such mechanistic models often consider the interactions between electrostatic forces and charge diffusion processes in the Poisson-Nernst-Planck system of equations centered around the EDL covering mineral grains in electrolyte-fluid systems.

The formulation of mechanistic models often involves the partition of charges between the Stern and the diffuse layer, each assigned a distinctive charge mobility. In tightly packed systems, prevailing models often consider the Stern layer as the dominant polarization source, yet a contribution from the diffuse layer cannot be

dismissed because of the role it plays in counterbalancing the charge deficiency and Stern layer polarization to maintain charge neutrality (Leroy et al. 2017). In addition to charge mobility and partitioning between Stern and diffuse layers, another key parameter often considered in mechanistic models is the cation exchange capacity (CEC), a parameter associated with surface charge density, and of geochemical significance in terms of ion adsorption/desorption (Leroy and Revil 2009). The derivation of mechanistic SIP models has been conducted for multiple model systems, such as those for clay, calcite, and metallic minerals. A detailed description of these models is beyond the scope of this chapter; the interested reader can find more details in relevant literature (e.g., Leroy and Revil 2009; Revil and Florsch 2010; Leroy et al. 2017).

In general, mechanistic models are critical for understanding the underlying physicochemical processes driving observed electrical signals and to improve the application and acceptance of these methods beyond the geophysical community. A key drawback of mechanistic models lies in the challenge of applying them to complex, natural systems with complex mineral composition, texture, and electrolyte geochemistry, as all models rely on significant simplifications of the systems studied. The superposition principles often applied to such systems utilizing volume mixing formulas (Lesmes and Morgan 2001) become unmanageable, and the parallel process assumption may not hold in complex, natural systems. As a result, mechanistic models often perform well when applied to laboratory results in simple systems but fall short when applied to complex systems in both lab and field. A brief example of mechanistic model application during calcite precipitation is presented in a later section.

3 Current Applications

3.1 Metal Sulfides

The first successful biogeophysical applications were the result of research to improve the efficacy of microbial induced metal sequestration as a remediation tool (Ntarlagiannis et al. 2005; Williams et al. 2005). For any remediation effort to be successful, characterization and monitoring of the controlling processes, and end products, is required at high spatial and temporal resolution at field-relevant scales. In the case of metal contaminants, there is a need to monitor the microbial activity and the metal precipitates to understand where, when, and at what rates bioremediation is occurring (Williams et al. 2005).

Metal sulfide mineralization is expected not only to create a new mineral phase but also to change the bulk electrical properties of the host porous media since the end product is highly conductive and possibly polarizable. Ntarlagiannis et al. (2005) and Williams et al. (2005) used SIP to successfully monitor FeS and ZnS precipitation in laboratory columns. SIP appeared to be very sensitive in monitoring the formation of new biominerals, coagulation due to aging, and also the microbial

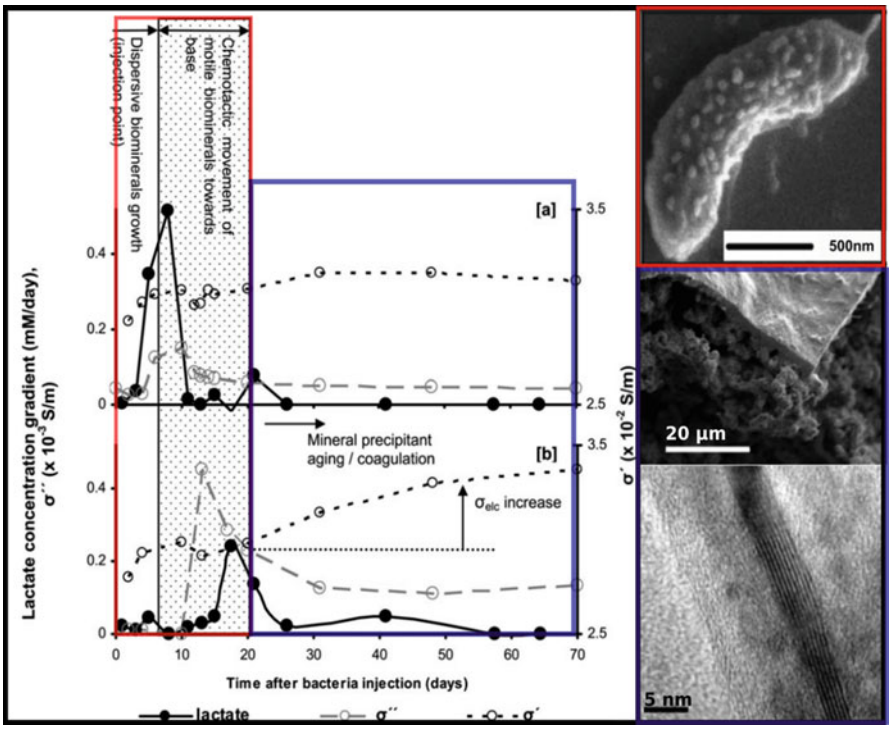

Fig. 4 Imaginary and real conductivity, the two SIP components, appear to closely track the formation on Fe and ZnS biominerals; the responses change with the progression of biomineralization and can track both early mineralization dominated by motile sulfide-encrusted microbes (red) and late mineralization with dense sulfide precipitates on porous media (blue); modified from Williams et al. (2005) and Ntarlagiannis et al. (2005)

activity driving the process (Fig. 4). Furthermore, the use of seismic methods to monitor the same processes was examined by Williams et al. (2005). The acoustic seismic signals became increasingly attenuated in response to biomineralization. Their time dependence and partial signal rebound further suggested that acoustic seismic signals are sensitive to the mineralization progress.

Further research on metal sulfide biomineralization not only confirmed the sensitivity of the SIP method to sequestration but also showed that SIP is sensitive to dissolution processes (Slater et al. 2007; Personna et al. 2008). This very important finding strongly suggests that SIP can be used as a monitoring tool during active metal contaminant bioremediation, providing real-time information on mineralization progress. In addition, SIP can be used to monitor the long-term stability of a treated area, providing information on any possible release of contaminants in the event that subsurface conditions change and lead to mineral dissolution.

Although most biogeophysical research on metal sulfide monitoring is still confined to laboratory settings, the existing field investigations to date have shown

very encouraging results. Indeed, FeS biomineralization was tested as a remediation treatment for uranium contamination at the Rifle IFRC (Integrated Field Research Center) site, and complex conductivity was used as the monitoring tool (Flores Orozco et al. 2011). Complex conductivity signals were very successful in identifying, and monitoring, hotspots of biogeochemical activity, where FeS precipitated during active treatment. Furthermore, SIP was successfully used to monitor the long-term effectiveness of the treatment for a period of almost 2 years (Flores Orozco et al. 2011). The work of Flores Orozco et al. (2011) highlights that SIP is mature enough to be utilized in situ as a monitoring tool during field investigations at contaminated sites.

3.2 Carbonates

Wu et al. (Wu et al. 2010) present an example of the early studies on the SIP signals stemming from calcite precipitation. To reduce compounding effects, a simplified experimental setup utilizing glass beads of uniform size and abiotic mixing of reactants was implemented in their experiments. A significant increase of the SIP signals was observed during the onset of calcite precipitation which was attributed to the increased surface charge and therefore polarization resulting from newly precipitated calcite crystals (Fig. 5). A shift of the peak signal frequency to lower values helped to link signal changes to the growth of the calcite crystals themselves. The lower frequency was driven by the polarization of particles of increasing diameter. While the initial SIP signals follow a linear correlation with calcite formation mass, a later reversal of the signal trend was attributed to particle aggregation that acted to reduce the effective polarization surface area.

Following Wu et al. (Wu et al. 2010), multiple studies have validated the SIP and IP signals from calcite precipitation in both abiotic and biotic processes (Saneiyan et al. 2018, 2019, 2020; Izumoto et al. 2020). Specifically, Leroy et al. (2017) developed a mechanistic model to simulate SIP responses from calcite precipitation based on a previous model developed for borosilicates (Leroy et al. 2008). In Leroy et al. (2017), the EDL-based model of the calcite-electrolyte interface was used (Heberling et al. 2011). The model simulates the electrochemical polarization of charge in the Stern layer at the calcite surface. The model of Leroy et al. (2017) successfully simulated the experimental observations presented in Wu et al. (2010) and contributed to improving the understanding of the mechanistic processes driving SIP signals during calcite precipitation.

Additional studies from Saneiyan et al. (2018, 2019, 2020) expand earlier results and demonstrate the applicability of SIP at field scales for monitoring microbially induced carbonate precipitation (MICP). Additional studies in small-scale flow-through systems (Izumoto et al. 2020) further revealed the effect of pore fluid chemistry on the SIP signals of calcite. Together, these results demonstrated how electrical geophysical methods, specifically SIP, can be used to study

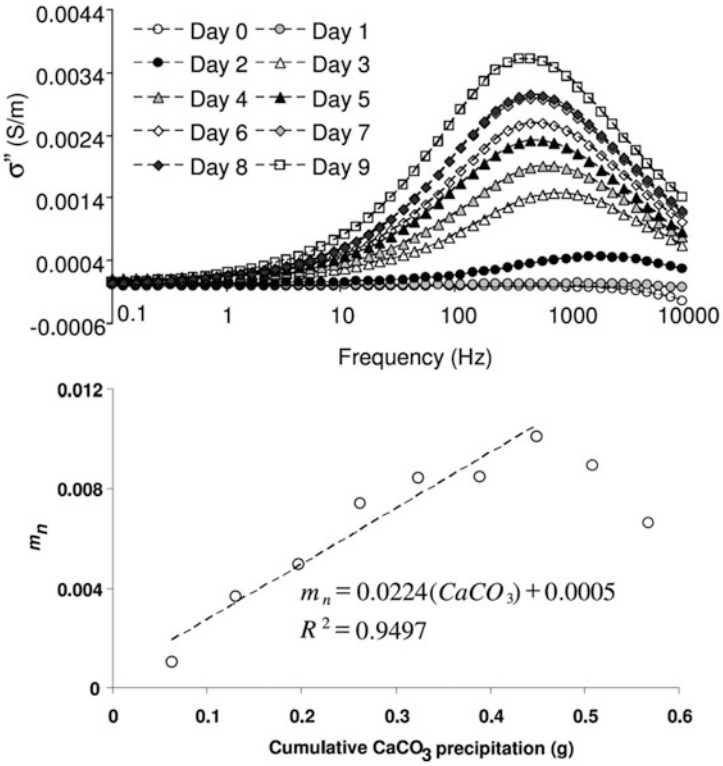

Fig. 5 Imaginary conductivity changes during calcite precipitation over time (top); quantitative correlation between the mass of calcite precipitation and normalized chargeability from the SIP signals (bottm). Figures modified from Wu et al. (2010)

biomineralization processes involving calcite at both milli- and microscales in the laboratory and at the field scale.

3.3 Iron Cycling

The most active area of research in biogeophysics is currently on Fe cycling as it relates to contaminant biodegradation (Atekwana et al. 2014; Ameen et al. 2014; Abdel Aal et al. 2014; Atekwana and Abdel Aal 2015; Lund et al. 2017). The environmental abundance and the redox activity of its soluble and (bio)mineral forms make its biogeochemical cycle particularly important for all near-surface biogeochemical processes. We now know that Fe acts as a catalyst for the degradation and cycling of multiple elements, including contaminants such as hydrocarbons, and that its cycling is mostly through biotic pathways.

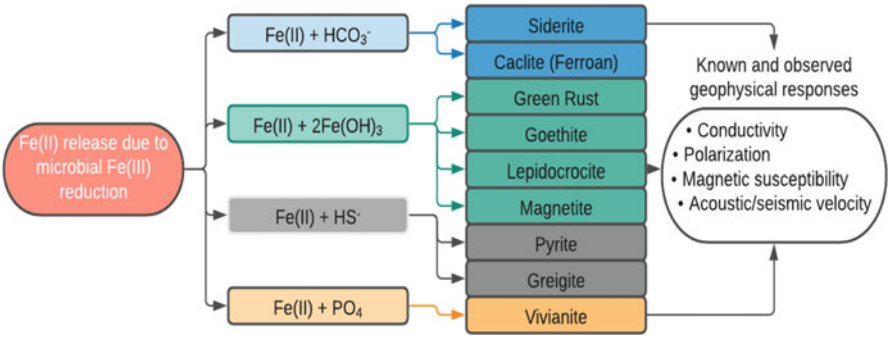

Fig. 6 Conceptual model showing different biomineralization pathways and the resulting common iron mineral phases observed at hydrocarbon-contaminated sites undergoing microbial degradation (modified from Atekwana and Abdel Aal 2015)

Magnetic susceptibility has recently emerged as a potential characterization and/or monitoring tool for hydrocarbon biodegradation because of the role of magnetite in bioremediation. Fe reduction, for example, is a common, and very important, process occurring at hydrocarbon-impacted sites. Microbial-driven hydrocarbon degradation will lead to the formation of new Fe-bearing minerals, or the transformation of existing Fe minerals depending on environmental conditions and Fe cycling (Fig. 6) (Atekwana et al. 2014; Lund et al. 2017). The presence of biogenic magnetite and its transformations, mainly due to iron-reducing microbial activity, seem to dominate the MS signal at the National Crude Oil Spill Fate and Natural Attenuation Research Site in Bemidji (MN) (Atekwana et al. 2014; Atekwana and Abdel Aal 2015; Lund et al. 2017). Atekwana et al. (Atekwana et al. 2014) showed enhanced MS responses across the site, with highest values in the water table fluctuation zone above the source zone, based on an extensive set of MS borehole logs. Follow-up research revealed the dynamic nature of the MS signal, with decreasing trends that are attributed to the continuous biomineral transformations driven by iron-reducing microbes (Lund et al. 2017). The opportunity exists to utilize MS as a non-invasive tool to study Fe cycling and Fe mineral transformations, particularly at hydrocarbon-contaminated sites.

4 New Applications and Opportunities

Geophysical methods offer non-invasive and real-time monitoring advantages but often suffer from non-uniqueness and ambiguity in data interpretation. The joint utilization of multiple geophysical methods is often adopted to reduce ambiguity. By tackling multi-physics problems from different angles utilizing multiple types of geophysical signals, interpretation fidelity and uncertainty reduction can be improved. In biomineralization studies, joint applications of (S)IP, acoustic and magnetic susceptibility, nuclear magnetic resonance (NMR), and self-potential

(SP) can be utilized to improve process understanding and quantification (Williams et al. 2005; Slater et al. 2008; Personna et al. 2008; Wu et al. 2011; Mewafy et al. 2011; Atekwana et al. 2014). For example, in the recent MICP field demonstration, DC resistivity was used to characterize the geology of the site, IP and SIP were used to monitor the biomineralization front, while borehole seismic and NMR confirmed the predicted porosity reduction and stiffness increase (Saneiyan et al. 2019, 2020; Ohan et al. 2020). In addition, coupling geophysical approaches with flow and reactive transport models provides a way to improve the mechanistic understanding of biomineralization processes and the underlying drivers of measured geophysical signals (Wu et al. 2011; Mellage et al. 2018; Izumoto et al. 2020).

Dynamic mineral precipitation and dissolution yields a distinct environment-dependent geochemical signal directly related to biological turnover. The sensitivity of geophysical methods to the surface charge, conductive and magnetic properties of biominerals provides a unique non-invasive sensing opportunity to capture real-time biogeochemical information in environmental samples, field investigations, and laboratory experiments. In dynamic subsurface environments, biomineral precipitates can be short-lived, and reductive dissolution or parallel reactions can mask the extent of a specific reaction pathway, resulting in missed information when applying traditional sampling methods (Posth et al. 2014).

The small nucleation sites of biominerals dictate that these are often found as nano-sized precipitates of high surface area and reactivity. Owing to their nano-size, biominerals are important players in (bio)geochemical cycling and contaminant turnover. For example, pyrite nanoparticles precipitated during reducing conditions can act as a source of electrons for denitrification (Bosch et al. 2012). Cycles of oxidized and reduced conditions can yield precipitation of mineral metal-oxide coatings (both of biotic and abiotic origin) onto aquifer substrate, which can increase the metal-binding capacity of a system (Teutsch et al. 2005). Biominerals are typically surrounded by microbes themselves, and secreted extrapolymeric substances provide additional (to those of the precipitates) binding sites for metal sorption (Ferris 2005). The latter can act to enhance the detectability of iron and manganese oxides that yield low-intensity geophysical signals in comparison to conductive and magnetic biominerals (see Fig. 2).

The conclusive identification of biomineral type requires the use of traditional sampling and analytical tools that rely on sample extractions (e.g., Mössbauer, EDS/X, X-ray diffraction). However, geophysical methods can provide dynamic temporal information, a key requirement for determining reaction kinetics and ultimately the timescales of processes of interest. Thus, the integration of magnetic and electric methods as monitoring tools can force a paradigm shift in the detection and monitoring of biomineral formation and dissolution and parallel reactive and sorption processes that act to modify subsurface electrical properties. It is conceivable that geophysical signals can yield information related to, for example, nitrate turnover coupled to the reduction of pyrite nanoparticles. In particular, the ability to extract quantitative information from such responses would be enhanced via the joint interpretation of measured data with reactive transport and/or surface complexation models (Kessouri et al. 2019).

In conclusion, biogeophysics is a relatively young discipline that made great strides forward in less than two decades since its conception. Especially for biomineralization processes, biogeophysical studies identified the most promising methods and established qualitative links between biominerals and geophysical signals. For biogeophysics to truly contribute in biomineralization studies, these links have to become quantitative. This objective is not far-fetched with recent research showing early steps toward the right direction. Theoretical mechanistic models describing the links between biomineralization and geophysical signals, are in development (Leroy et al. 2017). Furthermore, laboratory research showed that SIP signals can be used to quantify FeS precipitation (Ntarlagiannis et al. 2010). Finally, applications of biogeophysical methods are increasingly transitioning from the safe laboratory space to field applications (Flores Orozco et al. 2011; Lund et al. 2017; Saneiyan et al. 2020) highlighting the progress in data acquisition and understanding of the fundamental mechanisms.

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The Molecular Genetics of Microbial Biomineralization

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Contents

Abstract Microbial organisms are responsible for the synthesis of some of the most elaborate of biominerals. In particular, diatoms make intricate silica frustules and coccolithophores make morphologically complex $CaCO_3$ scales. The significance of these algae and their biominerals in the natural environment, as well as the potential to use them in biotechnology, makes understanding the molecular genetic underpinnings of biomineralization in these organisms an important research area. In this chapter I discuss our current understanding of the molecular genetics of biomineralization in diatoms and coccolithophores while highlighting gaps in our knowledge. I also compare these intracellular biomineralization processes with those in magnetotactic bacteria, to emphasize commonalities and differences in the genetic blueprints of these biominerals. After considering the regulation of coccolithophore

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and diatom biomineralization, outstanding question, methodological opportunities, and future directions of research are discussed.

1 Introduction

Although single-celled microbes are often considered simpler systems than multicellular organism, some of the most morphologically intricate biominerals are in fact made by microorganisms, in particular eukaryotic algae. As biologists, we are all aware that cells can make fabulously complex structures on a minute scale (think of the ribosome), but there is something especially intriguing about the inorganic nature of biominerals: that the cells appear to be almost 'building' something non-self, analogous to how humans use inorganic materials. Beyond their intrinsic fascination, biomineralizing algae occupy key positions in global food webs and biogeochemical cycles. For example, silicifying diatoms and calcifying coccolithophores together contribute around 50% of marine primary productivity, and their mineralized cellular coverings are thought to be crucial to this ecological success (Lopez et al. 2005; Monteiro et al. 2016). Coccolithophore calcification is a key component of the 'carbonate counter pump' which affects the degree to which CO_2 is drawn down (or degassed) from the ocean's surface, while biominerals can also ballast single particles in the oceans, helping to lock away carbon in sediments on the sea floor (Sanders et al. 2010). Analysis of algal minerals from sediments is a key technique in palaeoclimatic reconstruction (Hermoso 2014), in turn helping us to predict how the Earth system will respond to anthropogenic climate change. Beyond their environmental importance, algal biominerals have received attention because of their potential in materials science and nanotechnology. For example, diatom silica has already found potential application in diagnostics, biosensors and drug delivery (Mishra et al. 2017), and coccolithophore calcite also has biotechnological potential (Skeffington and Scheffel 2018; Lomora et al. 2021). The fact that algae can produce these complex structures using only salt water and sunlight makes them particularly attractive systems to develop as we move towards a low-carbon economy.

In order to understand how biomineralizing microbes will respond to global change, and in order to exploit these organisms for biotechnology, it is important to gain an understanding of the molecular genetic program underpinning the synthesis of the minerals. Since the very beginning of algal biomineralization research, it has been clear that the mineral architecture is genetically determined. After inoculating a culture with a few hundred cells of a given species, you will soon have millions of daughter cells coated in mineral of near identical morphology, and the morphology of that mineral is generally relatively insensitive to a range of growth conditions. Indeed, traditional taxonomy of biomineralizing algae was based to a large degree on mineral morphology, and molecular analyses over the

past decades have confirmed the view that cells generating a particular morphology form genetically distinct lineages. Since the molecular biology revolution, researchers have been interested in understanding the 'genetic blueprint' for different biominerals. This includes identifying the cellular machinery responsible for biomineral production and control of morphology, as well as understanding the genetic underpinning of differences in mineral structure and mineralization processes between species. Over the past quarter century, an increasing range of genetic resources and tools have become available, driving this field forwards. Although interesting biominerals are found in a range of microbial eukaryotes (e.g. silicification in Bolidophytes and some radiolarians, the production of strontium sulphate skeletons in acantharian radiolarians and silicification or calcification of dinoflagellate cysts), research has focused on two groups, the diatoms and the coccolithophores, due to their a bundance in the natural environment, the relative ease with which certain species can be cultured and the complex nature of the biominerals they produce. This chapter will focus on our understanding of the molecular genetics of biomineralization in these two groups and point out the parallels between these seemingly very different systems. However examples will also be drawn from other branches of the tree of life, in particular from the magnetotactic bacteria, as an example of a prokaryotic biomineralization system for which the genetics are well understood. These bacteria are presented in detail in other chapters of this book, so these are only discussed here where pertinent comparisons can be made to diatoms and coccolithophores and where lessons can be learned from the advanced genetic experiments that have been performed in these species.

The first part of this chapter briefly introduces the reader to the biology of the systems that will be discussed. Subsequent sections discuss the molecular genetic machinery necessary to synthesize a biomineral, how that machinery may be regulated by the cell and what we still have to learn about the molecular genetics of microbial mineralization.

2 Molecular Genetic Models for Microbial Biomineralization

This section outlines the basic biology of the systems which will be discussed in the remainder of the chapter. Given the large scope of this work, it is not possible to be comprehensive, so below I also point the reader to key reviews for more detailed treatments of particular topics.

Coccolithophores (Fig. 1a, b) are single-celled algae found throughout the world's oceans, with cells coated in calcitic scales known as coccoliths. Two types of coccoliths are often distinguished. The first, called heterococcoliths, are typical of the diploid phase of coccolithophore life cycles, and the individual calcite crystals within the coccolith have complex shapes. The second, known as holococcoliths, are

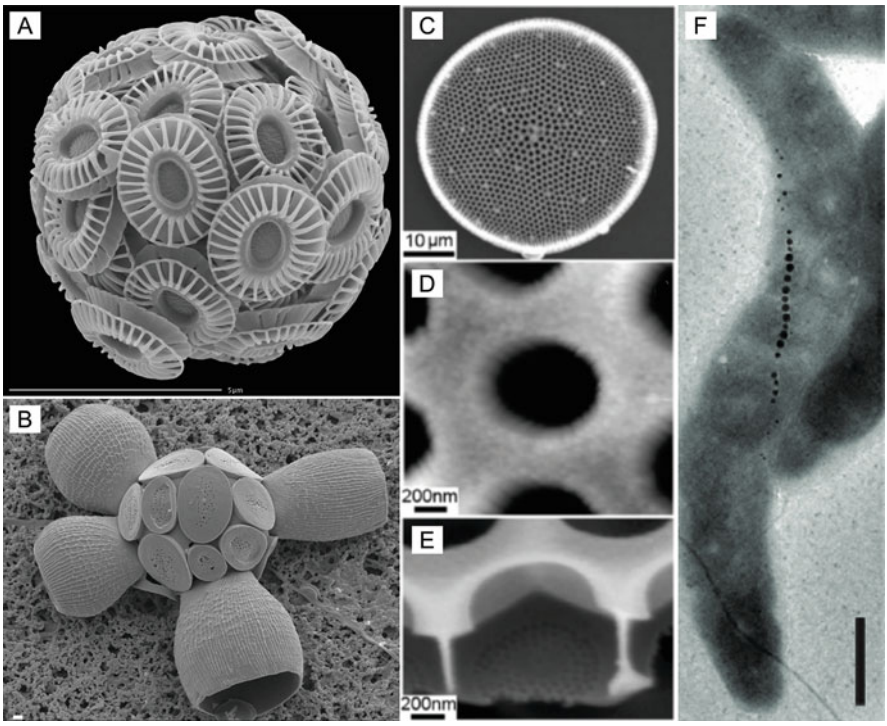

Fig. 1 Biominerals formed by the groups of organisms that are the focus of this chapter. (**a**) SEM micrograph of the coccolithophore *Emiliania huxleyi* (image credit: Dr. Jeremy Young, University College London, www.mikrotax.org/Nannotax3, scale bar: 5 µm), (**b**) SEM micrograph of the coccolithophore *Scyphosphaera apsteinii*, which produces two types of coccoliths on a single cell: large cup-shaped lopadoliths and flat muroliths (image credit: Dr. Jeremy Young, University College London, www.mikrotax.org/Nannotax3, scale bar: 1 µm). (**c–e**) SEM images of silica from a valve of the diatom *Thalassiosira eccentrica*, showing the hierarchical organization of pores in the silica (modified from Mitchell et al. (2013), under terms of the Creative Commons Attribution Licence). (**f**) TEM micrograph of the magnetotactic bacterium *Magnetospirillum gryphiswaldense*, scale bar 500 nm (modified from Zeytuni et al. (2014), under terms of the Creative Commons Attribution Licence). A chain of magnetosomes can be observed in the centre of the cell

produced by the haploid life cycle phase of some coccolithophore species and consist of amalgamations of small rhombohedral calcite crystals. Coccolithophore biomineralization research has focused almost exclusively on heterococcolith formation, so that is also the focus of this chapter, and heterococcoliths will simply be referred to as coccoliths from this point on. Coccoliths are formed in a specialized intracellular vesicle called the 'coccolith vesicle' and are exocytosed onto the cell surface when their synthesis is complete. Coccolith morphologies and the shapes of their constituent calcite crystals differ enormously between species, with coccolith shapes ranging from discs to funnels to cups and spines. There has been a lot of research focused on physiology of coccolithophores, which has contributed to our knowledge of ion transport processes involved in coccolith formation. However,

genetic tools are in their infancy for these organisms, so our knowledge of the molecular genetic machinery underlying coccolith formation is still very basic. *Emiliania huxleyi* is the only coccolithophore species with a sequenced genome (Read et al. 2013) and has been the focus of many experiments, along with another species called *Pleurochrysis carterae* (the name was recently updated to *Chrysotila carterae*). For more detail than can be achieved in this chapter, the reader is directed to some of the excellent reviews available (Young 2003; Monteiro et al. 2016; Brownlee et al. 2020).

Diatoms (Fig. 1c–e) are unrelated to coccolithophores, being found in a different eukaryotic supergroup. They are found throughout the world's fresh and salt water bodies as pelagic organisms and are also important components of biofilms on natural and man-made substrates. They are characterized by a cellular covering (the frustule) made of amorphous silica, which displays species-specific, hierarchical porous nano-patterning (Fig. 1c–e). The silica is produced inside the cells, in silica deposition vesicles (SDVs) before being released to the cell surface. The membrane around the SDV is known as the silicalemma. Two main groups of diatoms are distinguished, the pennates, with bilateral symmetry, and the centrics, with radial symmetry. Although biomineralization has been investigated in both groups, most molecular genetic studies have been performed with centric species, and in particular *Thalassiosira pseudonana*. These species have two types of SDVs: One type produces the radially symmetric frustule ends called valves (Fig. 1c), and the other produces the 'girdle bands' that surround the cylindrical part of the cell. The large body of work describing the biochemistry of diatom silica formation combined with more recent experiments involving genetic manipulation means that we understand more about the molecular genetics of diatom frustule formation than we do about any other algal biomineralization system. The last review of Mark Hildebrand provides an excellent introduction to diatom biomineralization (Hildebrand et al. 2018).

Magnetotactic (Fig. 1f) bacteria are ubiquitous in the low-oxic and anoxic zones of marine sediments and are characterized by chains of magnetosomes: membrane-bound organelles filled with magnetic iron minerals (often magnetite (Fe_3O_4) and sometimes greigite (Fe_3S_4)). These chains allow the bacteria to orientate such that they can efficiently move to optimal positions within chemical gradients in the sediment. Magnetotactic bacteria are found among a number of phylogenetically diverse lineages of gram-negative bacteria. Biomineralization in magnetotactic bacteria is reviewed thoroughly in Chapter 8 of this book, but since they are by far the best genetically characterized prokaryotic biomineralization system, I will use them as an example to contrast with the eukaryotic systems which are described in more detail in this chapter. The exceptional progress in understanding the molecular genetics of biomineralization in this system is largely due to the establishment of *Magnetospirillum magneticum* and *Magnetospirillum gryphiswaldense* as model organisms that can be relatively easily cultured in the lab and genetically manipulated. Both species make chains of cuboctahedral magnetite crystals. In addition to Chapter 8 in this book, the reader is directed to two recent reviews (Uebe and Schüler 2016; McCausland and Komeili 2020) for more in-depth information on biomineralization in magnetotactic bacteria.

3 The Genetic Blueprint of a Biomineral

Given that biomineralization has arisen independently in many diverse taxa and the wide range of minerals that these taxa produce, we should expect to find an equally diverse genetic and molecular machinery underpinning biomineralization processes. Despite this, commonalities can be found between unrelated systems, both at a conceptual level and in terms of the data that supports our understanding of their biology. For example, a mechanism must exist to ensure that mineralization occurs in the 'right' place. This may be transporters concentrating ions in a particular compartment, or the complementary mechanism of molecules that prevent mineralization in the 'wrong' place, despite high enough concentrations of the ions for mineralization to occur spontaneously. In addition, cellular molecules must be involved in the control of the mineralization processes including the generation of the final morphology. The prime candidates are the complex biological macromolecules involved in essentially every cellular process: proteins and polysaccharides. Given that the machinery must exist to generate these macromolecules, as well as to modify them and target them correctly with appropriate timing, we can be reasonably confident a priori that biomineralization processes are likely to be directly dependent on the activities of at least tens and probably hundreds of genes. In the remainder of this section, I will sketch our knowledge of the genetic underpinnings of biomineralization in diatoms, coccolithophores and magnetotactic bacteria, highlighting similarities between the systems. I also draw on examples from additional prokaryotic and eukaryotic systems where data is available.

3.1 Generating the Mineralization Compartment

It is probably no coincidence that the most intricately patterned of microbial biominerals are formed in intracellular compartments, in which the conditions for mineral growth can be very precisely regulated by the cellular machinery. In principle the compartment boundary could consist of any molecular system capable of restricting the diffusion of the key biomineral precursor species (e.g. ions or small particles) while permitting control of macromolecular complement of the compartment. Classical lipid bilayer bound organelles are the obvious 'solution' to these requirements and form the biomineralization compartment in diatoms, coccolithophores and magnetotactic bacteria. However, alternative solutions have also evolved. For example, intracellularly calcifying cyanobacteria contain amorphous calcium carbonate (ACC) granules (Couradeau et al. 2012; Benzerara et al. 2014) which are coated by a ca. 2.5-nm-thick electron dense envelope (De Wever et al. 2019). This is too thin to be a lipid bilayer, and it has been suggested that it is likely to be a protein shell. If so, then this would be a new example of a proteinaceous 'bacterial microcompartment', joining more famous examples such as the carboxysome (Kerfeld et al. 2018). Beyond the biomineralizing organelles described

above, it is intriguing that liquid-liquid phase separation is increasingly being found to define subdomains within previously known cellular compartments (Boeynaems et al. 2018; Abbondanzieri and Meyer 2019). It will be interesting to see if future research yields examples of this process generating biomineralizing compartments or subcompartments in microbes.

Electron microscopy studies of a variety of coccolithophore species have convincingly demonstrated that the coccolith vesicle develops from Golgi cisternae (reviewed in Young 2003). Other aspects of the ultrastructure of calcification vary from species to species. For example, the coccolith vesicles in *E. huxleyi* and *Coccolithus pelagicus* ssp. *braarudii* are associated with a complex membrane structure known as the reticular body (Wilbur and Watabe 1963; Taylor et al. 2007), while coccolith vesicles of *Pleurochrysis* (*Crysotila*) *carterae* are associated with small vesicles termed 'coccolithosomes' (van der Wal et al. 1983). To add to the complexity, some species (such as *P. carterae*) produce unmineralized organic scales which pass through the Golgi system in parallel to the coccoliths (van der Wal et al. 1983), and other species produce more than one type of coccolith on the same cell (Young et al. 2009; Drescher et al. 2012).

The origins of SDVs in diatoms are more mysterious. Although there have been suggestions that the SDV is Golgi derived, based on the fact that Golgi membranes have been observed close to the SDV in some studies (e.g. Reimann 1964; Schnepf et al. 1980), the reality is probably more complex (Bedoshvili and Likhoshway 2019). This view is supported by the fact that the earliest stage of SDV formation that could be identified in *Navicula pelliculosa* was a vesicle that already contained a small amount of silica, ran the length of the cell under the plasmalemma and had a diameter much smaller than that of a Golgi dictyosome (Chiappino and Volcani 1977). Now that protein markers are becoming available for the silicalemma (Tesson et al. 2017; Yee et al. 2020), it may become possible to use super-resolution microscopy, to trace the origins of the membrane before silica begins to form.

In both diatoms and coccolithophores, we can assume that a substantial protein machinery is involved in biogenesis of the mineralization compartment, but we are almost completely ignorant of its nature. In model cell biology systems such as yeast, the maturation of Golgi vesicles and the regulation of vesicle fusion events involve a large number of factors, including SNAREs, golgins and Rab GTPases among others (Witkos and Lowe 2017). The increasing availability of genome and transcriptome information for diatoms and coccolithophores (Read et al. 2013; Keeling et al. 2014; Osuna-Cruz et al. 2020; Falciatore et al. 2020) presents an opportunity to search for homologues of such factors and for evidence of evolutionary innovations which may be specific to membrane trafficking in biomineralization processes. Indeed there is already some evidence for a specific syntaxin-1 SNARE that correlates in expression with calcification in *E. huxleyi* (Von Dassow et al. 2009). In the context of calcification, it may be particularly interesting to examine the role of annexins, which are known to bind membrane phospholipids in a Ca^{2+}-dependent manner (Konopka-Postupolska and Clark 2017). It is also possible that Ca^{2+} itself helps to regulate membrane fusion events, since it is known to directly regulate membrane curvature (Grieve et al. 2012).

The protein complement of an organelle is normally crucial to its identity and function, yet our knowledge of the proteins associated with the membranes of the coccolith vesicle and the SDV, and the mechanisms by which these proteins are targeted to their destination, is limited. There is some biochemical and immunological evidence for a V-type ATPase in the coccolith vesicle membrane (Araki and González 1998; Corstjens et al. 2001), although its exact role in calcification has yet to be determined (Mackinder et al. 2010). Beyond this, we have very little knowledge of the protein content of the coccolith vesicle or of how proteins are targeted to this compartment. In diatoms we know a little more thanks to the genetic tools that are available in these organisms. Tesson and colleagues have identified a small family of silicalemma-localized proteins with a single transmembrane domain and a silica-rich region (Tesson et al. 2017). The exact roles of these proteins are unclear, but strains with putatively reduced expression of these proteins displayed some minor defects in frustule morphology. Another study has shown that a short, lysine-rich sequence is sufficient to target GFP to the silica (Poulsen et al. 2013), presumably via the SDV, but the generality of this targeting mechanism is unclear.

The relative ease of generating knock-out mutants in magnetotactic bacteria means that we have a better understanding of the genes that are necessary for the formation of magnetosomes, which arise from invaginations of the cytoplasmic membrane of the cell. Genetic evidence suggests that a protein named MamB plays a key role in orchestrating this process since it has the most extreme membrane phenotype of any *mam* gene in knock-out mutants, although it is also clear that a large number of other magnetosome proteins are required (Uebe and Schüler 2016). The biochemical and structural basis of formation of the magnetosome membrane has yet to be elucidated.

3.2 Ion Transport and Buffering

For intracellular biomineralization to occur, the precursor ions must first be transported from the extracellular environment to the compartment where the mineral is formed. This often involves a process of concentration, effectively pumping the ions 'uphill' against a concentration gradient, and thus comes with an energetic cost. The transport of ions must be achieved in a way that provides the necessary flux while not interfering with ion homeostasis in other cellular compartments. Mineralization processes are also often pH dependent, and sometimes generate protons, so cells need mechanisms to control the pH in the mineralizing compartment. In the following section, I will describe how the requirements are achieved in diatoms, coccolithophores and magnetotactic bacteria.

3.2.1 Ion Transport in Diatom Silicification

The substrate for diatom silicification is orthosilicic acid, which is a small, uncharged molecule at circa neutral pH and can thus diffuse freely across biological membranes. Such diffusive uptake is likely to be a major mode of silica uptake at high environmental silica concentrations (Thamatrakoln and Hildebrand 2008), but at low concentrations (10 μM is typical in surface waters where diatoms grow to highest densities (Tréguer et al. 1995)), protein-based transport systems are involved. Evidence for such systems included saturable uptake at relevant concentrations (Thamatrakoln and Hildebrand 2008), and dependence on a transmembrane sodium gradient (Bhattacharyya and Volcani 1980). The molecular genetic basis of these observations has now largely been elucidated. The first silica transporters (SITs) were identified from cDNAs that were induced by low silicic acid concentrations and conferred Ge transport capacity to *Xenopus* oocytes (Hildebrand et al. 1997). More recently silicic acid transport by SITs has been directly measured and sodium silica symport confirmed as the mode of transport (Knight et al. 2016). The same study demonstrated that conserved glutamine residues in the SITs are crucial for transport and are likely to have a role in substrate binding. A wide-ranging phylogenetic analysis has shown that SITs are by no means unique to diatoms, but (along with related transporters) probably underpin silicification in a number of eukaryotic supergroups, and have an origin deep within the eukaryotic lineage (Marron et al. 2016).

Although we now understand the fundamentals of silica transport in diatoms, there is still much to be discovered. For example, diatom genomes often encode multiple SIT genes, and the roles of the different paralogues are unclear. When three SIT genes were localized in *T. pseudonana* (Shrestha and Hildebrand 2015), TpSIT1 and TpSIT2 were found to localize to the plasma membrane, while TpSIT3 displayed an ambiguous intracellular localization. Knock-down of *TpSIT1* and *TpSIT3* resulted in slower silica accumulation in cells recovering from Si limitation (Shrestha and Hildebrand 2015), suggesting that they are the major uptake system under low Si conditions. It is not known whether SITs are involved intracellular transport of silica into the SDV, or whether particular SITs become more or less important under certain environmental conditions or at particular stages of the silicification process. Intriguingly, several studies have estimated silica concentrations in diatom cells well in excess of the 1–2 mM solubility limit (reviewed in Martin-Jézéquel et al. 2000), raising the questions of how silica is distributed within the cell, what factors drive its intracellular distribution and what mechanisms operate to prevent ectopic condensation reactions and silicification outside of the SDV.

In addition to the transport of silica, the nature of silica chemistry means that diatom cells must precisely regulate the pH in SDVs to ensure appropriate silicification. SDVs have been shown to be acidic and to increase in acidity during the valve formation process (Vrieling et al. 1999). Orthosilicic acid ($Si(OH)_4$) readily oligomerizes when concentrations exceed its solubility limit, and this initial oligomerization is accelerated by the presence of ionized orthosilicic acid molecules

(Belton et al. 2012). The pKa of orthosilicic acid is 9.8; however as larger oligomers and small particles form, the pKa of the Si-OH (silanol) groups drops to about 6.8 meaning that the particles tend to carry a net negative charge at biologically relevant pH and repel each other. This means they continue to grow as individual particles. If the pH drops substantially below 7, or if molecules (e.g. salts, amines or basic amino acids) that bridge or neutralize the surface charges are present, then the particles will tend to coalesce to form a 3D gel network which is generally the arrangement of silica to be found in diatom silica (Hildebrand et al. 2006). It has been shown that pore sizes decrease in the silica of diatoms (*Thalassiosira weissflogii*) grown at low pH, supporting the idea that low pH promotes coalescence of silica particles in vivo (Hervé et al. 2012).

At a molecular level, control of pH in SDVs has been shown to be dependent on the activity of V-type H^+ ATPases (VHAs) (Vartanian et al. 2009; Yee et al. 2020). A GFP tagged subunit of the complex accumulates in actively silicifying SDVs, and pharmacological inhibition of VHA prevented silica frustule formation and cell division in *T. pseudonana* (Yee et al. 2020). Partial inhibition of VHA activity led to cells with aberrant valve morphology in both *T. pseudonana* (Yee et al. 2020) and *P. tricornutum* (Vartanian et al. 2009). Interestingly, Yee et al. found that the insertion of an SDV membrane protein was also compromised by VHA inhibition, suggesting that regulation of SDV pH may in turn regulate recruitment of frustule biogenesis machinery.

In the future it will be interesting to learn how silica transport and SDV pH regulation are coordinated and adjusted to respond to changing external conditions such as Si availability, pH and salinity.

3.2.2 Ion Transport in Coccolithophore Calcification

Some coccolithophore species can form coccoliths at rates of one per hour, requiring large fluxes of Ca^{2+} and HCO_3^- from the external medium to the coccolith vesicle, and large fluxes of H^+ generated by the precipitation of $CaCO_3$, out of the cell. The available evidence suggests that both photosynthesis and calcification use HCO_3^- as a substrate (Bach et al. 2013), but the route of HCO_3^- transport is not clear. Estimates of membrane potentials and the HCO_3^- gradient suggest that it could diffuse passively into the cell (Nimer and Merrtt 1992; Anning et al. 1996; Mackinder et al. 2010), but inhibitor studies also support the role of a SLC4-type (HCO_3^-/Cl^-) anion exchanger (Herfort et al. 2002), corroborated by the fact that a SLC4 homologue is upregulated in calcifying cells of *E. huxleyi* compared to non-calcifying cells (Von Dassow et al. 2009).

The pathway of Ca^{2+} transport to the site of calcite precipitation is also uncertain, but it is clear that there is a requirement to maintain low calcium concentrations in the cytosol to allow Ca^{2+}-dependent cellular signalling mechanisms to function. Low cytosolic calcium concentrations effectively generate a kinetic barrier to uptake into the endomembrane system. Given that a high flux of Ca^{2+} to the coccolith vesicle must be maintained despite this barrier, research focused on potential routes

that calcium could take through the endomembrane system to reach the coccolith vesicle. Although experiments have been performed to investigate whether fluid phase uptake directly into the endomembrane system plays a role, the results have been negative to date (Raven 1981; Brownlee et al. 2015). An alternative is that the cytoplasmic Ca^{2+} concentration is locally higher in the space between the plasma membrane and the cortical ER, enabling high rates of uptake into the endomembrane system immediately after transport across the plasma membrane. The principle that the cytosol is not homogenous but consists of distinct domains has gained traction in recent years (Boeynaems et al. 2018), so it is not impossible that regions of the cytosol have biophysical properties that allow Ca^{2+} to accumulate to higher than normal concentrations. Multiple studies have noted that in some species the coccolith vesicle is close to the nuclear envelope for most of the calcification process (Westbroek et al. 1984; Taylor et al. 2007; Drescher et al. 2012; Yin et al. 2018), leading to speculation that Ca^{2+} could be transported across the narrow intermembrane space with locally raised Ca^{2+} concentrations. There have also been suggestions that calcium accumulating in acidocalcisome-like organelles, which are found in a wide variety of mineralizing and non-mineralizing algae (Gal et al. 2018), may have been co-opted as part of the calcium transport pathway in coccolithophores (Sviben et al. 2016). However, there is as yet little evidence to directly support this hypothesis (Gal et al. 2017). Electron micrographs of calcifying *P. carterae* cells often show small vesicles with an electron dense cargo close to the coccolith vesicle (Outka and Williams 1971), and there is compelling evidence that these contain calcium complexed with acidic polysaccharides and that these are delivered to the coccolith vesicle (van der Wal et al. 1983; Marsh 1994). However, calculations have shown that there is only enough of the polysaccharide to complex a relatively small proportion of the calcium required for building coccoliths (Marsh 1996).

Uptake of calcium directly at the coccolith vesicle membrane has the advantage that it could be mediated by a Ca^{2+}/H^{+} exchanger and thus contribute to the alkalinization of the vesicle that is required for calcite precipitation (Mackinder et al. 2010). Indeed, a CAX-like Ca^{2+}/H^{+} antiporter is upregulated in calcifying cells (MacKinder et al. 2011). Having removed protons from the coccolith vesicle, they must also be removed from the cell. An important study of coccolithophore plasma membrane physiology (Taylor et al. 2011) identified a voltage-gated H^{+} conductance in two coccolithophore species and the genes that are likely to encode the protein channel responsible. More recently, a novel class of voltage-gated sodium channels called EukCatB channels have been characterized in coccolithophores (Helliwell et al. 2020). Since coccolithophore plasma membranes are known to be excitable (Taylor et al. 2011, Helliwell et al. 2020), these data have led to the hypothesis that the firing of action potentials might be the mechanism by which H^{+} is removed from the cell (Brownlee et al. 2020). One plausible scenario put forwards by Brownlee and colleagues is that cation entry could depolarize the membrane and trigger opening of the voltage-gated proton channel followed by H^{+} efflux from the cell. The membrane would repolarize via ATP-dependent pumping of cations out of the cell. Less than one action potential per second would be required

to remove the H^+ generated by calcification in this manner in *C. braarudii* (Brownlee et al. 2020). Whether Ca^{2+} or Na^+ influx carries the depolarising current has consequences for the energenic cost of repolarization, since Ca^{2+} could be consumed by calcification and then would not have to be pumped out of the cell. Since the cost of cation efflux will be dependent on the external pH, the exact mechanisms in play here will have consequences for the physiological responses of coccolithophores to ocean acidification (Brownlee et al. 2020).

Although there may be commonalities in the ion transport mechanism operating in different coccolithophore species, we currently lack the genetic and physiological data to identify the aspects that are widely conserved. However, there is increasing evidence that there are aspects of ion transport which differ between species (recently reviewed in Brownlee et al. 2020). For example, the trace elemental composition of coccolith calcite differs between species (Stoll et al. 2002; Bottini et al. 2020), and differences in isotope fractionation indicate that ions are subject to somewhat different transport events in different species (Rickaby et al. 2010), or even in different types of coccoliths produced by the same species (Meyer et al. 2020).

3.2.3 Ion Transport Magnetotactic Bacteria and Commonalities with Calcification

Magnetite accumulation in magnetotactic bacteria has similarities with calcification in that the substrate (free ferric or ferrous iron vs. free calcium) concentrations must be kept low in the cytosol. In the case of iron, this is because free iron can readily participate in the Fenton reaction and related reactions that can generate free radicals and damage cellular components. It seems that the general iron uptake mechanisms in MSR do not participate in biomineralization since deletion of a transcriptional master regulator of these systems only cause minor changes in magnetite formation (Uebe et al. 2010; Qi et al. 2012; Wang et al. 2015). However deletion of two GTP-dependent Fe^{2+} transporters which are distributed throughout the cytoplasmic membrane of the bacterium do drastically decrease magnetite formation (Rong et al. 2008; Rong et al. 2012). This suggests that Fe^{2+} is first transported into the cytoplasm and subsequently taken up into magnetosomes. There is also data to suggest that iron is complexed at the membrane by an organic substance such as ferritin and delivered directly to the magnetosome membrane (Faivre et al. 2007). Genetic evidence indicates that uptake into the magnetosome is mediated, with some redundancy, by two proteins (ManB and MamM) belonging to the cation diffusion facilitator (CDF) family (Uebe et al. 2011; Keren-Khadmy et al. 2020) as well as MamH and MamZ which belong to the major facilitator superfamily (Raschdorf et al. 2013).

A further similarity with calcification is that protons are released by precipitation of magnetite and that these need to be removed from the site of mineralization in order to maintain the alkaline pH required for mineralization. A protein called MamN has similarity to Na^+/H^+ antiporters and so has the potential to carry this

flux (Jogler and Schüler 2006). A knock-out mutant of this protein displayed reduced magnetosome size and number compared to wild type (Lohße et al. 2014).

3.3 *The 'Organic Matrix' of Diatom SDVs: Control of Mineral Nucleation and Growth*

Forty years ago it had already been recognized that when inorganic crystals generated by an organism take on complex yet reproducible and genetically inheritable shapes, mineralization must be guided and controlled via interactions with organic components, for which the term 'organic matrix' was coined (Lowenstam 1981). Much biomineralization research over the subsequent decades has been focused on characterizing these organic components from different biominerals and attempting to deduce their role in mineralization through in vivo and in vitro experiments.

Our understanding of the organic matrix involved in diatom silica cell wall formation is particularly advanced, to a large degree thanks to work in the laboratories of Manfred Sumper, Mark Hilderbrand and Nils Kröger. Three broad classes of organic molecules have been found in association with diatom silica: long-chain polyamines (LCPAs), polysaccharides (especially chitin) and proteins (Hildebrand et al. 2018). Recently it has been directly demonstrated that organic molecules are intimately associated with developing silica inside the SDV (Heintze et al. 2020). LCPAs are entrapped within diatom silica and different species synthesize distinct complements of LCPAs (Kröger et al. 2000). The abundance of LCPAs in silica, and the fact that LCPAs catalyse the polymerization of silicic acid to silica in vitro, has led to the hypothesis that they are likely a key part of the silicification machinery. This is supported by the fact that *T. pseudonana* cells grown with an ornithine decarboxylase inhibitor display aberrant frustule morphology (Frigeri et al. 2006), although this inhibitor will also affect synthesis of short-chain polyamines required in multiple cellular functions, so the effects could be secondary. Polyamine metabolism genes are also overrepresented in diatom genomes relative to other eukaryotes (Bowler et al. 2008). To build LCPAs, an S-adenosyl methionine decarboxylase (SAMDC) is required to generate the aminopropyl moiety for addition to the growing LCPA by an aminopropyl transferase (APT) activity. Diatoms are unique among eukaryotes in that they contain fusion proteins containing SAMDC and APT domains, and it is hypothesized that these bifunctional proteins could be responsible for LCPA synthesis in diatoms (Michael 2011).

Chitin (β-linked N-acetylglucosamine) has been found associated with the surface of diatom silica (Durkin et al. 2009) and embedded within it (Tesson et al. 2009), forming a meshwork that makes up between 25% and 40% of the organic content of the silica (Brunner et al. 2009). All the enzymes necessary to synthesize chitin from fructose are encoded in the *T. pseudonana* and *P. tricornutum* genomes, and chitin synthase genes have been detected in many diatom species (Durkin et al. 2009). Chitin is a common component of the organic matrix of mineralized structures of

several organisms, including molluscs and corals (Ehrlich 2010), so it is possible that chitin has a role in the templating of mineralization in diatoms, although definitive evidence for this has yet to be found. Studies focused on chitin synthases in diatoms (Wustmann et al. 2020) should begin to provide further evidence of the role of chitin. Other polysaccharides identified in diatom silica include mannose-rich polymers (Ford and Percival 1965; Tesson and Hildebrand 2013) as well as the β-1,3 glucan callose. Indeed, treatment of cells with a β-1,3 glucan synthesis inhibitor resulted in alterations to silica morphology (Tesson and Hildebrand 2013).

Proteins that have been identified as associated with silicification in diatoms are generally grouped according to the biochemical method used to extract them (Hildebrand et al. 2018). A number of proteins have been identified from ammonium fluoride dissolution of detergent-cleaned frustules, suggesting that these proteins are integral to the silica. The silaffins from *T. pseudonana* are proteins that fall into this category, and they nicely illustrate the complexities of the molecular genetic underpinnings of diatom silica formation. Silaffins are proteins, first identified in *Cylindrotheca fusiformis* (Kröger et al. 1999, 2002), which are rich in lysine and hydroxyl-bearing amino acids as well as being post-translationally modified by phosphorylation and polyamine modification of lysine residues. In *T. pseudonana*, two very similar genes (tpsil1 and tpsil2) each encode a protein that is proteolytically cleaved to a high (H) and low (L) molecular weight product (Poulsen and Kröger 2004). The H products of the two genes were isolated and biochemically characterized together (tpSil1/2H), as were the L products (tpSil1/2L). A third, unrelated, gene encodes tpSil3. LCPAs isolated from the same cell wall preparations do not induce silica precipitation in vitro and neither do any of the silaffins on their own. Mixtures of LCPAs and silaffins could induce precipitation, but the exact response depended on the silaffin concerned. As the concentration of tpSil1/2L was increased in the reaction, the rate of silica precipitation increased, generating nano- to microscale silica sphere. However, tpSil3 only had silica precipitation activity over a certain window of concentrations, resulting in silica spheres of various sizes, while tpSil1/2H only had activity at rather low concentrations and yielded silica sheets with irregular pores. It was hypothesized that the glycosylated and sulphated residues in tpSil1/2H tend to have more of an inhibitory effect on silica formation, while phosphate groups that dominate the chemistry of tpSil1/2L have a purely enhancing effect on silica formation, similar to the effect of inorganic polyanions incubated with LCPAs. The above illustrates that the role that silaffins play in vivo will depend on numerous factors, including their localization within the SDV, their final absolute concentrations, their concentrations relative to each other, the timing of proteolytic cleavage and potentially their stability. Numerous factors must be involved in silaffin production (e.g. enzymes leading to glycosylation, phosphorylation, sulphation and proteolytic cleavage), and genetic variation at loci encoding these factors could also potentially have an impact on silicification. To further add to the complexity, other silica integral proteins such as the silacidins (peptides derived from cleavage of an acidic, phosphoprotein in *T. pseudonana* (Wenzl et al. 2008)) have also been shown to promote silica formation in vitro. We clearly have much more to learn about this complex system.

Although mixtures of ammonium fluoride solubilized proteins and LCPAs are clearly sufficient to promote silica precipitation, alone they do not generate the complex patterning exhibited by diatom silica. This is thought to be partly determined by components that remain insoluble after ammonium fluoride treatment. Various insoluble organic matrices have been isolated from diatom silica, including proteinaceous 'microrings' (Scheffel et al. 2011) from girdle bands in *T. pseudonana* which have silica-forming activity in vitro and contain proteins called cingulins which are rich in serine, lysine and aromatic residues. Valve-associated insoluble organic material has also been isolated from a number of other species (Scheffel et al. 2011; Tesson and Hildebrand 2013) including *T. pseudonana* (Kotzsch et al. 2016), and proteomic analysis of the latter identified several novel 'SiMat' proteins as well as the silaffin tpSil1 and several cingulins. Elegant experiments with organic 'microplates' isolated from the valves of *T. pseudonana* showed that subject to remineralization, a small proportion of the plates developed hierarchical porous silica patterns with distinct similarities to the valves of the native diatom silica (Pawolski et al. 2018). When the assay was performed in the presence of ammonium fluoride soluble material from dissolved silica frustules, the proportion of plates displaying these complex porous patterns rose to over 60%. This strongly supports the hypothesis that the insoluble organic material acts as a template for mineralization, which is further promoted or inhibited at certain positions by the soluble organic material (proteins and polyamines).

A third class of proteins associated with silicification in diatoms are membrane proteins that are likely to be associated with the silicalemma. A protein called silicanin (Kotzsch et al. 2017) and a group of proteins called SAPs (Tesson et al. 2017) from *T. pseudonana* are likely associated with the silicalemma via single transmembrane domains. It seems that for silicanin and TpSAP3 at least, the SDV luminal parts of the proteins are cleaved and incorporated into the silica. TpSil1/2 also appears to have a single transmembrane domain (Hildebrand et al. 2018). These proteins potentially transfer positional information from components in the cytoplasm (such as the cytoskeleton) to the biomineralization machinery within the SDV (Hildebrand et al. 2018).

Although a large number of SDV proteins have now been identified, the challenges involved in the genetic manipulation of diatoms mean that the roles of these protein have only been tested using reverse genetics in a few cases. *T. pseudonana* cells transformed with antisense constructs targeting the silacidin gene were reported to contain less silica-associated silacidin than wild type and to display increased cell size, but no difference in silica nano-patterning (Kirkham et al. 2017). No decrease in silacidin transcript levels was observed in these lines, suggesting that more work may be needed to fully understand the molecular phenotype of the transformants. Transgenic *T. pseudonana* lines containing antisense constructs targeting TpSAP1 and TpSAP3 also could not be confirmed at the transcript level, but reduced silicification was observed on the distal side of the valve across several independent lines and multiple technical replicates (Tesson et al. 2017). Another gene (Thaps3_21880) was selected for gene knock-down because its expression pattern suggested a role in cell wall biogenesis (Trofimov et al. 2019). Applying a neural

network to image analysis, the authors could identify differences in the nano-patterning between transformants and wild type, but the lack of molecular characterization of the transformants makes this work difficult to interpret. In the first application of genome editing to the problem of diatom cell wall synthesis, Görlich and colleagues generated knock-outs of silicanin-1 (Sin1) which were confirmed at the protein level by western blotting. This resulted in changes to the nano-patterning of the valve silica such as a decrease in the number of silica connections between radial bands of silica called costae (Görlich et al. 2019). Although fairly subtle, these morphological changes had a dramatic impact on the strength and stiffness of the cell walls.

3.4 The 'Organic Matrix' of Coccolith Vesicles: Control of Crystal Nucleation and Growth

Heterococcolith calcite has several remarkable features that make it especially interesting from a materials science perspective (Young 2003). Firstly, the orientation of both of the major crystallographic axes of the mineral (the *c*-axis and the *a*-axis) is controlled during the crystallization process. Secondly, individual crystals display remarkably complex, yet reproducible, shapes. These crystals interlock in an intricate manner to form a structurally cohesive unit. Thirdly, the coccoliths display chirality such that the crystals are orientated at a defined angle relative to a tangent to the edge of the coccolith. Fourth, in some species such as *E. huxleyi*, the entire coccolith develops (while still intracellular) a curvature that is approximately the same as that of the cell surface (Wilbur and Watabe 1963). It has long been assumed that the above features largely result from nucleation of the crystals on an organic template (Wilbur and Watabe 1963) combined with organic molecules selectively binding certain crystal faces to regulate their growth. Unlike in diatom mineralization, very little of this organic material ends up inside the mineral itself, as evidenced by the very minor distortions to the calcite lattice in coccoliths relative to pure calcite (Hood et al. 2016).

Some of the properties of coccolith calcite probably arise from the fact that the crystals nucleate on an organic 'base plate' within the coccolith vesicle (Manton and Leedale 1969; Westbroek et al. 1984). These disc-like structures vary from species to species, being, for example, very thin and delicate in *E. huxleyi* and much more substantial in *Pleurochrysis* species. Due to their stability, base plates have been most studied in *Pleurochrysis* species. Two types of calcite crystals with different morphologies and crystallographic orientations have been shown to alternate around the rim of the base plates (Young et al. 1992; Marsh 1999; Young et al. 1999) and have direct contact with the base plate or its rim (Walker et al. 2020). It has been hypothesized that base plates have distinct sites which promote the formation of the two types of crystals (Young et al. 1992), and it inferred that competition for space between crystals during growth probably contributes to the morphology (Walker

et al. 2020). In a revealing in vitro study, Gal and colleagues isolated base plates of *P. carterae* and found that soluble polysaccharides extracted from the coccoliths bind to the edge of the base plates, in the presence of calcium, as nanoscale particles (Gal et al. 2016). The particles bound in two concentric rings at the edge of the base plate, supporting the notion that it contains binding sites with distinct chemistries, although no alternating pattern along the circumference was noted. This study also showed that the base plates alone do not have capacity to induce calcite formation or encode all the information to make a coccolith. The results of another study (Sakurada et al. 2018) imply that one particular *Pleurochrysis* polysaccharide (PSII) is responsible for directing calcium to the base plate and also that mineralization requires components that can be extracted from the base plate by detergent treatment, suggesting that proteins and polysaccharides within the base plate may be involved. Despite its importance, we know surprisingly little about the biochemistry of base plates. They are composed of multiple layers of fibres arranged both concentrically and radially (Manton and Leedale 1969; Brown and Romanovicz 1976; Marzec et al. 2019), and there is evidence that the rim is rich in primary amines (Marzec et al. 2019). Non-calcified scales from *Pleurochrysis scherffelii*, which have a similar fibrous structure, have shown to be largely cellulosic but also to contain some other polysaccharides and proteins (Brown et al. 1969). However, the chemistry of coccolith base plates differs crucially from the chemistry of the non-calcified scales, since the latter do not interact with coccolith-derived polysaccharides to direct calcium to the rim of the scale (Gal et al. 2016).

Abundant acidic, sulphated, coccolith-associated polysaccharides (CAPs) (Borman et al. 1982) are thought to play key roles in calcification, not least because of the evidence described above that they can form aggregates with calcium at the base plate rim. Different species produce CAPs of different molecular weight and composition (Marsh 2003). Strains of the same species also display differences (Lee et al. 2016; Rickaby et al. 2016) which have been hypothesized to be relevant for associated differences in morphology (reviewed in Brownlee et al. 2020). CAPs have been demonstrated to be localized to coccolith vesicles (van Emburg et al. 1986; Marsh et al. 1992) and have strong effects on calcite precipitation in vitro, both in terms of the amount and morphology of the crystals produced (Kayano et al. 2011), but also the $CaCO_3$ polymorph (Walker et al. 2019). Intriguingly, the cations present as well as the pH can both modulate the ability of a CAP from *E. huxleyi* to bind to steps in calcite crystals (Henriksen and Stipp 2009), suggesting that the transport of trace elements and control of pH could impact coccolith morphology via regulation of CAP binding.

In seminal work, Mary Marsh took a genetic approach to investigate the roles of the three CAPs identified in *P. carterae*. Mutagenesis, followed by screening for low-density mutants defective in calcification, identified two independent mutants which lack the CAP known as PS2 (Marsh and Dickinson 1997). This polysaccharide has a very broad molecular weight distribution, being made up of variable numbers of repeating units, and is rich in glucuronic, tartaric and glyoxylic acids, with an extremely high Ca^{2+}-binding capacity. The mutants lacking this polysaccharide exocytosed base plates with no or very little calcite. Where calcite did form,

it was positioned on the edge of the base plate, and the mature crystals had the typical anvil-like shape of wild-type coccoliths, suggesting that the primary role of PS2 may be in substrate delivery or nucleation, rather than maturation of the calcite. In two other studies, Marsh and colleagues identified two mutants of PS3 (Marsh 2000; Marsh et al. 2002), which is a sulphated galacturonomannan of a more defined molecular weight, somewhat similar to the *E. huxleyi* CAP (Fichtinger-Schepman et al. 1981; Marsh et al. 1992). Intriguingly, these mutants secreted coccoliths similar to immature coccoliths at an early stage of development in wild-type cells, where the crystals have not developed their complex, interlocking morphologies. This suggests that PS3 may be involved in the maturation of the crystals, but is not involved in nucleation. The limitations of *P. carterae* as a genetic model do however mean that these conclusions must be treated as preliminary. There remains the possibility that unknown mutations in the genome unrelated to PS2/PS3 synthesis are responsible for the coccolith phenotype, and without the possibility of using classical genetic methods (e.g. repeated backcrossing to wild type and mapping the mutation) or genome resequencing, Marsh et al. were unable to exclude this possibility.

Clearly coccolithophores invest substantial resources in the production of CAPs, and they are likely to have key roles in coccolith formation; however we have very little idea of the genes that might be involved in their synthesis. Presumably they are synthesized in the ER/Golgi system and require a number of nucleotide-sugar transporters to provide the substrates in this compartment. Then a variety of glycosyltransferases and other enzymes will be required to synthesize the CAPs. Datasets available at present provide no strong clues as to the molecular identity of these enzymes.

The surprising discovery of SITs in sequence data from certain coccolithophores (*Coccolithus braarudii*, *Calcidiscus leptoporus* and *Scyphosphaera apstenii*) led to the finding that Si was essential for normal heterococcolith formation in these species (Durak et al. 2016). When the cells are starved of Si, or when Si transport is inhibited by Ge, the cells produce high proportions of malformed coccoliths. Growth of *C. braarudii* was not affected by the very low silica treatment, indicating that the effect on calcification is likely to be direct. Other coccolithophores in contrast (*E. huxleyi* and *P. carterae*) were unaffected by low Si or Ge, implying that there are fundamental differences in calcification mechanisms between species. Interestingly, the holococcolithophore-bearing haploid cells of *C. braarudii*, *C. leptoporus* and *S. apsteinii* do not have a silica requirement for normal calcification (Langer et al. 2021). Furthermore, blocking Si uptake with Ge in heterococcolith-producing *C. braarudii* sometimes resulted in the cells producing simple calcite rhombs instead of coccoliths. These data suggest that Si has a key role in calcite crystal maturation in certain coccolithophore species, but the biochemical basis of this effect has yet to be discovered.

The protein that has received most attention with respect to coccolith morphogenesis was named GPA for glutamate-, proline- and alanine-rich protein (Corstjens et al. 1998). It was identified by screening a cDNA library with an antibody raised against an intracellular polysaccharide-rich extract of *E. huxleyi*, which also contained some protein material. It is predicted to be highly acidic due to a high

glutamic and aspartic acid content and has motifs relating to Ca^{2+}-binding EF hands. Indeed, the recombinant protein had Ca^{2+}-binding activity. Expression of the gene encoding GPA was shown to correlate negatively with calcification, indicating that it might have a negative regulatory role (MacKinder et al. 2011). There are different strains of *E. huxleyi* with different coccolith morphotypes, and polymorphisms were discovered in the 3'UTR of GPA which correlated with coccolith morphology (Schroeder et al. 2005). As the authors of the study noted, this may well not be a causal relationship. Genotypes are likely to be highly 'structured' in the small sample of strains used: i.e. many genetic loci will have co-evolved in these strains along with coccolith morphology, and thus you would expect polymorphisms at many loci to correlate with morphotype. However it is certainly an observation worthy of further investigation. In conclusion, there are almost certainly many proteins associated with the growing coccolith and the coccolith vesicle that we are unaware of, and future work should be focused on closing this gap in our knowledge.

3.5 The Role of Disordered and Low Complexity Proteins in the Control of Crystal Nucleation and Growth

Many studies of biomineral-associated proteins, from mollusc shells to egg shells to human bone, have found that the proteins have a tendency to be biased in amino acid composition, low in sequence complexity and have high levels of predicted intrinsic disorder (Evans 2019; Skeffington and Donath 2020). The significance of these trends has yet to be established, but it's possible that the biochemistry of the amino acids in the protein, and their modifications, is more important for biomineralization than the 3D structure of the protein. This idea may make sense if the principal roles of these proteins are to bind to the mineral surface at particular positions and promote or inhibit mineralization. Given that many proteins have evolved as binding partners for other globular proteins with complex 3D shapes, the comparative simplicity of mineral surfaces may have favoured the evolution of mineral-binding proteins with comparatively low complexity sequences or without a well-defined 3D structure in solution.

In coccolithophores, we do not as yet have enough examples of coccolith associated proteins to examine trends in terms of sequence bias, complexity and intrinsic disorder. In diatoms we do have enough examples of silica and SDV associated proteins, but these variables have not been systematically examined. Using a bioinformatic toolkit designed for this purpose (Skeffington and Donath 2020), I compared the sequence complexity and degree of predicted disorder for the proteins discussed in Sect. 3.3 to the rest of the *T. pseudonana* proteome, and the results are presented in Fig. 2a–b. We can see that there is a clear tendency for these proteins implicated in silica formation to be more biased and intrinsically disordered than the remaining diatom proteome.

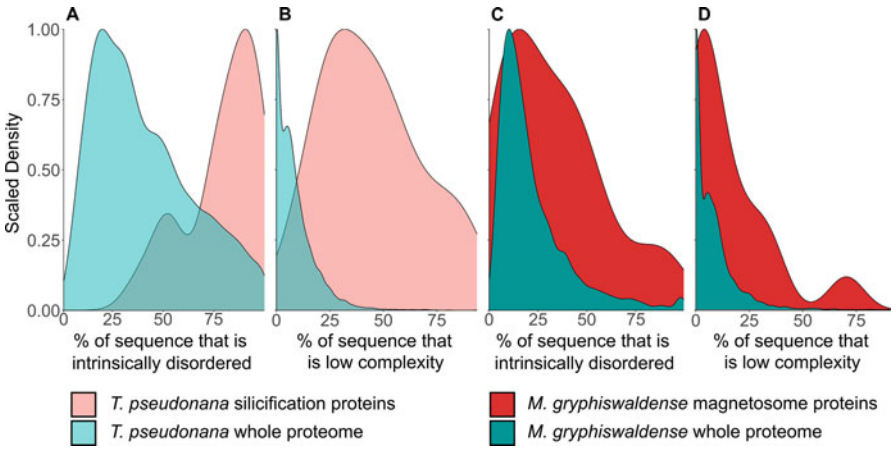

Fig. 2 The prevalence of low complexity and disordered protein regions in proteins implicated in biomineralization in the diatom *T. pseudonana* and the magnetotactic bacterium *M. gryphiswaldense* compared with the background proteomes in these organisms. The *T. pseudonana* silicification proteins consist of the silaffins, cingulins, SiMat proteins, silicanin and SAPs. The *M. gryphiswaldense* magnetosome proteins consist of all proteins encoded by the *mms6*, *mamGFDC*, *mamAB* and *mamXY* operons. Analyses performed with ProminTools (Skeffington and Donath 2020)

Given that intrinsic disorder is relatively rare in prokaryotic proteomes (Ward et al. 2004), it was of interest to perform the same analysis on magnetosome related genes. Comparing the magnetosome proteins (all proteins encoded by the *mms6*, *mamGFDC*, *mamAB* and *mamXY* operons) of *M. gryphiswaldense* to the background proteome of the organism revealed that this protein set has significantly more tendency to disorder than the background proteome (Fig. 2c, Wilcoxon rank sum test, $p = 0.03$). There was a less significant tendency for the magnetosome proteins to be low complexity compared to the background proteome (Fig. 2d, Wilcoxon rank sum test, $p = 0.07$), although some individual proteins (MamG and Mms6) were composed largely of low complexity sequence. Interestingly, the proteins containing the highest proportions of intrinsically disordered sequence (ManI 89%, MamJ 79%, MamL 94%, Mms6 66% and Mms36 55%) and those with high proportions of low complexity sequence (MamG 71%, Mms6 65%, MamC 36%, MamD 35%, MamJ 30%, MamF 29% and Mms36 25%) all (with the exception of MamJ) seem to be involved in the control of crystal growth, with mutants being affected in the size of the crystal generated (Lohße et al. 2014). Mutants lacking the most disordered protein, MamL, do not produce any discernible magnetite, while the second most disordered MamI only produces very small magnetite particles (Lohße et al. 2014). These data suggest that disorder and low complexity are general features of biomineralization proteins from both prokaryotes and eukaryotes and support the hypothesis that these proteins are often directly involved in mineral binding and regulation of crystal growth. Orthologue identification is notoriously difficult for low complexity proteins, which complicates cross-

species comparisons of biomineralization machineries. For example, the proteins identified as low complexity above have all been classified as specific to the genus *Magnetospirillum* (Uebe and Schüler 2016), but this raises the question of whether functionally equivalent proteins with similar amino acid composition but differing primary sequences are of importance in other groups of magnetotactic bacteria. To understand biomineralization fully, we are clearly going to have to gain a better understanding of the evolution of low complexity proteins.

3.6 Control of Crystal Growth from Outside the Compartment: The Cytoskeleton

It is clear that the cytoskeleton has a major role in the development of the mineralizing compartment in both diatoms and coccolithophores. Although inhibitors of cytoskeletal function are crude tools that likely affect many cellular functions, inhibitors of the actin and microtubule cytoskeletons affect mineralization in both groups of organisms. In diatoms, actin and microtubule depolymerization drugs have been shown to have distinct effects on valve morphology (Van de Meene and Pickett-Heaps 2002; Van De Meene and Pickett-Heaps 2004), while the coccolithophore *Emiliania huxleyi* produces an increased fraction of malformed coccoliths on treatment with such inhibitors (Langer et al. 2010). In diatoms, imaging work also supports a role for the cytoskeleton. Microtubules have been observed in close association with developing valves (Chiappino and Volcani 1977), and the ends of microtubules seem to be positioned adjacent to certain pores in the valve (Tesson and Hildebrand 2010a), consistent with mispositioning of the pores on treatment with a microtubule inhibitor (Tesson and Hildebrand 2010b). Actin rings have been shown to localize at the edge of growing valves (Van de Meene and Pickett-Heaps 2002; Van De Meene and Pickett-Heaps 2004; Tesson and Hildebrand 2010a) and to correlate with the patterning of the silica structure as the valve develops in a variety of species (Tesson and Hildebrand 2010a). This latter observation raises the possibility that the position of actin filaments encodes information that determines the pattern of silicification. How actin positioning is determined around the SDV and how actin might affect the biochemical processes occurring within the SDV is unknown, but an exciting future direction of research. In this context it will be interesting to uncover the roles of diatom-specific, actin-related proteins that have been identified through phylogenetic analyses (Aumeier et al. 2015; Morozov et al. 2018).

3.7 Genomic Organization of Mineralization Genes

In bacteria, it is often the case that functionally related genes are clustered on the chromosome and, in some cases, they are even transcribed on the same mRNA,

facilitating the co-regulation of the genes. Most genes involved in magnetosome synthesis are clustered in a genomic region known as the magnetosome island which is organized into five operons in *M. gryphiswaldense* (Uebe and Schüler 2016). Such an organization means that entire pathways may easily undergo horizontal gene transfer (HGT) to different species, and indeed it has been postulated that HGT has played a key role in the parallel evolution of magnetotaxis in different bacterial lineages (Monteil et al. 2020).

Although gene clusters have been identified in eukaryotes, they are rare and mostly restricted to genes involved in metabolism in fungi and plants (Nützmann et al. 2018). In a transcriptomic analysis of silica limitation in *T. pseudonana*, three genes were identified with similar chromosomal locations (Mock et al. 2008), but the significance of this is unclear. When the positions of the diatom silicification proteins discussed in previous sections of this chapter are examined in the PLAZA diatoms genome browser, no striking physical clusters are observed. The contribution of HGT to the genetics of biomineralization in coccolithophores and diatoms has yet to be investigated.

4 Cellular Regulation of Biomineralization

As yet we have little knowledge of the mechanism by which biomineralization is controlled and regulated in microorganisms. Calcification in coccolithophores is subject to multiple layers of regulation which differ from species to species, but we are completely ignorant of the underlying molecular mechanisms. For example, *E. huxleyi* and *C. pelagicus* only produce one coccolith at a time (Taylor et al. 2007), so what control mechanisms operate to prevent the formation of multiple coccoliths simultaneously in a cell, or even in the same vesicle? What controls the final size of a coccolith, and how does a cell sense that a coccolith is complete and ready for exocytosis? The rate of calcification is responsive to light (Nimer and Merrtt 1992), and the supply of nutrients (Anning et al. 1996; Kayano and Shiraiwa 2009), so what underlies these responses? We do not yet know if there is circadian as well as light regulation of coccolith secretion. In *P. carterae* the cell stops making coccoliths when the cell surface is completely covered and resumes coccolith synthesis if the cell's coccoliths are dissolved away (van der Wal et al. 1987), so how does the cell sense its 'coccosphere' and switch coccolith formation on and off? *C. pelagicus* rotates within its coccosphere when calcifying to allow secretion of coccoliths in appropriate positions (Taylor et al. 2007), raising similar questions about how the cell senses the state of its coccosphere. In *C. braarudii* cell cycle progression appears to be dependent on maintenance of an intact coccosphere (Walker et al. 2018), so how are these processes linked? Another particularly interesting example of regulation is found in *S. apsteinii*, which makes increasing numbers of barrel-shaped lopadoliths as light intensity increases (Drescher et al. 2012). Coccolithophores manifest different calcification 'programs' depending on their life cycle phase, often producing holococcoliths (agglomerations of simple rhombohedral calcite

crystals) or no coccoliths at all in the haploid phase while producing complex heterococcoliths in the diploid phase (Houdan et al. 2004). *E. huxleyi* cells infected with giant DNA viruses also shed their coccoliths (Trainic et al. 2018; Johns et al. 2019). The genetic regulation underlying switching between these different calcification programs is unknown.

In both diatoms and coccolithophores, mineralization involves a large number of cellular components and de novo synthesis of macromolecules and thus is associated with a large energetic cost. In coccolithophores the energetic cost of forming one mole of calcite is estimated to be on the order of a quarter to a third of the cost of fixing one mole of CO_2 through photosynthesis (Brownlee et al. 2020). Given the costs, it is perhaps surprising that more examples of mineralization being regulated in response to external stimuli have not been observed. One of the few examples comes from studies showing that diatoms increase silicification in the presence of predators (Pondaven et al. 2007; Grønning and Kiørboe 2020), presumably as a defence response (Pančić et al. 2019). How this response is mediated at the molecular level is unknown. The diatom with the most flexible silicification machinery described to date is *Phaeodactylum tricornutum*, which can switch between three morphotypes (Borowitzka and Volcani 1978) and is the only diatom studied that can grow without silica (D'Elia et al. 1979). In nutrient replete, favourable conditions, the cells are planktonic and take on their triradiate or fusiform morphotypes, which are non-silicified. However in less favourable conditions, the cells transition to a benthic oval morphotype with a silicified cell wall (De Martino et al. 2011). This may be an adaptation to the brackish, changeable estuarine conditions in which this diatom is often found, but it raises the question of why more diatoms have not adopted facultative silicification. Indeed, in other well studied diatoms, silicification is intimately linked to the cell cycle (Hildebrand et al. 2007), and if silica is removed from the medium, then cell division ceases. However even these diatoms have cell types within their life cycle which are not silicified (Armbrust 2009), and we have little knowledge of the genetic regulation that prevents silicification when it is not appropriate.

5 The Future of Biomineralization Research Depends on Genetics

Genetics has a uniquely powerful position in the tool box for the study of biomineral formation. Forward genetics (i.e. mutagenesis, screening for a phenotype of interest and identifying the genetic locus that has been mutated) has the potential to expand our knowledge of the mineralization machinery in unexpected directions, while reverse genetics (i.e. inducing and isolating mutants in a locus of interest) has the power to test hypothesis about the roles of particular components. The latter can also yield surprises. A good example is the MagA locus from magnetotactic bacteria, which encodes a gene similar to ion transporters, and was postulated to be key for

magnetosome biogenesis. However, deletion mutants at this locus make magnetosomes that closely resemble those from wild-type cells, providing strong evidence against an important role for MagA in mineralization.

Genetic transformation of diatoms was first achieved around 25 years ago (Dunahay et al. 1995; Apt et al. 1996), and since then many more tools have been developed (Falciatore et al. 2020) including Cas9-mediated genome editing, which has recently been applied to biomineralization research (Görlich et al. 2019). Expression of transgenes from episomes has also been achieved (Karas et al. 2015), which may be useful for avoiding the genomic rearrangements that seem to result from biolistic transformation (George et al. 2020). In contrast, genetic tools for coccolithophores are still in their infancy. The transformation of *P. carterae* was reported in 2016 (Endo et al. 2016), but this technique has not yet been used in any further publications. Ideally, a model system with tools for genetic modification should also be amenable to classical genetics, meaning that researchers can control the life cycle of the cells and perform genetic crosses. This makes forward genetic screens more viable and allows researchers to study genetic interactions between loci, such as dominance and epistasis, which can be important data to constrain hypotheses about the molecular function of proteins of interest. Among diatoms, *Seminavis robusta* is a particularly promising future model system; since sexual crosses can be routinely performed, the molecular basis of sexual system is beginning to be understood (Vanstechelman et al. 2013), and excellent genomic and transcriptomic resources have recently been developed (Osuna-Cruz et al. 2020). Another diatom in which the mating system is well understood is *Pseudo-nitzschia multistriata* (Russo et al. 2018), which may also be a useful model in the future. Although life cycle transitions have sometimes been observed in cultured coccolithophores, no reliable methods to induce syngamy and meiosis or to perform crosses have been reported.

In order to gain a systems-level understanding of biomineralization in diatoms and coccolithophores, an excellent molecular genetic model organism is required for each. Given that hundreds of genes are likely to be directly involved in biomineralization processes, methods need to be developed to the point where high-throughput generation of targeted mutants is possible and multiple knock-outs can be achieved simultaneously. For example, although knock-out of the Silicanin-1 gene in the diatom *T. pseudonana* was shown to effect silica formation (Görlich et al. 2019), there is an orthologous gene (source: PLAZA diatoms database) encoded in the *T. pseudonana* genome, so to understand the true significance of Silicanin-1-like proteins, a double mutant should be made. Ideally, the cells of the model should also be viable in the absence of biomineralization; otherwise genetic approaches to study the roles of genes essential for mineralization become vastly more complicated. In diatoms the only species known to meet this criterion is *P. tricornutum*, which can grow and divide without producing a silica frustule (De Martino et al. 2007). In coccolithophores, *E. huxleyi* can grow without calcifying, and non-calcifying mutants sometimes arise spontaneously in culture (Klaveness and Paasche 1971), whereas many other species appear to have an obligate requirement for calcification (Walker et al. 2018). In addition to such 'workhorse models', methods for genetic

manipulation of additional organism across the relevant phylogenetic spectrum should be developed. This will allow hypotheses about the nature of the ancestral biomineralization genetic program in the group to be investigated, as well as allowing researchers to explore the genetic basis of species-to-species variation in mineral architecture. To this end, large-scale genome sequencing projects, such as the Darwin Tree of Life (www.darwintreeoflife.org) project, combined with studies that screen strains and species for ease of genetic transformation (Faktorová et al. 2020) will be invaluable. Comparison of unrelated species which synthesize similar biominerals will also be informative. For example, it will be fascinating to see if similar principles underlie silicification in diatoms and silicifying haptophytes (Durak et al. 2016).

To test our understanding of biomineralization, recapitulating the mineralization process in a synthetic setting will be a key approach in the future. This has already been achieved in magnetotactic bacteria, where the transfer of 30 genes into *Rhodospirillum rubrum*, which does not normally produce magnetosomes, leads to magnetosome formation in this organism (Kolinko et al. 2014). Similar experiments in other recipient strains have successfully magnetized additional species (Dziuba et al. 2020). In vitro approaches have been used to recapitulate aspects of biomineralization in diatoms (Pawolski et al. 2018) and coccolithophores (Gal et al. 2016); however given the intimate connections between mineralization and cell biology, such cell-free systems are unlikely ever to recapitulate the process fully. In coccolithophore calcification, calcite is deposited on organic base plates which appear superficially similar to organic scales produced by many other haptophytic algae that do not calcify. Thus, it may be the case that coccolith formation evolved by building upon the existing organic-scale synthesis machinery. Loss of certain components of this machinery could have led to an absence of calcification in the Isochrysidales, which are very closely related to *E. huxleyi*. Given that a genetic transformation system has been developed for *Isochrysis galbana* (Prasad et al. 2014; Faktorová et al. 2020), in the future it may be possible to increase our understanding of calcification by attempting to 'restore' calcification in *I. galbana* by introduction of genes from *E. huxleyi*. Another intriguing (although futuristic) possibility is that ancestral state reconstruction methods could be used to reconstruct the mineralization machinery of extinct coccolithophore species. The function of this machinery could be tested in a model system, to see if any aspects of the morphology of fossil coccoliths from extinct species preserved in the fossil record can be reproduced.

As well as identifying the nature of the biomineralization machinery and the biochemical intricacies of mineral formation, an understanding of the genetics of mineralization should also begin to inform our understanding of the physiology and evolution of mineralized microbes. For example, by examining the physiology of cells in which the biomineral has been manipulated, we could learn about the effects of mineralization on photosynthesis and biotic interactions. Phylogenomic studies should soon be able to tell us when in evolutionary time different components of the mineralization machinery arose, and this will allow us to test ideas about the evolutionary drivers in biomineralization. For example, the silica requirement for

calcification in coccolithophores has been hypothesized to have been lost in certain lineages as an adaptation to the drastic decrease in oceanic silica concentrations resulting from the radiation of the diatoms (Durak et al. 2016). If we understood the genetic basis of the loss of the silica requirement in calcification, this hypothesis could be tested by examining the evolutionary timing of these genetic changes. Finally, as single-cell sequencing technology improves, it will be exciting to investigate how biomineral morphological diversity relates to the underlying genetics of natural populations. This will inform both our understanding of the genetic and environmental factors underlying evolutionary changes in biomineralization and should aid efforts to perform paleoenvironmental reconstruction based on assemblages of fossil diatoms and coccolithophores.

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Silicate Minerals Induced by Microorganisms

R. Brindavathy

Contents

Abstract Rocks are made up of minerals and they form the Earth's crust. Nearly 90% of Earth's solid material are silicate minerals. Rocks and minerals are the source and sink of most essential elements, without which the living forms cannot survive.

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This nutrient source has to be mineralized from the parent rock. The biological agents such as bacteria, fungi, algae, cyanobacteria, etc. effectively act on this mineralization process. Bioweathering is the destruction or decomposition of rocks by the ubiquitous microbial source. By this biomineralization, transformation of silicate minerals takes place by varied microbial metabolic activities. Biodissolution mechanism comprises acidolysis, extracellular polysaccharide production, pH fluctuation, chelation, organic acid secretion, and organic ligand production. These mechanisms vary with the variety of bioagents that trigger the silicate mineral formation. Biomineralization of silicate minerals leads to various biogeochemical processes, viz., soil formation, mineral transformation, and nutrient mobilization to plants and microbes itself which are streamlined naturally by this 'bio-miners' or biological agents, which balance nutrient cycling and maintain equilibrium. Such natural phenomenon supports the living forms in varied ecosystem. Exploration and bio-intervention of such novel microbes leads to more advantages in mineral formation and its allied processes. In this chapter, the author presents a critical review of mineral formation from silicate minerals, mechanisms, and its application aspects collected from existing literatures. An advancement and extensive research in this field would no doubt nourish the environment in ecofriendly approaches.

1 Introduction

Earth's crust is made of rocks. Rocks are hard mass of minerals, or combination of minerals. Minerals are naturally occurring, inorganic solid forms with definite chemical composition. Minerals vary with its parent rock, possessing identical properties. There are more than 3000 types of minerals on Earth's crust and only few form the dominant group. Among them, silicate minerals are the largest one with complicated composition, and as per the geologist's estimation, it comprises about 90% of Earth's solid material (Ehrlich 1998; Ehrlich and Newman 2009).

Due to high temperature and pressure, minerals are molded to form rocks. When microbes contact with oxygenated atmosphere, a variety of reactions takes place, yielding dissolution and release of minerals to soil organisms and also causing crystallization of stable clay component on Earth's surface (Adamo et al. 2002; Tazaki 2006).

Rocks and minerals are the source and sink of elements that are more essential nutrients for the biota on Earth. The elements have to be released from these reservoirs in available form for the metabolic activity of the living system. These include vital metals and nutrients like sulfur and phosphorus (Gadd 2007; Gadd et al. 2005, 2007). The geochemical fractionation of these elements is formed by the process called weathering. Such type of biogeochemical reactions happens from evaluation and continues with the formation of lithosphere comprising of mantle, crust, and its related structures. In this ecosystem the bioavailability of essential

nutrients for the living entity is facilitated by the alternate mineral deposition and weathering from the rock mineral reservoir. Due to these sequential processes like physical disintegration and chemical breakdown and release of elements such as silica, calcium, magnesium, phosphorus, potassium, and many trace elements take place, in a form directly available to the biota. Consequently, they add fertility to the soil and in turn boost the ecosystem productivity. Mineral weathering has direct impact on human well-being, by influencing agriculture, water resources, architectural stability, landscaping, and distribution of mineral resources (Brehm et al. 2005).

Bioweathering is nothing but the destruction and decay of rocks. Some researchers term it as biodeterioration (Gorbushina and Krumbein 2005). Other than carbon and nitrogen, for their survival, microbes meet out their essential elements from the bioweathering process (Hoffland et al. 2004a, b). Microbial biomineralization is the formation of minerals, mediated by microorganism, is considered as one among the important activities of microbes, and is being enforced in the scientific community. Its scope is much larger than initially thought, since it involves metals and minerals of tremendous range and kind (Beveridge 1989). In general, microbes process the weathering reactions through the production of organic metabolites which causes acidification and corrosion of rock minerals. Because of such mechanism, biological weathering is also referred to as organic weathering.

Earth's geosphere and biosphere are interlinked by the microbial kingdom. Microbes are ubiquitous found in sediments, extreme environments, lower temperatures, hot springs, and hydrothermal vents. Surprisingly, metabolically active cells have been discovered in rocks buried several kilometers below the Earth's surface. Microorganisms survive in diverse environment causing immense geochemical changes on Earth's surface. Microbial interactions with minerals are prevalent in numerous and sequential natural processes like mineral weathering, decomposition, and transformation. Microbes play a major role in the genesis of soil formation when they come in contact with silicate rocks. Microbes that come in close proximity with mineral substances and cause reactional changes are opportunists (Ehrlich 1997).

In nature, microorganisms exist in microbial communities as mats or biofilms growing upon a solid substrate. Their presence on a mineral substrate greatly influences the mineral texture and geochemistry of mineral rocks and their microenvironment. They grow inside (endoliths) and on rock surfaces (exoliths), and they totally depend on their niche for primary nutrient source and can be called as "critical compounds." These nutrients are utilized for their metabolic activity and in the production of cellular energy. Their metabolic products and its released structural components have greater influence on metal speciation, and its solubility, mobility, and bioavailability (Gadd and Griffiths 1978; Gadd 2007). Microbes influence the kinetics and sequence of reactions resulting in solubilization and release of different types of minerals, and they also influence the authigenic and diagenetic development of various minerals in the lithosphere and hydrosphere.

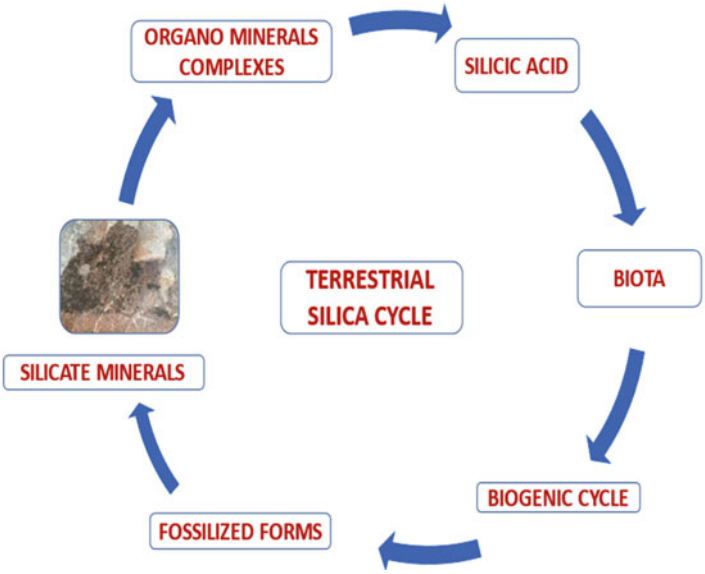

Fig. 1 Silica cycle

The reason why these microbes, particularly prokaryotes, take part in the biodissolution is that in anoxic environment, they obtain energy and electron from minerals as a result of these reactions. Numerous microbial processes are mediated by these minerals, for fulfilling their metabolic activities like energy production, respiration, nutrient acquisition, cell adhesion, and biofilm formation (Hochella 2002; Brown et al. 2008). In addition, they satisfy their trace element needs for their self-sustaining, and to enrich other microbes in that microenvironment with their resulting end product (Ehrlich 1996). Microorganisms are efficient living entity, which acts as mini-factories, generating mineralization even though they survive in extreme environmental conditions like pH, salinity, and water potential.

It is a question of surprise on how these tiny creatures perform in global cycling of silicon between the lithosphere and the biosphere and how they can mobilize and transfer silicon among different mineral phases. In fact, it seems that microorganisms are a vital ingredient to a functioning global silicon cycle and in turn other nutrients (Fig. 1). The following chapter will describe the importance of silicate mineral formation, its explorations, and experimental proofs for interactions between microorganisms and silicate minerals.

2 Classification of Silicate Minerals

In Earth's crust, silicate minerals are the dominant group and a common constituent. Among all elements oxygen and silicon are the most abundant where oxygen comprises 46.6% and silicon occupies 27.7% by weight. These elements help to make up the dominant group of rock-forming silicate minerals (Deer et al. 2004). The silica structure forms pyramid-like shape having silicon in center surrounded by four oxygen atoms, thus forming a silicate tetrahedron structure. The basic chemical unit is (SiO_4) tetrahedron-shaped anionic group with a negative four charge (−4). The silicon ion located in the center has a positive charge of four, while each oxygen has a charge of negative two (−2), and thus each silicon-oxygen bond is equal to one half (1/2) the total bond energy of oxygen. Here the oxygen is ready to bond with another silicon ion and hence links with other (SiO_4) tetrahedron and thus this linkage goes in this pattern. The complex structures thus formed with these silicate tetrahedrons are truly amazing. They progress as single and double units and further polymerize to chain structures, sheet patterns, rings, and framework structures (Hawthorne et al. 2019). Minerals that lack silicon are called nonsilicates.

Silica Structure The combination and linking pattern of silicate tetrahedrons are most interesting and make the largest silicate groups, and the most complex class of minerals. Here two different groups of classification are explained (Tables 1 and 2). Firstly, the important rock-forming minerals are described and then secondly the crystalline or polymerization groups (Tibor Zoltai 1960).

2.1 Important Silicate Minerals

The most important rock-forming minerals are quartz, feldspars, micas, amphiboles, pyroxenes, and olivine.

2.2 Polymerization

The size of $[SiO_4]^{4-}$ tetrahedral is relatively stable, with Si-O bond length varying from 0.161 to 0.164 nm at ambient conditions. Mostly silicate compounds have higher strength of S-O bonds with the dissociation energy of ~452 KJ/mol and provide thermal stability and chemical resistance (Hawthorne et al. 2019). Formation of polymers is common in silicate minerals. The tetrahedral clusters can be polymerized by forming link or bonding to each other through the bridging oxygen atoms. Polymerization process takes place by means of linkage with one, two, three, or four neighboring tetrahedra, forming Si-O-Si bonds. Silica bonds with other ions located in the silicate lattices such as aluminum (Al^{3+}), beryllium (Be^{2+}), boron (B^{3+}), calcium (Ca^{2+}), fluoride (F^{-}), lithium (Li^{+}), magnesium (Mg^{2+}), potassium

Table 1 Types of rock-forming silicate minerals

Types	Description
Quartz	Quartz (SiO_2) a framework silicate, hard, second-most abundant mineral in the Earth's crust, having glassy luster and conchoidal fracture with varying colors. Common is granite. Examples are sandstone, quartzite, and chert. Chert a sedimentary rock composed of microcrystalline quartz
Feldspars	Dominant hard mineral, occupies 60% by weight. Feldspars have two directions having two cleavages at nearly right angles with flat, glassy surfaces. Examples are granite and basalt. Two major types of feldspar minerals are orthoclase and plagioclase Orthoclase feldspar ($KAlSi_3O_8$) called as potassium feldspar group ranges from pink to white to gray. Plagioclase feldspar is white to gray or black. Its is classified into calcium-rich end member, called anorthite ($CaAl_2Si_2O_8$), and the sodium-rich end member albite ($NaAlSi_3O_8$)
Micas	Mica groups are sheet silicates with perfect cleavage in one direction causing it to split into thin sheets. These are common in metamorphic rocks, particularly schists. Muscovite is transparent variety or silvery-colored mica. Biotites are black or dark brown mica (contains Mg and Fe). A third common variety, *chlorite*, is green with small scales, rather than the large sheets of biotite and muscovite
Amphiboles	Amphiboles are double chain silicates producing two directions of cleavage, not at right angles, producing narrow, elongated crystals. Typically, dark in color, e.g., hornblende and augite
Olivine	Olivines are isolated tetrahedra silicate, normally found as masses of olive green to brown granules. They have no cleavage. Each sand-sized olivine crystal has conchoidal fracture. They contain Mg and Fe
Clay minerals	Clay minerals are also important sheet silicates. Their crystals are submicroscopic. On a macroscopic scale, they form earthy masses with very fine-grained flakes, dull, soft, smooth. They form as weathering products of other silicate minerals, e.g., kaolinite

(K^+), sodium (Na^+), zinc (Zn^{2+}), and ions of titanium, manganese, and iron linkages in various oxidation states. Some cations such as aluminum, boron, and beryllium are isomorphically substituted with silicon atoms in the silica-oxygen tetrahedra (ref). Mostly these ions are located on the outer framework and are in easily exchangeable positions. These ions play a major role in balancing the charge of the mineral and also serve as nutrient source in soil after mineralization.

2.3 Crystalline Silicates

There are several classification systems of crystalline silicates. The most comprehensive one was developed by Machatschki and Bragg in the 1930s, which formed the basis as well and had some changes in due course.

The silicates are divided into the following subclasses, not by their chemistry but by their structures (degree of polymerization of the $[SiO_4]^{4-}$ tetrahedral):

Table 2 Classification of silicate minerals by their degree of polymerization

Name of the minerals	Description of minerals
Nesosilicates (orthosilicates)	The simplest of all the silicate subclasses includes all silicates where the (SiO4) tetrahedrons are unbonded to other tetrahedrons. The negative charge of the anions is neutralized by the cations linked with it. Some classes have tetrahedral basic ionic units (PO_4 and SO_4) and thus they form several groups. Examples are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4)
Sorosilicates	Sorosilicates are silicates $[Si_2O_7]^{6-}$ containing clusters having two silicate tetrahedrons that are linked by one oxygen ion, and thus the basic chemical unit is the anion group (Si_2O_7) with a negative six charge (−6). The sharing of one oxygen atom between two neighboring tetrahedra results in formation of a dimer. It includes silicate tetrahedrons as well as the double tetrahedrons. They are further divided into epidote, containing chains of aluminum oxide and akermanite ($Ca_2Mg[Si_2O_7]$) and rankinite ($Ca_3[Si_2O_7]$) which are calcium-containing silicates
Cyclosilicates (rings)	**Cyclosilicates** are silicates with cyclic clusters of three $[Si_3O_7]^{6-}$, four $[Si_4O_{12}]^{8-}$, or six $[Si_6O_{18}]^{12-}$ tetrahedra. The silicon to oxygen ratio is 1:3. The rings can be made of the minimum three tetrahedrons forming triangular structures as that of benitoite; axinite has four tetrahedrons forming a rough square shape. Six tetrahedrons form hexagonal shapes in beryl types. There are many gemstone minerals found in this group, for its high hardness, luster, and durability
Inosilicates	**Inosilicates** are silicates which consist of one-dimensional $[SiO_3]_\infty{}^{2-}$, $[Si_2O_5]_\infty{}^{2-}$, and $[Si_4O_{11}]_\infty{}^{6-}$ chains or ribbons and charge balanced ions. Enstatite ($Mg_2[Si_2O_6]$) and diopside ($CaMg[SiO_3]_2$) are examples of chain silicates. In inosilicates all tetrahedra have two common oxygen atoms and two excess negative charges for cations which connect these chains to a framework. The length of these chains is defined by size of the crystal
Phyllosilicates (layered silicates)	**Phyllosilicates (sheet or layered silicates)** are silicates with two-dimensional layers of $[SiO_4]^{4-}$ tetrahedral sharing three oxygen atoms between each other. They form cleavage and split along definite smooth planar surfaces, for example, micas, talc, and kaolinite. A substitution of silicon atoms for aluminum atoms occurs very often in anionic frameworks of layered silicates. They are weakly bonded with water molecules, and other neutral atoms produce very soft minerals and are easily invaded by microbes
Tectosilicates (framework silicates)	**Tectosilicates** have a three-dimensional framework where all four oxygen atoms of each tetrahedral are shared by the adjacent tetrahedra. Examples are quartz, cristobalite, coesite, and stishovite which do not contain any cations. Mostly feldspars containing SI^{4+} cation replaced by Al^{3+} in tetrahedra providing negative charge of this anionic framework. This negative charge is balanced by cations, e.g., Na^+ in albite ($NaAlSi_3O_8$), K^+ in microcline ($KAlSi_3O_8$), and Ca^{2+} in anorthite ($CaAl_2Si_2O_8$)

- Nesosilicates *(single tetrahedrons)*
- Sorosilicates *(double tetrahedrons)*
- Inosilicates *(single and double chains)*
- Cyclosilicates *(rings)*
- Phyllosilicates *(sheets)*
- Tectosilicates *(frameworks)*

These polymerization and structural identity are explained for it would be easy to understand the transformation of silicate minerals during bioweathering and mineral formation process.

3 Biomineralization of Silicate Minerals

Rocks are a rich reservoir of minerals on Earth that cannot escape weathering. The biomineralization process has been emerged and parallelly performed along with evolution. Consequently, weathering arose as the study during the end of the nineteenth century and presently more emphasis is given in this section. Microorganisms play an essential role in the mineralization processes by contributing to the release of nutrients from minerals that are essential for its own nutrition and in turn augment the soil, which in turn becomes as a nutrient source, influencing other microbial communities.

For this reason, the biodissolution potential has a strong foundation in economic geology, where bioleaching of essential elements from ores is attained (Ehrlich and Brierley 1990). Microbes can intensely modify the rate of reaction and products of mineral dissolution by controlling mineral availability and solubility. This has greater environmental impact, and its importance is focused because it leads to geochemical cycles of major nutrients, viz., Si, Al, Fe, Ca, K, Na, and trace elements. Mineralization and redistribution of the listed elements serves as a source for plant nutrition. It is well known that biologically mediated reactions can affect both the rate and stoichiometry of mineral weathering compared to predominately abiotic processes. The biodissolution and mineral formation are the results of microbial metabolic reaction (Fig. 2).

3.1 Bacteria

Bacteria are extraordinary tiny creatures having tremendous phylogenetic and metabolic diversity, with high adaptability, and are able to colonize at extreme environments that cannot be tolerated by other organisms. They have the potential to form biofilms wherever they grow and possess highest surface area-to-volume ratio (Barker et al. 1997). When bacteria encounter mineral surfaces, they attach themselves onto it creating a microenvironment that protects them from adverse

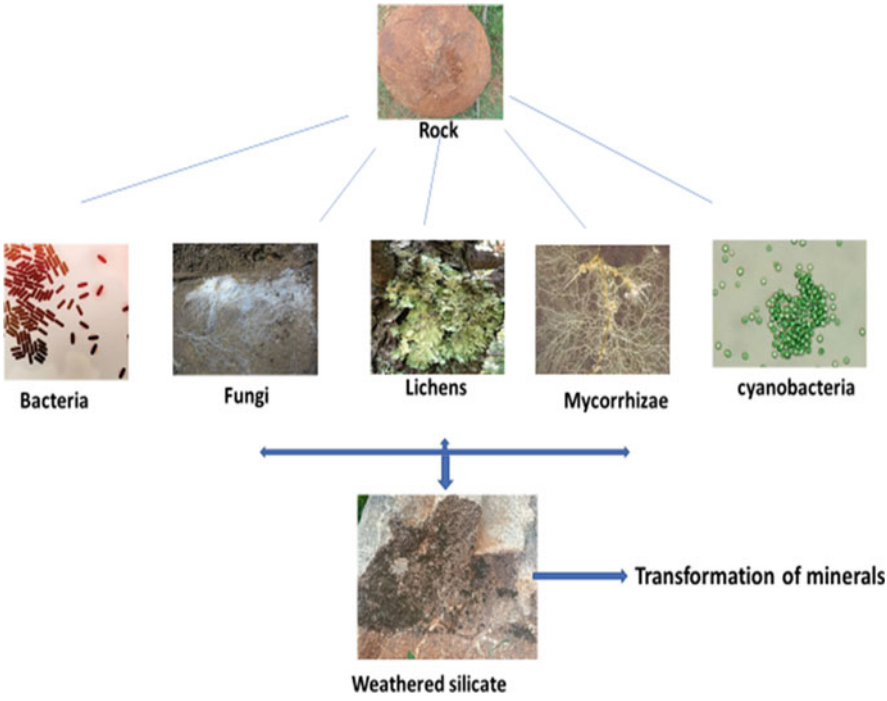

Fig. 2 Bioagents of silicate mineralization

environment. From this niche these bacteria extract energy and nutrients from the mineral matrix. The bacteria produce organic acids and chelates that act as a weathering agent, and they take part in many oxidoreduction reactions that trigger the mineralization from rocks.

The formation of minerals by bacteria from parent rock is a complex biophysical and biochemical process where bacteria experience physiological changes due to the variation of external environment where they live. Among microbes, bacteria have a peculiar pattern of mineral dissolution, which comprises two processes. At first, the metal ions surrounding the cell interact with the charged compounds in their cell structure, resulting with an electrostatic charge prevailing between them. Consequently, an energy drop takes place in the system initiating further mineral dissolution and deposition. Thus, the biomineralization in bacterium occurs mainly due to the physicochemistry of its cell surface and the chemistry of the cell's environment, where the organisms itself has no control over it. The actively metabolizing bacterial plasma membranes have some role in inhibiting mineral formation, since the cell wall is enriched with protons causing a competition between metal cations (Sand and Gehrke 2005).

Bacterial colonization has been noticed and reported in different primary silicate minerals such as granite, limestone, apatite, plagioclase, quartz, or a mix of phlogopite and quartz (Gleeson et al. 2006; Carson et al. 2007). Major elements such as

aluminum, silica, and calcium contained in the parent rock have significant role on their colonization and biofilm formation. That is why there exists affinity between metal type and bacterial species. Biodissolution of minerals are induced by microbial metabolism, which represents an alternative interactive pathway between minerals and microbes. There are many research evidences both in vitro and in vivo that have focused on mineral transformations promoted by dissimilatory metal-reducing bacteria. Few such interesting evidences are explained here to know the transformational changes of silicate rocks and the mineral formations.

Silicate-weathering bacteria are widely distributed in nature, and some common ones are *Bacillus mucilaginosus*, *Bacillus circulans*, and *Bacillus edaphius*. These bacteria actively take part in mineral formation, diagenesis, and mineralization of major silicate rock (Zhu et al. 2011a, b). The so-called silicate bacterium is referred as *Bacillus mucilaginous*, which was first reported and isolated from silicate minerals (Aleksandrov 1958). Microbes isolated from either natural smectite or soil extract can reduce the structural formation of ferruginous smectite (Stucki et al. 1987) and nontronite (Wu et al. 1988). The physiochemical properties of smectite, such as clay-particle flocculation, dispersion, swelling, surface area, and cation and anion exchange capacity, have been influenced significantly by *Shewanella*. *Shewanella* is a gram-negative rod, mostly found in extreme aquatic habitats where the temperature is very low and the pressure is very high. These bacteria are facultatively anaerobes that depend on the parent rock material for its metabolic activity (Gates et al. 1993; Stucki and Kostka 2006; Kim et al. 2005; Jaisi 2007). The potentiality of this bacterium to decompose minerals makes it a good candidate for the extraction of Si and Al from bauxite in the metallurgical industry (Monib et al. 1986).

Bentonite is composed mainly of the layered silicate smectite having small amounts of quartz and feldspar. It has been widely used in environmental and geotechnology-related applications (Emmerich et al. 2009). In an interaction study between this mineral and *Bacillus mucilaginosus*, *the* bacterial colonies increased and produced a certain amount of metabolites that resulted in an acidic environment. And more flagella were produced by mineral stimulation. The results of the bacterial activity were as follows: the dissolution of K and Fe increased, and composition of Al decreased the remaining solid minerals. The XRD and micro-FTIR results supported major transformational changes in the bentonite. Contact between solid minerals and bacteria appeared to have stimulated the production of bacterial flagella which caused the release of ions from minerals which led to phase changes in bentonite (Zhu et al. 2011b).

Bacterium-mineral complexes and the mineral grain were tightly enclosed with newly formed structures which were explained with apatite. The mineral grain forms plump capsules when the bacterium *B. mucilaginous* grows and reproduces on the solid substrate. As a result, a greater amount of extracellular polysaccharides were secreted, leading to the formation of a biofilm on the mineral surface. At this juncture a relatively closed microenvironment was formed where a continuous acceleration and dissolution of the mineral proceeds (Lian et al. 2002; Friedrich et al. 1991; Welch et al. 1999).

3.1.1 Biotransformation of Silicate Minerals

Polymerization of silicate leads to different forms of minerals. Natural selection of metal types by bacteria has greater impact. Some organisms release monomeric forms of silicate minerals. Monomeric form means mineral having H_2SiO_4 or $Si(OH)_4$ and this on polymerization Si-O-Si forms dimer. By microbial activity it becomes a monomer which attains available form. One such example is *Proteus mirabilis*, a mesophilic bacterium, mediates the monomer silicate ions formation, dissolution, and accumulation. Another example is *Bacillus caldolyticus*, thermophilic bacterium. These two bacterium were examined for the silicification studies. The extreme thermophile, *Bacillus caldolyticus*, seemed a good choice, because it survives naturally in a high monomer silica concentration and the bacterial mats have the tendency to attach themselves to the rock surface (Lauwers and Heinen 1974).

Proteus mirabilis caused destruction in naturally occurring polymer silica, and similar interaction was also seen in *Pseudomonas* and in some soil bacteria (Webley et al. 1960). The interaction between silicate minerals and bacterial surfaces is caused by the adsorption of silica onto other mineral oxides like Fe and Al that are electrostatically bound to the bacterial cell surface (Ferris et al. 1989; Walker et al. 1989).

Therefore, the role of bacteria in silica and silicate mineralization is to concentrate Fe and Al through adsorption and/or precipitation reactions leading to transformational changes in mineral. (Warren and Ferris 1998; Konhauser et al. 1998). Bacteria serve as bases or perhaps templates, for ionic precipitation, and these oxide mineral, forms surface complexes with aqueous silica that are the precursors in the formation of silica and silicate minerals (Douglas 2005). Another example for biotransformation is *Thiobacillus* promoted rapid formation of amorphous silica at low pH values; hence in acidic conditions, bacteria create a platform and act as a reactive interface that facilitates heterogeneous nucleation and enhances the precipitation kinetics (Yee et al. 2003).

3.2 Fungi

"Geomycology," a term coined by Professor Geoffrey M. Gadd and his team, implicates the functional role of fungi on geological processes, including the alteration, weathering of rocks and minerals, and accumulation of metals, and finally their role in nutrient cycling. Initially fungi are well known for its carbon cycle and organic degradation, but recently it is explored for biomineralization, biomining, and biogeochemical cycle.

Although many studies on microbe-mineral associations on geomicrobiology have been published in recent years, more emphasis has been shown on prokaryotes. Recently, many research works laid foundation on the myco-families that have biomineralization potential. Fungi are ubiquitous components of the microflora commonly found on rocks. Among the fungal types, epilithic and endolithic forms

Fig. 3 Disintegration of mineral rock by fungal growth showing cracks

encompass a significant group of the microflora along with cyanobacteria, chemolitho- and chemoorganotrophic bacteria, and algae proliferating onto the varying range of silicate rock types, viz., silica, silicates, and aluminosilicates, and also other rocks like granite, gypsum, limestone, marble, and sandstone (Gadd 2010).

Fungal invasion greatly influences on proliferation of other microbial communities on the mineral substrates (Barker and Banfield 1996). Fungi invade the solid rock material using both physical and chemical tools. That is, fungi put forth its mycelial growth form and exploit the weaker spots on the rock or grain surface. Later the hyphae units enter the scratches, ridges, and grooves and by penetrating pores or tunnels formed on the rocks and initiate weathering by releasing their chemical tool (Fig. 3). Here the chemical tool is the hypha along with its metabolic excretion (Hoffland et al. 2002). The fungal invasions are more pronounced by their mycelium, a structural entity, that increase the biomass, than the prokaryons. Rock-inhabiting fungi have been reported to dwell in extreme atmospheric conditions like cold and hot deserts and also seen in siliceous, igneous, and sedimentary rock types (Staley et al. 1982; Ehrlich 1998). The redox reaction that hastens the geochemical process is pronounced more in prokaryotes than these fungal counterparts. But the ability of spreading habit and ubiquitous presence of the fungi, bridge their distance and comes equal or near to bacterial weathering potential (Banfield et al. 1999; Sterflinger 2000). The growth of fungal hyphal tips is often accompanied by the production of organic anions and protons which helps to break down weak spots in solid rock substrates and paves pathway for further intrusion.

The unavailability of moisture, nutrient deficit, and exposure to solar radiation are limiting factors for rock-dwelling microorganisms. Nevertheless, many fungal species and lichen, a microsymbiont, were evolved in such environment and thrive by exploiting a microhabitat within and on the surface of rocks. They occupy in preexisting cracks and subsurface of rocks as endoliths, and they are also found in rock fissures, mineral pores, and cavities called as cryptoendoliths. Lichens usually colonize on rock surfaces as epilithic forms (Ehrlich 1981; Urzi et al. 1995; Sterflinger 2000).

An important contribution of these fungal colonies to the mineral formation is the production and excretion of cell metabolites like H^+, organic acids, metal-binding ligands, etc. which leads to the dissolution of the host rock through chemotaxis (Gadd and Sayer 2000). In addition, the oxidative or reductive reaction on the reactive mineral constituents enforces mineral weathering (Grote and Krumbein 1992). Biodissolution of fungi and lichens releases soluble nutrients that are essential for their survival, and by their saprophytic processes, they also release nutrients like phosphorus, sulfur, trace metals and organic metabolites, which helps the proliferation of other microbial forms in their niche (Gadd and Sayer 2000). Consequently, fungi also play an important role in secondary mineral formation by the precipitation of organic ligands like oxalates and, through their metabolism activity, further formation of metal ions and fungal cell wall complexes to their external surfaces as well.

3.2.1 The Major Fungi Taxa Involved in Weathering

3.2.1.1 Lichen-Forming Fungi

Lichens are the microsymbionts that have mutualistic relationship between fungi and algae or cyanobacteria. Lichens have played an important role in weathering and soil genesis from mineral rocks (Chen et al. 2000). Such association between fungi and rocks is more important in stabilizing mineral grains, and a biogenic micro-fabric is formed in mineral substrates (Goudie 1996). It has been evidently proved that, lichen-covered rocks weather with an order of magnitude, faster than bare rocks (Stretch and Viles 2002). Sequentially, in addition with in the algal symbiont, endolithic fungal partner found below the rock surface also accelerates weathering by the development of mycelial mat over the mineral grains. These mats travel and form groove-like structures as they spread over the grains and accelerate weathering.

Because fungi first come in close proximity with the mineral interface, the weathering ability of lichens is mainly enforced by the fungal counterpart. Carbon substrates released by the algal symbiont stimulate growth of fungal partner. These microorganisms have sequential processes, directly or indirectly by loosens the mineral aggregation,which increases the hydration, causes dissolution. They later enhance the secondary mineral formation and release nutrients like calcium, potassium, iron, clay minerals, etc. (Banfield et al. 1999).

Below fungi-mineral interfaces, mineral surfaces are exposed for dissolution, mediated by the metabolic byproducts. By forming porosity and permeability in their niche, fungi increase the colonization, and thus through this indirect process, they release minerals. Many have reported the association of lichen and rock minerals, viz., microperthitic feldspar, ferriannite, quartz, and ferrohastingsite (Barker and Banfield 1998).

Secondary silicates minerals were formed in biotite, K rich silicate mineral by the interpenetration of lichens, where the fungal hyphae move along cleavages and cause the transformational changes (Gorbushina et al. 2001). Crustose saxicolous lichens, *Rhizocarpon grande* and *Porpidea albocaerulescens*, have found to pierce the rock surface and protrude to a depth of 10 mm. After the invasion of this symbiont within the intact rocks, they form amphibole surfaces, and corrosion takes place along hyphae-filled cracks. Later the mycelial growth proliferates, spreading into exploited grain boundaries and cleavages, and protrudes the cracks for accession to mineral surfaces. Thus, after their invasion, small cleavage-bounded mineral fragments are accumulated in their lower thallus.

Biotite is partially transformed to vermiculite by the metabolic activity of lichens. Here this mineral encounters the symbiont, where it is being eroded by the penetration and formation of cleavages (Barker and Banfield 1996). These changes are formed by the growth of the fungal partner and their hyphal dissemination. It showed no siliceous relics in that region.

3.2.1.2 Mycorrhizal Invasion

Ectomycorrhizal fungi, or sheath mycorrhizae and ericoid mycorrhizal types, were recognized for their mineral weathering ability (Landeweert et al. 2001). Silicate minerals such as feldspars, granitic bedrock, and hornblendes were weathered by the excretion of organic acid like citric, formic, oxalic, succinic, and malic acid from fungal hyphae, on the host rock. In this microenvironment, by their organic excretions, they cause mineralogical changes like transformation of mica and chlorite to 2:1 expandable clays types. Here ectomycorrhizosphere surroundings are formed where the dissolution of potassium and magnesium ions are produced by mycorrhizal hyphae (Arocena et al. 1999).

3.2.1.3 *Saprotrophic Fungi*

Many saprophytic fungi are found to involve in this biomineralization and one such example is *Aspergillus niger*, which use relatively simple carbohydrate sources for quick proliferation under favorable conditions and initiate dissolution as they grow.

3.2.1.4 Yeasts

Black yeasts and many stress-tolerant saprotrophic ascomycetes induce biodissolution of silicate minerals by the use carbohydrate sources in their niche (Sterflinger and Krumbein 1997).

3.2.1.5 White Rot and Brown Rot Fungi

These fungal groups excrete large amounts of organic anions especially oxalate which directly or indirectly forms minerals. This ligand serves as a source for the production of hydrogen peroxide and for the formation of Mn chelates which are used for the oxidation of a range of phenolic compounds and that act as a potential weathering agent (Dutton and Evans 1996).

3.3 Cyanobacteria

Cyanobacteria are a major group of phototrophic prokaryotes that play an important role in the textural development of silica located in sinters in geothermal and in other rocky environments (Douglas 2005; Benning et al. 2005). Biosilicification is an important process in cyanobacteria and leads to the formation of silica nanoparticles then resulting into larger silica assemblages. This purely happened as the result of metabolic activity of these phototrophs leading to silicification process (Fig. 4). In general presence of cyanobacteria and their complex surface structures on rock surface initiates dissolution. The more important process of silica precipitation causes no changes in the rate cyanobacterial metabolism. Production of higher quantity of extracellular polysaccharide helps in the construction of aggregation. If this silicification process proceeds further, it causes cell death, lysis, and finally fossilization takes place. By fossilization the silica is again immobilized. This mechanism of mineral-microbe interaction was further explored by a series of algal studies. Interestingly *Calothrix*, a freshwater alga that forms chain pattern of cells enclosed by a thick sheath woven by polysaccharide and often found as

Fig. 4 Invasion of alga on the rock surface leading to decomposition on minerals

biofilms in hydrothermal environments, was observed (Jones and others, Jones et al. 1998).

The silicification reaction takes place between surface of the algal cell wall sheath and the aqueous silica where the cell wall itself acts as most reactive component (Phoenix et al. 2002). A series of reaction occurs in this silicification process. Initially the cell as a whole along with the sheath was subjected with high intensity of silica. Later the sheath is enriched with carbohydrate components and this extra cellular polysaccharides become more thicker leading to silicification. Further amorphous silica precipitation takes place, making the cell microenvironment with higher concentrated of Si. Eventually the sheath acts as the mineral deposition site, thus providing a physical barrier against colloidal silica deposition, and then this protects the cell wall and cytoplasm from mineralization (Phoenix et al. 2000).

3.4 Diatoms

Diatoms are single-celled algae having siliceous cell wall and actively take part in biodissolution of silica from naturally occurring rock host. Diatoms have a highly organized, polysilicate structures formed by the dissolved orthosilicate obtained from their microenvironment. These structures are species specific and the pattern various with organisms and duration of silicification (Ehrlich 1996; Gadd 2010). Species variation occurs by the intricately designed frustule that is formed by the silicate deposition. The adsorption and deposition of silica into the algal frustule structure is an active and integrated process that is mediated by the metabolic activity and an energy-conserved process in the cell. The rate of silicate uptake by diatoms can be quantified from time of speciation, the mechanism involved in mono-silicate uptake into the cell. This silicification and incorporation into the frustules is a question of investigation. It is clear that without diatoms, the mono-silicate forms would not have been organized in its frustules and this arrangement of silica lays foundation to biosilicification process. Thus, the microorganisms are highly reactive and metabolically sound in the biodissolution of silicate from the parent rock along with the production of essential nutrient mediated by its own genetically driven process. These metabolic activities are specific to its own group.

4 Mechanism

Microbes exploit minerals for their survival and thus they process mineral formation or dissolution potential. Thus, by dissolving minerals, they use it as a source of energy, or as a terminal electron acceptor in respiration, or as a trace element requirement for their growth. In some cases, they detoxify poisonous inorganic species or use them in active or passive transport for its cell growth or use it in their protective structure and make the environment safe. They also create

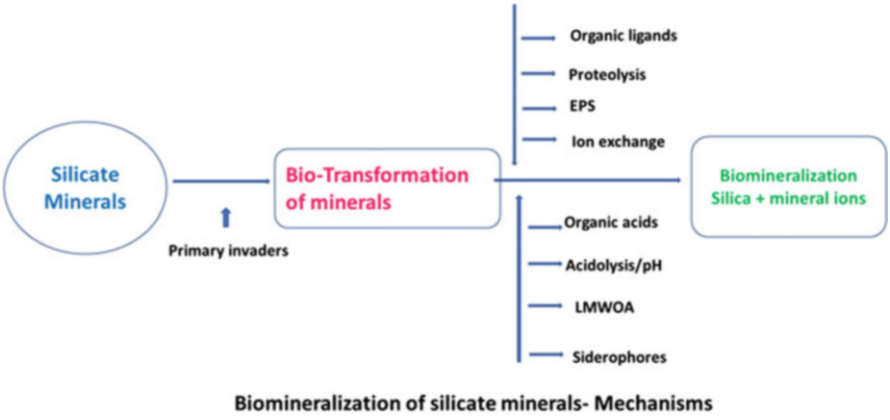

Fig. 5 Chart indicating the mechanism of biomineralization

competitiveness among microbial communities by causing nutrient limitation in the region they live (Ehrlich 1996).

Minerals are formed by the interaction of microbes with host rock, where both are prevalent in nature. They cause a number of environmental processes like decomposition, mineralization, transformations of rock-forming minerals, and finally biodissolution of nutrients (Fortin et al. 1998; Ehrlich 1998; Dong 2010). Several microbes-minerals interactions were studied and documented. Biomineralization mechanism (Fig. 5) comprises acidolysis, alkaline hydrolysis, ligand degradation, enzymolysis, capsule absorption, extracellular polysaccharide, redox reaction, etc. (Lian et al. 2002) (Table 3). The biological agents employ these substances to dissolute metals and make available in their intracellular and extracellular environment. Algae, fungi, and bacteria comprising lithobiontic communities synthesize an array of organic compounds that have been shown to affect the mobility of metal ions from the parent rock (Drever and Vance 1994).

4.1 Extracellular Polysaccharides (EPS)

Production of extracellular polysaccharides is the distinct process in prokaryotes that are involved in mineral formation. The chemical composition of EPS varies with their microenvironment. Aquatic bacteria possess peculiar characteristic structures that are not found in terrestrial ones. The cells are enclosed by several hundred nanometer thicker envelope than its cell volume. The diffusion barrier becomes thicker, acts as a boundary layer, extending many microns away from the cell wall, and protects the cell from the higher concentration of metabolic products. These layers are formed by the polymers like capsules or slimy layer produced and deposited onto its cell surface. Totally these interwoven structures are called “extracellular polymeric substance” or extracellular polysaccharides (Douglas and

Table 3 Biomineralization of minerals and their mechanisms

Microorganism	Minerals	Mechanism	References
Bacillus mucilaginosus	Phosphorite	Protein production	
Apatite and silicate	Native bacteria	Raise in pH	Singh and Kapoor (1998), Lian et al. (2002)
Adamellite and feldspar	*Bacillus mucilaginous*	Extracellular polysaccharide production	Binbin and Bin (2011)
Rock phosphate and feldspar	*Bacillus* strains	Organic acids, i.e., oxalic, fumaric, citric, and tartaric acid	Girgis et al. (2008)
Silicate minerals	Lithobiontic communities	Oxalic acid, extracellular microbial polymers production	Barker and Banfield (1996)
Aluminosilicate	Bacteria	Acid polysaccharide production	Malinovskaya et al. (1990)
Tectosilicates (quartz and feldspar)	In vitro studies	Aluminum ion concentration	Amrhein and Suarez (1988), Brady and Walther (1991)
Illite-smectite	*Bacillus mucilaginous*	Polymers production	Zhang et al. (2004)
Apophyllite, olivine, and ca- and Zn-silicate	*Pseudomonas*	Ketogluconic acid	Duff and Webley (1959), Henderson and Duff (1963)
Basalt and granite	Fungi	Citric acid	Silverman and Munoz (1970)
Smectite	Lichens	Organic ligands	
Silica sinter	Cyanobacteria	Extracellular polysaccharide that they produce. Exopolymeric sugars	
Feldspars	Bacteria	Oxalic acid and soluble oxalate complexes	Drever and Stillings (1997)
Quartz	Diatoms and *Radiolaria*	Production of chelates and mineral or organic acids	Brehm et al. (2005)
Quartz	Bacteria	Organic acids such as citric and oxalic acid	Bennett et al. (1988)
Phlogopite	*Agrobacterium* and *bacillus Burkholderia*	Gluconic acid production, aluminum chelation, and acidic dissolution	Page and Huyer (1984), Kalinowski et al. (2000), Kim et al. (2005)
Olivine and goethite/hornblende	*Azotobacter* sp. or *Streptomyces* sp.	Siderophores production	Page and Huyer (1984)

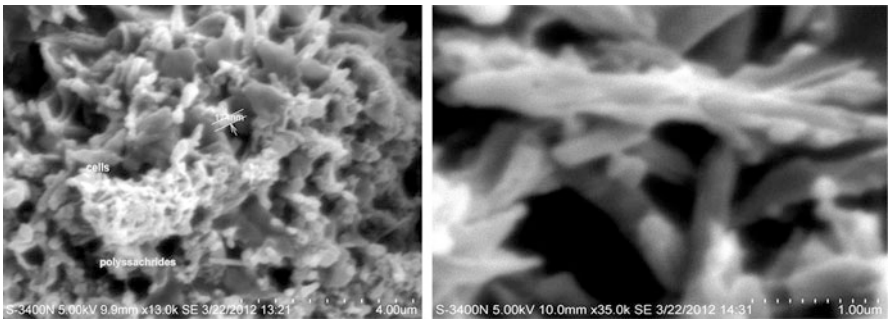

Fig. 6 SEM photograhpy of EPS production in the presence of biotite by *Bacillus mucilaginous* (in vitro studies by the author)

Beveridge 1998). At neutral pH, the negatively charged polymer, have strong influence on microbial mineral formation (Geesey et al. 1988; Little et al. 1997).

Production of extracellular polysaccharide by the bioagent played important roles in the formation of microbe-mineral complexes and maintaining the special properties of the microenvironment (Fig. 6). For example, when the polysaccharides strongly adsorbed the organic acids and attached to the surface of the mineral, they create an environment of high concentration of organic acids near the mineral (Liu et al. 2006). In a microbe-mineral study with feldspar and *B. mucilaginous*, leaching of K from feldspar had occurred, as a result of the participation of both EPS and organic acids (Girgis et al. 2008). Formation of bidentate complexes with metal ions tends to be more effective in enhancing dissolution than monodentate ligands formed by acetate or propionate (Welch and Ullman 1993).

Consequently, biologically mediated weathering involves a complex dissolution, selective transport, and a recrystallization mechanism occurring within the acidic extracellular gels coating all mineral surfaces. This specialized weathering microenvironment formed around each mineral grain initially produces minute phyllosilicate crystallites. Before initiating weathering a rind of clay minerals or a polymer-bound aggregates are formed around the dissolving parent phase. Filamentous fungi have a peculiar process where the hyphae entangle soil particles, forming stable microaggregates and also polysaccharide aggregates that are tightly held with these sticky polymeric substances (Lunsdorf et al. 2000).

These organic layers are formed around feldspar and quartz, facilitating the mobility and transport of A1, Ca, K, and clay minerals. They form polysaccharide coatings around themselves, separated by a few micrometers, and generate a polysaccharide-bound mass of clay minerals (Barker and Banfield 1996). Thus, it is possible that EPS, unlike other classes of organic molecules often implicated in bioweathering, has greater influence in mineral formation, its transport, recrystallization, and transformations of silicate minerals. Biogeochemical processes are well pronounced by many mechanisms, namely, (1) proton-based and (2) ligand-based agents (3) organic acids comprising low molecular weight organic acids, lichen acids, etc.

4.2 Proton-Based Agents

Proton-based agents include respiratory CO_2 or carbonic acid and other organic acids produced by microorganisms. They enhance mineral dissolution rate by producing and excreting such agents that interact with the mineral surface. Carbonic acid concentration increases at mineral surfaces by their respiratory mechanism and particulate degradation and also by dissolved organic carbon content which accelerates mineral weathering; further it intensifies the mineralization rates by a proton-promoted dissolution mechanism (Barker and Banfield 1998).

4.3 Ligand-Based Weathering Agents

Ligand-based weathering agents include organic anions, lichen acids, LMWOA, siderophores, other polyphenolic acids, and acid polysaccharides.

4.3.1 Low Molecular Weight Organic Acids (LMWOA)

Low molecular weight organic acids are the most important group of weathering agents, acting as both proton-based and ligand-based groups. Mostly, they combine with metal-binding sites, and are exuded as anions of oxalate and citrate which have a strong affinity to bind with the tri- and divalent metal cations like Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+} (Casarin et al. 2003). As the result of the binding process with, the source of free cations will be reduced in the surrounding and in soil solution. A low saturation state of ions takes place and they further erode of ions from minerals and thus trigger mineral weathering. This type happens in lichen where oxalate production mediates the reaction. Ectomycorrhizal fungi produce citrate and malate (Landeweert et al. 2001), whereas ericoid mycorrhizal fungi, specifically the heavy metal-tolerant strains, produce oxalates (Martino et al. 2003).

4.4 Proteomics

Microbiological proteomics deals with proteins in close relation with microbial activities, and functional genome expression under different environmental conditions. Proteins are the product of physiological function that directs the embodiment of life phenomenon. However, bacterial proteomics deals partially with bacterial physiology, mechanism of environmental adaption, and reconstruction (Liang et al. 2002; Ding et al. 2006). Meagre studies were done related to enzyme activities and recently it's an emerging division in mineralogical weathering. Proteomic study

would give a concete idea and paves a way for new approaches in mineral formation and also forms a platform for studying the molecular mechanism of bioweathering.

In a study with *Bacillus mucilaginous* and phosphorite mineral, the bacterium produces plump capsules with a greater amount of extracellular polysaccharides and forms of a biofilm on the mineral surface. In addition with the protein production, bacterial biomass was also increased, leading to higher absorption of ions (Douglas and Beveridge 1998). The rise of bacteria colonies resulted in bacterial self-regulation which initiates weathering. Signal proteins were found to involve in protein translation, in determining the activation, stability, and metabolism of proteins (Tjalsma and van Dij 2005). *B. mucilaginous* produced many new protein spots and the formation of new protein patterns was closely related with environmental changes.

The proteins thus formed may promote mineralization, which is dependent with enzymatic function during weathering (Dziurla et al. 1998; Neal et al. 2003). On the other hand, the newly synthesized proteins were related to cell metabolizability such as regulation of transcription, transcriptional factors, growth factors, and signal transportation (Madsen 1998). More work on this kind of research is needed further for probing the role of protein in mineral formation.

4.5 pH Production

Microbial metabolites cause mineral corrosion, where reduction in pH takes place and breaking down of crystal structure of minerals by chelation and by the bacterial enzyme (Sun and Zhang 2006). Acidolysis is the main accepted mechanism of microbes weathering silicate minerals (Jongmans et al. 1997; Cameselle et al. 2003; Sha et al. 2006). During the dissolution process, the bioagents, either bacteria or fungi or lichens, dissolves the minerals by co-action of acidolysis and ligand formation. Mineralization of silicate are greatly influenced by the pH production.

4.6 Acidolysis and Chelation Reactions

Acidolysis is another mechanism involved in biomineralization. Mineral dissolution can also be due to carbonic acid formed from CO_2 by bacterial respiration or to nitric and nitrous acid produced by nitrifying bacteria (Barker et al. 1997; Sverdrup and Warfvinge 1995). Mineral weathering process takes place either by (a) adhesion of organic acids onto mineral surfaces and extraction of nutrients by electron transfer or; (b) breaking the oxygen links or; and (c) creating an imbalance between cation and anion concentrations in the solution by the chelation reaction through carboxyl and hydroxyl groups (Welch et al. 2002). Acidolysis and complexolysis processes can be used simultaneously by bacteria to affect the mineral stability. *Agrobacterium* and *Bacillus* strains were described for their ability to weather phlogopite via aluminum

chelation and acidic dissolution of the crystal network (Leyval and Berthelin 1989). Bacteria produce gluconic acid, which harbors both acidifying process and chelating reactions, as reported for a strain of *Burkholderia* (Kim et al. 2005).

4.7 Organic Acids

Some bacteria and fungi can accelerate dissolution of silicates and aluminosilicates. The bioweathering reactions have been attributed to the production of varied organic acid, e.g., acetic, oxalic, citric, formic, fumaric, glyoxylic, gluconic, succinic, and tartaric acids. Organic acids act as acidulants and/or ligand, or base in the form of NH_3, and causes acidification of specific capsular slime produced by bacteria. Among the organic acids, 2-ketogluconic acid produced by some bacteria and citric and oxalic acids produced by some fungi have proved as effective bioagents for dissolution of silicates (Duff et al. 1963; Vandevivere et al. 1994; Welch and Ullman 1993). They supply protons that help in breaking Si-O and A1-O bonds through protonation and catalysis. At the same time, some of the acids function as ligands that exude cations from the crystal lattice framework, facilitating further breakage of framework bonds. The mineral surface is occupied by active microbes which form biofilms, and the metabolic products they produce critically encounter the silicate or aluminosilicate at relatively high concentration, thereby causing higher range of mineral solubilization. Production of soluble organic acids by bacteria is by three mechanisms, viz., fermentation, catabolism, and excretion.

(a) ***Fermentation***

Fermentative bacteria produce organic acids like acetic acid, butyric acid, and lactic acid as final metabolic byproducts. Fermentation is generally limited in aquifers and sediments to zones where alternative electron acceptors (O_2, Mn^{4+}, Fe^{3+}, NO^3, SO_4^{2-}) are unavailable.

(b) ***Catabolism***

Decomposition of macromolecules such as proteins, cellulose, and lignin in aerobic conditions can also lead to the production of organic acids. By the degradation mechanism, it is thought that amino acids and a large number of aromatic organic byproducts are produced (Thurman 1985).

(c) ***Excretion***

Aerobic bacteria excrete organic acids when grown in the absence of essential nutrients (Neijssel and Tempest 1975 and Tempest and Neijssel 1992). Organic acids are excreted in the presence of sufficient carbon substrate, but aerobic growth is inhibited by the lack of nutrients. Abiotic factor like temperature acts as an important criterion where excretion was greater at lower temperatures (5 °C) than at higher temperatures (20 °C and 35 °C), that is, the dissolution rate is greater at lower temperatures.

4.8 Impact of Polymers on Mineral Dissolution

Components of microbial cell, as a whole, have some affinity on dissolution. Cell walls, hyphal structures, and extracellular polymers produced have greater impact on mineral solubility. A well-known fact is that, the bacterial cell wall, has metal binding capability, which indirectly enhances solubility by forming metal complexes in solution (Beveridge and Fyfe 1985; Mittelman and Geesey 1985; Geesey et al. 1987; Ferris et al. 1989; Walker et al. 1989). These compounds or other metabolic byproducts also inhibit mineral dissolution. Many organic compounds are known to irreversibly adsorb on mineral surfaces or to react with surfaces and solutions to produce stable secondary phases (Davis 1982; Kirchman et al. 1989). Thus, an alternate adsorption and precipitation process have the effect on the exchange between the mineral surface and the surrounding fluid. Polymers produced by bacteria have direct or indirect impacts on dissolution rates. This mainly depending on the nature of the compound, its type of interaction, concentration of other dissolution enhancing or inhibiting compounds and pH (Welch and Vandevivere 1995).

4.9 Nutrient Limitation

Many important microbial processes, viz., energy generation, nutrient acquisition, cell adhesion, biofilm formation, etc., can be influenced by minerals (Hochella 2002; Brown et al. 2008). Essential nutrients may be acquired from mineral surfaces, and this concentrates these substances above surrounding environmental levels, e.g., C, N, P, Fe, essential metals, and various organic compounds (Vaughan et al. 2002). Nutrient-limited conditions trigger the bacterium to pull the nutrients from the nutrient-rich mineral surface, thus indirectly affecting the dissolution and also inducing organic acid production which in turn enhances mineralization.

4.10 Siderophores

Siderophores are low molecular weight organic compound produced by the microbes for search of iron. Metal mobilization from rocks, minerals, soil, and other substrates can be achieved by Fe-binding siderophores (Burgstaller and Schinner 1993; Jacobs et al. 2002a, b; Huang et al. 2004; Lian et al. 2008). Chelating ability is also characteristic of another group of molecules containing carbonyl structures with a strong affinity for iron, the siderophores. Under iron deficiency conditions, some bacteria excrete such compounds into the medium in which they chelate and transport iron ions into bacterial cells. Interestingly, catechol derivatives produced by *Azotobacter* sp. or *Streptomyces* sp. are supposed to increase

dissolution of, respectively, iron-containing minerals like glauconite, goethite, and olivine or hornblende (Page and Huyer 1984; Kalinowski et al. 2000).

4.11 Other Mechanisms

Bioweathering cause many transformation changes in silicate rocks when there is disturbance in the polymerized structures. This is because of the formation cleavage of Si-O-Si (siloxane) or Al-O bonds or removal of cations from the crystal lattice which leads to the structural collapse of rock silicates and aluminosilicates.

The mechanisms of attack may include microbially produced ligands of cations or organic or inorganic acids that serve as a source of protons or production of alkali like ammonia or amines or by the extracellular polysaccharides that act at acidic pH. These compounds individually or in combination are excreted in the bulk phase in addition with the formation of biofilm on surfaces of silica or silicates resulting in etching (Bennett et al. 1996, 2001).

Clay compounds like aluminosilicates exert many effects on microbes in soil and trigger the microbial metabolism (Theng and Yuan 2008) where clay acts as buffers and as sorptive agents for cells, metabolites, ions, and enzymes and causes indirect physicochemical effects on the microenvironment (Tazaki 2006; Ehrlich and Newman 2009).

The common formation of biofilms is significant, aiding colonization and survival, with the metabolites also capable of forming metal complexation, and weakening the mineral lattice through repeated wetting and drying cycles and subsequent expansion and contraction. The production of efflorescence or salting involves secondary mineral formation through reaction of anions from excreted acids with cations from the stone. Such secondary minerals can cause physical damage leading to blistering, flaking, scaling, and granular disintegration leading to rock decay (Wright 2002).

4.12 Oxidoreduction Reactions

Unlike eukaryotes, some bacterial taxa use nitrate and sulfate as alternative terminal electron acceptors for their metabolic activity. Some use minerals as a whole as electron acceptor. Iron containing minerals such as goethite or hematite are some examples. Bacterial cells acting on these are insoluble forms and have direct contact with the mineral surface (Newman 2001). It was suggested that this electron transfer could occur by excreted and membrane-associated molecules such as quinones, extracellular cysteines, or heteropolymers of melanin (Hernandez et al. 2004; Croal et al. 2004). Thus, the reduction or oxidation of a chemical compound entrapped in a complex structure leads to the instability of the mineral crystal, and, therefore, dissolution of silicates occurs.

5 Application of Mineral Rock Sources

There is a greater opportunity in near future, and no doubt that these efficient tiny, live-mini factories would replace chemical fertilization. These microbes can enhance the plant growth by releasing fixed mineral sources from solid crusts as available nutrient forms.

Such bio-intervention or biofertilization might be economical and yield a pollution-free environment in crop production. Rock powders are an abundant byproduct of the quarry industries and have been widely used as fertilizers or soil conditioners in agriculture. When mica was used as potassium source in wheat, vermiculitization of trioctahedral micas occurred after a few weeks of wheat cultivation (Mojallali and Weed 1978). Similarly, mica was used in soybean (Hinsinger et al. 1992) and in Italian ryegrass (Hinsinger and Jaillard 1993) as a raw material for K nutrition; mineral transformation had occurred by the exchange of K^+ ions between the clay lattices. These research works have shown the biological transformation of mineral in simplified nutrient available form.

Symbiotic microorganisms in the rhizosphere increased the availability of K from biotite weathering, increased K uptake, and improved the growth of *Zea mays* (Berthelin and Leyval 1982). Silicate rock materials are cheaper sources of P and K nutrition but not readily available to a plant because the minerals are released slowly and their use as fertilizer for long-term approaches often causes significant yield increase in maize (Zapata and Roy 2004). Illite mineral performed as a good K source, when used in powdered form in cotton and rape along with potassium releasing bacterial NBT strain *Bacillus edaphicus* as biological source which enhanced the biometrics of both the crop (Sheng 2005). In another study, the bio-intrusion of waste mica with potassium-solubilizing microorganism (*Bacillus mucilaginous*) could be another alternative and viable technology to solubilize insoluble K from mica into plant-available pool, and this can be used efficiently as K fertilizer for sustaining crop production and maintaining soil K (Nishanth and Biswas 2008 and Basak and Biswas 2010a).

Silicate-weathering bacteria such as *Bacillus circulans*, *Bacillus edaphicus*, and *Bacillus mucilaginous* were widely distributed in nature and contribute to weathering, biogenesis, and mineralization of silica, a major rock-forming mineral. These organisms dissolve K-rich silicate minerals like mica and illite and can extract P from apatite and have proved as an efficient biological fertilizer to accommodate plant growth in barren soil (Boyle and Voigt 1973; Lian 1998; Liu et al. 2006; Li et al. 2007).

Many research workers have reported the beneficial effect of typical silicate bacterium, *B. mucilaginous*; its ability in biogeochemical cycling of potassium, phosphorus, and other soil elements; and its utility in agriculture, bioleaching, and wastewater treatment. Lian (1998) have reported that *Bacillus mucilaginous* is a novel silicate-solubilizing bacterium that produces a variety of exopolysaccharides. This was utilized in agriculture, extensively as a multifunctional microbial fertilizer, which can make the availability of K, P, and other beneficial elements in soil by dissolving insoluble minerals. Many such examples can be listed for the bio-intervention and using silicate minerals in agriculture (Table 4 and Fig. 7).

Table 4 Bio-intervention of microbes and silicate minerals as a source of nutrient in agriculture

Silicate mineral	Bio-intervention	Crop	Findings	References
Micas	Rhizosphere bacteria	Wheat	Improved crop growth	Mojallali and Weed (1978)
Biotite	Microorganisms in the rhizosphere	*Zea mays*	Promoted biotite weathering and K uptake	Berthelin and Leyval (1982)
Phlogopite	Rhizosphere microorganisms	Pine	K source	Leyval and Berthelin (1991)
Biotite and microcline	Mycorrhizal fungi	Pine	Improved K uptake by releasing K from mineral structure	Wallander and Wickmann (1999)
Illite powder	*Bacillus edaphicus* NBT	Cotton and rape	Dry matter yield and K content increased	
Illite and rock phosphate powder	*Bacillus mucilaginous* (KSB) and *Bacillus megaterium* (PSB)	Eggplant	Enhanced plant growth and nutrient uptake	Han and Lee (2005)
Muscovite and biotite local	Rhizobacterial strain (K-31, K-81)	Wheat	Improved grain yield and K status of soil	Mikhailouskaya and Tchernysh (2005)
Feldspar and illite	*Bacillus edaphicus*	Wheat	Accumulated more K, N, and P	Sheng and He (2006)
Feldspar	*Bacillus cereus*	Sorghum	Yield and K uptake increased	Badr et al. (2006)
Feldspar	*Bacillus cereus*	Tomato	Maximum K use efficiency, total K uptake	Badr (2006)
Illite and rock phosphate powder	*Bacillus mucilaginous* (KSB) and *Bacillus megaterium* var *phosphaticum* (PSB)	Pepper and cucumber	Increased availability of P and K in soil and uptake by plants	Han et al. (2006)
Microcline, orthoclase, and muscovite mica	*Bacillus mucilaginous*	Groundnut	Yield and oil content increased and K status in soil improved	Sugumaran and Janarthanam (2007)
Phosphate and potash rocks	*Acidithiobacillus*, oxidizing bacteria	Sugarcane	Available P, K and exchangeable Ca and Mg increased	Stamford et al. (2008)
Waste mica	*Bacillus mucilaginous*	Sudan grass	Improved biomass yield and K uptake by Sudan grass as well as soil K status	Basak and Biswas (2009)
Waste mica	(*Bacillus mucilaginous*)	*Sorghum vulgare* Pers.	Solubilized insoluble K	Nishanth and Biswas (2008) and Basak and Biswas (2010a)

(continued)

Table 4 (continued)

Silicate mineral	Bio-intervention	Crop	Findings	References
Waste mica	*Bacillus mucilaginous* (KSB) and *Azotobacter chroococcum* (N fixer)	Sudan grass	Biomass yield, K, and N uptake increased	Basak and Biswas (2010b)
Feldspar	*Bacillus mucilaginous*	Maize	Plant growth and K uptake increased	Abou-el-Seoud and Abdel-Megeed (2012)
Feldspar (KUE) as compared to K_2SO_4	*Bacillus cereus*	Tomato	More fruit yield and potassium use efficiency	
Waste mica	*Aspergillus awamori*	Potato-soybean	Significantly increased yield K uptake	Biswas (2011)
Feldspar increased K uptake by maize and wheat	*Bacillus pasteurii*	Peanut and sesame	Yield enhancement	Youssef et al. (2010)
Waste mica	*Aspergillus awamori*	Soybean	Improved soybean yield and K uptake	Meena and Biswas (2013)

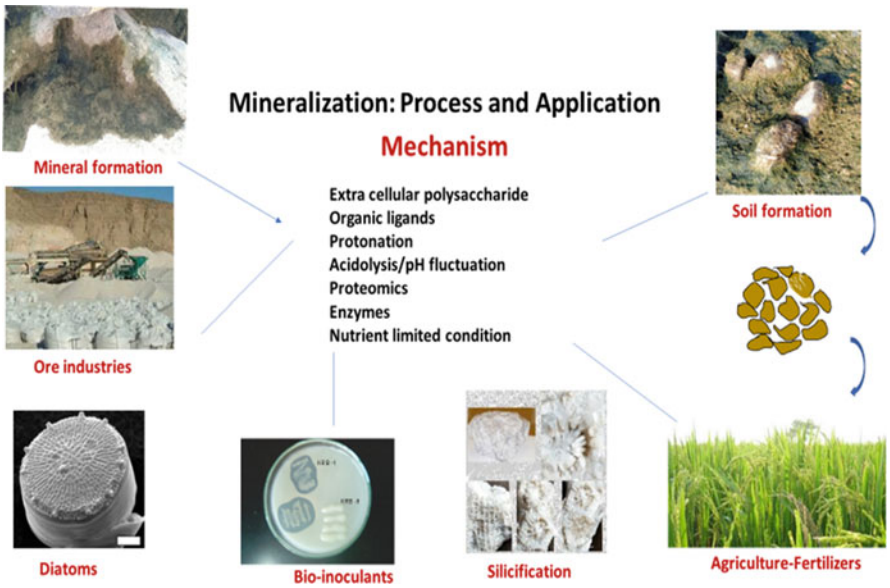

Fig. 7 Mineralization: process and application

6 Conclusion and Future Approaches

This chapter has thrown light on the importance of silicate minerals, as a source of nutrients. This approach has to be probed thoroughly, and more research investigation on finding new biological sources and its mechanism has to be done. Since most of the research works are confined to in vitro conditions, in-depth studies on popularization and application aspects have to be done in long-term experiments. The inference incurred from this research will highlight the importance of silicate mineral resources. Moreover, many indigenous microbial sources, with novel species having greater bioweathering potential, can be obtained. However, having a handful of scientific evidence on molecular mechanisms and genomics, more emphasis has to be given on enzymatic and proteomic studies as integrated approaches. Ecological process of this microbial domain remains a challenge to the scientist in the field of mineralogy. Many unanswered questions in this field, should be explored in future, to develop a newer pathway in mineralogical applications.

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Non-silicate Minerals (Carbonates, Oxides, Phosphates, Sulfur-Containing, Oxalates, and Other Organic Crystals) Induced by Microorganisms

Anne Jantschke

Contents

Abstract Microorganisms inhabit almost every natural environment on Earth. Since the beginning of life, microorganisms have played a fundamental role in the geochemical cycling of elements and shaped our current environments. Microorganisms that form minerals, a process known as biomineralization, contribute substantially to these processes. Over half of the essential elements required by living organisms are incorporated into biominerals. More than 60 different biominerals are known in nature, including oxides and hydroxides, carbonates, phosphates, sulfates and sulfides, silicates, and organic crystals.

Biominerals are composite materials that often exhibit superior properties when compared to their abiotically formed counterparts. Their well-designed architectures and hierarchical structures offer structural support and protection, but also fulfill a wide variety of other functions. Biominerals often reflect the physicochemical properties of the environment the biomineral was formed in. Fossilized biominerals are therefore useful tools for paleoceanographic and paleoclimate reconstructions. Biomineralization not only fascinates biologists, it also provides sophisticated models for functional materials in materials science and affects the global aspects of the earth sciences.

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The chapter gives an overview over non-siliceous biominerals formed by microorganisms and lists them in tabular form ordered by taxonomic criteria. It features carbonates, oxides and hydroxides, phosphates, sulfur-containing biominerals, and organic crystals.

1 Introduction

Microorganisms inhabit almost every natural environment on Earth. They populate the deepest oceans (Kato and Bartlett 1997), driest deserts (Wierzchos et al. 2011; Chan et al. 2012), the coldest climates (Cockell et al. 2010), and even extreme acidic environments (Johnson and Hallberg 2003). Since the beginning of life, microorganisms have played a fundamental role in the geochemical cycling of elements and have shaped our current environments. Microorganisms that form minerals, a process known as biomineralization, contribute substantially to these geochemical processes.

Over half of the essential elements required by living organisms are incorporated into biomineral deposits. The earliest microbial biomineralization process, the production of magnetite by magnetotactic bacteria, dates as far back as 3.5 billion million years (Lin et al. 2017). More than 60 different biominerals are known in nature, including oxides and hydroxides, carbonates, phosphates, sulfates and sulfides, silicates, and organic crystals. Among non-siliceous biominerals, calcium-based minerals are widespread. This can be explained by the high availability of environmental calcium and the low solubility of calcium salts, making them thermodynamically stable within biological environments. Precipitation of calcium salts also provides effective means to maintain cellular calcium homeostasis (Mann 2001).

Two types of biomineralization pathways can be distinguished: **biologically induced mineralization** and **biologically controlled mineralization** (Lowenstam 1981; Lowenstam and Weiner 1989). In biologically induced mineralization, precipitation occurs due to a modification of the local microenvironment caused by the organism. This could be the result of metabolic activity, or simply of the presence of adsorption and nucleation sites provided by cellular components, such as cell walls or extracellular polymeric substances (EPS). The organism does not exert any active control over the mineralization process.

In **biologically controlled mineralization**, the organism exerts a high degree of control over all steps of mineral formation: the selective uptake and accumulation of elements from the local environment, as well as nucleation and growth of the mineral phase. All of these processes are genetically controlled. Typically, the formation of biominerals requires local areas with sufficient ion supersaturation. Such privileged environments have to be created within a biologically controlled system in order to isolate harmful elements (Weiner and Dove 2003). For this reason, controlled biomineralization processes often take place in specialized, membrane-delimited spaces, such as vesicles, where an organism can exert control over mineralization.

In addition, these confined spaces also influence mineral crystallization (Meldrum and O'Shaughnessy 2020).

Generally, mineral precipitation often reflects the physicochemical properties of the environment the biomineral was formed in, e.g., water or mineral chemistry, temperature, pH, pressure, and light intensity. Fossilized biominerals are therefore a useful tool for paleoceanographic and paleoclimate reconstructions (Weiner and Dove 2003; Li et al. 2013).

Furthermore, biominerals are composite materials that often exhibit superior properties, e.g., in mechanical testing, when compared to their abiotically formed counterparts. Typically, the inorganic mineral is intimately associated with organic matrix constituents that influence the material's properties. These "natural additives" are also believed to play an integral part in mineral formation.

The well-designed morphologies and hierarchical structures of biominerals offer structural support and protection, but also fulfill a wide variety of important biological functions such as motion, buoyancy, storage, and optical, magnetic, or gravity sensing (Mann 2001). The "eco-friendly" formation of complex three-dimensional architectures with exquisite structural control under ambient conditions is beyond the reach of current human technology.

These properties make biomineralization a highly interdisciplinary research area: The architectures emerging from biological self-organization not only fascinate biologists and medical scientists, they also provide sophisticated models for functional materials in materials science (Nudelman and Sommerdijk 2012) and affect the global aspects of the earth sciences.

The chapter gives an overview over non-siliceous biominerals formed by microorganisms and lists them in tabular form ordered by taxonomic criteria. It features carbonates, oxides and hydroxides, phosphates, sulfur-containing biominerals, and organic crystals. For this overview, organisms up to 1μm in size were considered to be microorganisms. Taxonomic description is given according to the Lifemap project (de Vienne 2016) available at http://lifemap-ncbi.univ-lyon1.fr/.

2 Carbonates

Calcium carbonate biominerals are the most abundant biogenic minerals found in nature occurring both in freshwater and marine organisms. Three anhydrous calcium carbonate polymorphs exist: the two thermodynamically stable forms aragonite and calcite and the metastable vaterite. All of these polymorphs can be found biogenically as **carbonate biominerals formed by microorganisms** (**Table 1**). Calcite is the thermodynamically most stable form under ambient conditions (Jamieson 1953). Sometimes marine biogenic calcites contain up to 30 mol% Mg^{2+} ions in their lattice, which is referred to as Mg-calcite. Calcium carbonate can also occur in hydrated form as amorphous calcium carbonate (ACC), monohydrocalcite (MHC), calcium carbonate hexahydrate, and the recently discovered calcium carbonate hemihydrate (CCHH) (Zou et al. 2019).

Table 1 Carbonates in microorganisms

	Biomineral	Species	References
BACTERIA			
Non-specified	Calcite ($CaCO_3$)	~50 marine bacterial isolates	Morita (1980)
	Mainly aragonite, Mg-calcite ($CaCO_3$), and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	Heterotrophic marine bacterial (and fungal) isolates	Krumbein (1974, 1979)
	Calcite ($CaCO_3$)	31 calcifying bacterial isolates (*Bacillus*, *Arthrobacter*, *Kingella*, and *Xanthomonas*)	Cacchio et al. (2003)
Proteobacteria			
Alphaproteobacteria			
Rhodospirillales	Siderite ($FeCO_3$)	*Acidiphilium* sp.	Sánchez-Román et al. (2014)
	ACC (and magnetite)	Several species, at least two genomic undescribed genera	Monteil et al. (2020)
Betaproteobacteria			
Burkholderiales	Calcium carbonate ($CaCO_3$)	*Alcaligenes*	Rivadeneyra et al. (1985)
	ACC and Mg-calcite spherulites	*Curvibacter lanceolatus*	Zhang et al. (2017a)
	Rhodochrosite ($MnCO_3$) and MnO_x	*Leptothrix discophora*	Zhang et al. (2002)
Gammaproteobacteria			
Oceanospirillales	Mg-calcite, aragonite ($CaCO_3$), and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Halomonas eurihalina*	Rivadeneyra et al. (1998)
Pseudomonadales	Aragonite ($CaCO_3$)	*MB-1* (marine *Pseudomonas*)	Greenfield (2006)
	Calcite ($CaCO_3$)	*Pseudomonas fluorescens*	Appanna et al. (1997)
	Calcite and vaterite ($CaCO_3$)	*Freshwater isolates of Pseudomonas and Acinetobacter*	Zamarreño et al. (2009)
Thiotrichales	First calcium oxalate	*Achromatium*	Schewiakoff (1893)
	Calcite ($CaCO_3$)		West and Griffiths (1913), Bersa (1920), La Rivière and Schmidt (1992), Head et al. (1996, 2000b), Gray (2006), Gray and Head (2014), Salman et al. (2015)

Xanthomonadales	ACC	*Stenotrophomonas maltophilia*	Enyedi et al. (2020)
Alteromonadales	Siderite ($FeCO_3$)	*Shewanella algae*	Parmar et al. (2000)
	Siderite ($FeCO_3$), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], magnetite (Fe_3O_4), green rust*	*Shewanella putrefaciens*	Fredrickson et al. (1998)
	Vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] and siderite ($FeCO_3$)		Zachara et al. (1998)
	Magnetite (Fe_3O_4), ferrous hydroxy carbonate (FHC), carbonate, and ferric green rust*		O'Loughlin et al. (2013)
	Magnetite (Fe_3O_4), akaganeite (β-FeOOH), and siderite ($FeCO_3$)	*Shewanella algae*, *S. pealeana*	Roh et al. (2003)
Deltaproteobacteria			
Desulfovibrionales (SRB)	Ferroan dolomite [$CaMg(CO_3)_2$]	*Desulfovibrio*	Vasconcelos et al. (1995)
	Mg-calcite ($CaCO_3$) and Ca-dolomite [$CaMg(CO_3)_2$]	*Desulfonatronovibrio* sp., *D. hydrogenovorans*, *Desulfovibrio profundus*, and *SRB strains LVform1* and *LVform6*	Warthmann et al. (2000), Van Lith et al. (2003a, b)
	Greigite (Fe_3S_4), pyrite (FeS_2) and intermediates (FeS), sphalerite (ZnS), elemental sulfur, gypsum ($CaSO_4{\cdot}2H_2O$), struvite ($NH_4MgPO_4{\cdot}6H_2O$), magnesite ($MgCO_3$)	*Desulfovibrio desulfuricans*	Hallberg (1972)
	High Mg-calcite ($CaCO_3$), greigite (Fe_3S_4)	Bacteria (DSS-group) and archaea (ANME-1)	Reitner et al. (2005)
	Calcium carbonate ($CaCO_3$)	*Beggiatoa*	Boetius et al. (2000)
Myxococcales	Mg-calcite ($CaCO_3$)	*Myxococcus xanthus*	González-Muñoz et al. (2000),
	Vaterite ($CaCO_3$)		Rodriguez-Navarro et al. (2007)

(continued)

Table 1 (continued)

	Biomineral	Species	References
Terrabacteria			
Actinobacteria			
Propionibacteriales	Vivianite ($Fe_3(PO_4)_2.8H_2O$) [and siderite ($FeCO_3$)]	*Tessaracoccus lapidicaptus*	Sánchez-Román et al. (2014, 2015)
Micrococcales	Calcium carbonate ($CaCO_3$)	*Micrococcus*	Rivadeneyra et al. (1985)
	Calcite/vaterite ($CaCO_3$)	*Agromyces*, *Amycolatopsis*, *Brachybacterium*, *Nocardioides*, *Nocardiopsis*, *Paenibacillus polymyxa*, *Rhodococcus*, *Rothia*, *Streptomyces* sp., and *S. nitrosporeus*	Groth et al. (2001)
	Mg-calcite ($CaCO_3$)	*Brachybacterium*, *Paenibacillus polymyxa*, *Rhodococcus*, *Streptomyces*	
	Calcite, aragonite (CaCO3), and dolomite [$CaMg(CO_3)_2$]	*Nesterenkonia halobia*	Rivadeneyra et al. (2000)
	Calcite, vaterite ($CaCO_3$), and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Arthrobacter sulfonivorans* and	Rusznyák et al. (2012)
Corynebacteriales		*Rhodococcus globerulus*	
	ACC ($CaCO_3$)	*Rhodococcus degradans*,	Enyedi et al. (2020)
Firmicutes Bacillales		and *Bacillus simplex*	
	ACC and vaterite ($CaCO_3$)	*Lysinibacillus* sp.	Lv et al. (2017)
	calcite ($CaCO_3$)	*Bacillus megaterium*	Lian et al. (2006)
	Calcium carbonate ($CaCO_3$)	*Staphylococcus*	Rivadeneyra et al. (1985)
Urease-producing bacteria (UPB)	Calcite ($CaCO_3$)	*Bacillus*, *Staphylococcus succinus*	Stabnikov et al. (2013)
		Sporosarcina pasteurii = *Bacillus pasteurii*	Gollapudi et al. (1995), Stocks-Fischer et al. (1999), Bang et al. (2001), Bachmeier et al. (2002)
Clostridia	Magnetite (Fe_3O_4), akaganeite (β-FeOOH), and siderite ($FeCO_3$)	*Thermoanaerobacter ethanolicus*	Roh et al. (2003)

Cyanobacteria	Amorphous Ca-rich carbonates (ACC)	68 phylogenetically diverse strains	Benzerara et al. (2014)
Gloeobacterales	Amorphous Ca/Mg/Sr/Ba-carbonate spherules [benstonite, $(Sr_1Ba_{2.7}Mg_{1.4}Ca_{0.9})Ca_6Mg(CO_3)_{13}$]	*Cand. Gloeomargarita lithophora*	Couradeau et al. (2012)
	ACC granules		Li et al. (2016a)
		Gloeomargarita lithophora	Blondeau et al. (2018)
	Sr/Ba-enriched, core-shell structured ACC granules		Cam et al. (2016)
Nostocales	Calcite ($CaCO_3$)	*Scytonema julianum*	Schönleber (1936)
		Geitleria	Friedmann (1979)
Oscillatoriophycideae	Dypingite $[Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O]$	*Lyngbya* sp.	Power et al. (2007)
	Calcite and "nano-globules" ($CaCO_3$)	*Gloeocapsa* sp.	Bundeleva et al. (2014)
	ACC granules	*Cyanothece* sp.	Blondeau et al. (2018)
	Sr/Ba-enriched, core-shell structured ACC granules		Cam et al. (2016)
Spirulinales	Calcite ($CaCO_3$)	*Spirulina platensis*	Ramanan et al. (2010)
Synechococcales	Aragonite ($CaCO_3$) and ACC	*Rivularia*	Golubic and Campbell (1981)
	Calcite and aragonite ($CaCO_3$)	*Schizothrix calcicola*	Borowitzka et al. (1974)
	Calcite ($CaCO_3$)	*Synechococcus*	Dittrich et al. (2003)
	ACC, aragonite-like $CaCO_3$, calcite	*Synechococcus leopoliensis*	Obst et al. (2009)
	ACC granules	*Synechococcus calcipolaris*, *Synechococcus* sp., *Thermosynechococcus elongatus*	Li et al. (2016a), Blondeau et al. (2018)
	Gypsum ($CaSO_4{\cdot}2H_2O$), calcite ($CaCO_3$), and magnesite ($MgCO_3$)	*Synechococcus*	Thompson and Ferris (1990), Schultze-Lam et al. (1992)

(continued)

Table 1 (continued)

	Biomineral	Species	References
ARCHAEA			
SRB	High Mg-calcite ($CaCO_3$) and greigite (Fe_3S_4)	Bacteria (DSS-group) and archaea (ANME-1)	Reitner et al. (2005)
EUKARYA			
Amoebozoa			
Evosea			
Eumycetozoa			
Myxogastria	Calcite ($CaCO_3$)	*Fuligo septica*	Mangenot (1932)
	Calcite ($CaCO_3$)	*Didymium*	Pobeguin (1954)
Tubulinea			
Elardia			
Arcellinida	Calcite ($CaCO_3$)	*Paraquadrula*	Deflandre (1953)
Haptista			
Haptophyta	Aragonite ($CaCO_3$)	*Polycrater galapagensis*	Manton and Oates (1980)
Prymnesiophyceae/ Coccolithophyceae	Calcite ($CaCO_3$)	*Pleurochrysis carterae*, *Emiliania huxleyi*, *Coccolithus pelagicus*, *Calcidiscus leptoporus*, *etc.*	Wilbur and Watabe (1963), Isenberg et al. (2006) **Reviews:** Young (2003), Brownlee et al. (2015), Monteiro et al. (2016), Taylor et al. (2017)
SAR			
Alveolata			
Ciliophora	Calcium carbonate inclusions	*Prorodon*, *Lacrymaria*, *Trachelocerca*, *Cardiostonza*, *Loxocephalus*, *Pleuronema*, *Vorticella*, *Amphisiella*, *etc.*	Fauré-Fremiet and Gauchery (1957)
	MgCaP-rich inclusions	*Euplotes vannus*	Hausmann and Walz (1979)
	Calcite ($CaCO_3$), Ca-P-rich inclusions	*Spirostomum ambiguum*	Pautard (1970)
	ACC	*Coleps hirtus*	Lemloh et al. (2013)

Dinophyceae	Calcite ($CaCO_3$)	*Thoracosphaeraceae* (e.g., *Thoracosphaera heimii*, *Scrippsiella*, *Leonella*, *Calciodinellum*)	Wall et al. (1970), Keupp (1981), Tangen et al. (1982), Zonneveld et al. (2005), Wendler and Bown (2013), Jantschke et al. (2020)
	MgCaP-rich inclusions	*Calciodinellum operosum aff.*, *Leonella granifera*	Jantschke et al. (2020)
Stramenopiles			
Ochrophyta			
Crysophyceaea	Calcite ($CaCO_3$)	*Pseudokephyrion*	Tappan (1980)
PX clade	Calcite and aragonite ($CaCO_3$)	*Padina pavonica*, *P. australis*	Borowitzka et al. (1974)
Rhizaria			
Retaria			
Foraminifera	Calcite and aragonite ($CaCO_3$)	Diverse benthic and planktonic species, such as *Orbulina universa*, *Globorotalia*, *Ammonia* sp., *Amphistegina lobifera*, *A. lessonii*, *etc.*	Blackmon and Todd (1959) **Reviews:** Goldstein (1999), Erez (2003), de Nooijer et al. (2014)
Rhodophyta			
Florideophyceae	Calcite and aragonite ($CaCO_3$)	*Liagora cenomyce*, *Lithophyllum moluccense*, *Corallina cuvierii*	Borowitzka et al. (1974)
Fungi			
Dikarya			
Basidiomycota			
Agaricomycotina			
Agaricomycetes			
Boletales	Mixture of calcite ($CaCO_3$) and whewellite ($CaC_2O_4 \cdot H_2O$)	*Serpula himantioides* and *Cephalotrichum* sp.	Burford et al. (2006)
Ascomycota			
Saccharomyceta			
Pezizomycotina			
Ieotiomyceta			
Sordariomyceta			

(continued)

Table 1 (continued)

	Biomineral	Species	References
Lecanoromycetes	Hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$	*Stereocaulon vesuvianum*	Jones et al. (1982)
Viridiplantae			
Chlorophyta			
Core chlorophytes			
Chlorodendrophyceae			
Chlorocendrales	ACC micropearls, Sr/Ba-rich	*Tetraselmis*	Martignier et al. (2017, 2018)
Chlorophyceae			
Chlamydomonadales	Calcite ($CaCO_3$)	*Phacotus lenticularis*	Kamptner (1950), Hepperle et al. (1996), Schlegel et al. (2000)
Trebouxiophyceae			
Chlorellales	Calcite ($CaCO_3$)	*Nannochloris atomus*	Yates and Robbins (1998)
	Calcite ($CaCO_3$)	*Chlorella* sp.	Ramanan et al. (2010)
Ulvophyceae			
TCBD clade			
Bryopsidales	Calcite and aragonite ($CaCO_3$)	*Neomeris annulata*	
Dasycladales		*Halimeda cylindracea*, *H. macroloba*, and *H. opuntia*	Borowitzka et al. (1974)
Streptophyta			
Streptophytina			
Charophyceae	Calcite and aragonite ($CaCO_3$)	*Chara corallina*	Borowitzka et al. (1974)
Zygnemophyceae			
Spirogyra	Aragonite ($CaCO_3$)	*Spirogyra*	Mann et al. (1987)
Zygnematales	Calcite ($CaCO_3$)	*Oocardium*	Wallner (1933), Rott et al. (2010)

Of these, **ACC** is a particularly important actor in biomineralization, because it is a frequent precursor phase of calcite or aragonite (Beniash et al. 1997; Addadi et al. 2003; Rodriguez-Blanco et al. 2017). Several microorganisms also produce stable amorphous calcium carbonate (ACC) as a biomineral (cf. Table 1). ACC—as a precursor phase or stabilized biomineral—has been widely recognized in many groups of organisms (Addadi et al. 2003). Interestingly, more than one amorphous state of calcium carbonate exists, a phenomenon termed polyamorphism (Cartwright et al. 2012). ACC is a poorly ordered material that varies in its water content and short-range structure. Biogenic ACCs can exhibit distinct short-range structural order characteristic of specific polymorphs (calcitic, aragonitic, or MHC-like ACC) (Levi-Kalisman et al. 2002; Addadi et al. 2003; Cartwright et al. 2012).

Foraminifera and coccolithophores are the major producers of calcium carbonate in the oceans (Baumann et al. 2003). Along with pteropods these groups dominate the global flux of calcium carbonate to the ocean floor (Schiebel 2002). Their high abundance and global distribution in modern oceans together with a high degree of fossilization make them attractive model organisms and climate proxies. Both groups are therefore studied extensively. Trace element and stable isotope composition of their shells is frequently used for paleoceanographic reconstructions, providing information about past seawater parameters, such as temperature, salinity, and pH (Spero and Williams 1988; Spivack et al. 1993; Hastings et al. 1998; Gussone et al. 2003; Baumann et al. 2005; Stevenson et al. 2014; Keul et al. 2017). One of the key questions is to understand how shell composition of a biologically controlled mineralization process can accurately reflect environmental parameters present at the time of formation. A fundamental understanding of the (intra)cellular calcification processes and mechanisms is essential to interpret proxy signals accurately.

Foraminifera are unicellular amoeboid protists that produce shells, the so-called tests. They are divided into four categories based on their test features: organic tests, agglutinated tests, imperforate calcitic tests, and, the most abundant today, perforate calcitic tests. Foraminifera occur ubiquitously in both planktonic and benthic marine environments. Their attractiveness as a source of climate proxies lies in their abundance and their ability to record seawater conditions. Different mechanisms for calcification from seawater have been proposed, including endocytosis of seawater (Bentov et al. 2009), transmembrane ion transporters, ion-specific organic templates (Bentov and Erez 2006), and mitochondrial activity (Erez 2003).

A general model for foraminiferal biomineralization is still lacking, but rotaliid foraminifera grow their tests in discrete steps of new chamber additions. Calcification takes place within a defined space [the delimited biomineralization space (DBS)], which is created actively by the rhizopodial network and preforms the shape of the new chamber (Erez 2003). In this defined zone, primary calcite nucleation occurs on the surface of an organic template, the primary organic sheet (POS) (Banner et al. 1973; Hemleben et al. 1977; Spero 1988). This newly formed chamber wall is then overlain by another layer of secondary calcite that extends over the entire test. For more details the reader is referred to the excellent reviews on

foraminiferal biology (Goldstein 1999) and the complex and diverse nature of foraminiferal calcification (Erez 2003; de Nooijer et al. 2014).

Coccolithophores are a unicellular marine phytoplankton group characterized by a cell covering consisting of calcified scales called coccoliths. Coccoliths nucleate and grow within a specialized intracellular compartment, the Golgi-derived coccolith vesicle (for excellent reviews on coccolithophore calcification, see Young 2003; Brownlee et al. 2015; Monteiro et al. 2016; Taylor et al. 2017). This process starts with the nucleation of peripheral calcite crystals onto an organic baseplate (Walker et al. 2019; Marzec et al. 2019) inside the coccolith vesicle. Upon completion, the coccolith is subsequently extruded to the cell surface. Coccolith formation can be as fast as one per hour (Paasche 1962).

The biological mechanisms that control the intricate crystallization process are just starting to be understood. Recent studies using high-resolution cryoimaging revealed the presence of an intracellular compartment containing a calcium- and phosphorus-rich phase ([Ca] ~ 10 M) in the model organism *Emiliania huxleyi* (Sviben et al. 2016; Gal et al. 2017, 2018). By pulse-chase experiments using strontium instead of calcium ions, it was shown that the Ca-P-rich phase participates in coccolith formation and is used as calcium supply (Gal et al. 2017).

Recently, the structural similarity of this Ca-P-rich phase in coccolithophores and the Ca- and P-rich acidocalcisomes of the noncalcifying green alga *Chlamydomonas reinhardtii* was investigated (Gal et al. 2018). Acidocalcisomes are calcium-containing organelles that are considered the earliest form of an intracellular calcium pool (Ruiz et al. 2001; Docampo et al. 2005). Both Ca-P-rich compartments were shown to share many anatomical and chemical features, and based on these observations, a common dynamic calcium pool ancestor was suggested (Gal et al. 2018).

Interestingly, several other calcifying microorganisms possess similar intracellular, **membrane-bound granules** containing a disordered Ca-rich precursor phase that seem to be involved in mineral formation.

In members of **calcareous dinoflagellates**, dense **MgCaP-rich bodies** were identified by cryo-electron microscopy (Jantschke et al. 2020). These bodies seem to take part in calcium uptake, storage, and transport and are presumably secreted to the site of mineral growth, the outer matrix where the calcitic shell forms.

Similar **intracellular ACC inclusions** are known from cyanobacteria (cf. paragraph bacterial carbonate mineralization) and have been identified in the **green algae** *Tetraselmis cordiformis* (Martignier et al. 2017, 2018). Spherules of 0.4–1.2μm size were shown to consist of hydrated ACC. Because of the frequently observed internal zonation with alkaline-earth elements (Sr or Ba), these inclusions have been named "micropearls" (Martignier et al. 2017).

Intracellular "mineral concretions" have also been described in several **ciliate** species in the early twentieth century by Bernheimer (Bernheimer 1938) and Fauré-Fremiet (Fauré-Fremiet and Gauchery 1957). Even so, very little is known about biomineralization in ciliates. The first detailed description about the chemical nature of these inclusions was done by Pautard, who identified **intracellular spherules rich in calcium and phosphorus** in the ciliate *Spirostomum ambiguum* (Pautard 1970).

Furthermore, ciliates belonging to the genus *Coleps* form mineralized alveolar plates with a species-specific complex architecture. These alveolar plates are located within alveolar vesicles at the cell cortex. Recently, it has been shown that the alveolar plates are composed of an organic mesh-like structure that is mineralized with the **ACC** (Lemloh et al. 2013). Based on TEM observations, intracellular vesicles seem to be involved in calcium accumulation and transport.

A comprehensive study of the physiology and biochemistry of these precursor-rich spherules that extends over several phyla could shed light on the similarities and differences of these Ca-P-rich compartments and their ancestral origin.

Bacterial Carbonate Mineralization

Calcium carbonate deposits in **bacteria** are widespread and show a high degree of diversity. This is reflected by the variety of the calcium carbonate polymorphs found in bacterial cultures and in natural environments: Calcite, aragonite, vaterite, monohydrocalcite, and ACC have been identified in intra- and extracellular bacterial deposits (see **Table 1**).

Most of the bacteria precipitate calcium carbonate **extracellularly**, in close association with the bacterial cell wall (Beveridge and Murray 1976) and its extracellular polymeric substance (EPS) (Braissant et al. 2007; Dittrich and Sibler 2010; Flemming and Wingender 2010). Functional groups on the bacteria's surface, such as carboxyl, phosphate, hydroxyl, and sulfate, are able to complex and accumulate cations (such as Ca^{2+}). Calcium carbonate is subsequently formed as a result of alkalinization due to the bacterial metabolism, which is favoring precipitation.

During this process, **amorphous calcium carbonate (ACC)** has been observed to precipitate first and may transform into crystalline calcium carbonate polymorphs. ACC could be observed both in cultures, e.g., in vaterite-producing *Lysinibacillus* (Lv et al. 2017), Mg-calcite-producing *Curvibacter lanceolatus* (Zhang et al. 2017a) and aragonite-like calcium carbonate-producing *Synechococcus leopoliensis* (Obst et al. 2009), as well as in natural environments, such as cave sediments (speleothems) (Demény et al. 2016; Enyedi et al. 2020), marine ooids (Diaz et al. 2017), and hot springs (Jones and Peng 2012).

Recently, bacterial calcium carbonate mineralization has been applied in geotechnical engineering as a biocementation agent. Using urease-producing bacteria, the hydrolysis of urea into ammonium and carbonate is catalyzed. In the presence of Ca^{2+} ions, carbonate precipitation is initiated, a process called **microbially induced calcium carbonate precipitation (MICP)** (Seifan and Berenjian 2019). This novel and alternative type of construction material (De Muynck et al. 2010; Phillips et al. 2013; Chuo et al. 2020) is developing extensively and may be used for the strengthening of soil (Stabnikov et al. 2013), treatment of Ca-rich wastewaters (Hammes et al. 2003), oil recovery (Wu et al. 2017), or crack treatment (Gollapudi et al. 1995; Zhang et al. 2017b). In addition, the coprecipitation of other divalent cations such as Sr^{2+} and Ra^{2+} offers new possibilities for waste treatment (Kang et al. 2014).

Intracellular calcium carbonate inclusions are less common in bacteria. So far, intracellular calcite microspheres were only known from the large sulfur bacterium *Achromatium* (Head et al. 2000a; Gray 2006). These organisms accumulate microcrystalline calcium carbonate, in membrane-surrounded compartments filling most of the cell volume (Gray and Head 2014; Salman et al. 2015).

Recently intracellular amorphous calcium carbonate microspheres have been identified in several c**yanobacteria** species (for an overview see **Table 1**). Two phenotypes for ACC microsphere localization exist: They can be distributed randomly within the cell cytoplasm or lie at the cell poles (Benzerara et al. 2014; Li et al. 2016a). ACC biomineralization in cyanobacteria occurs within a microcompartment (Blondeau et al. 2018) and even in undersaturated extracellular solutions. Similar to other bacteria, *Gloeomargarita lithophora* has been shown to deposit other divalent cations with the ACC, even resulting in formation of core-shell globules (Cam et al. 2016). This accumulation of alkaline-earth elements is of particular interest for the remediation of radionuclides such as ^{90}Sr and Ra (Mehta et al. 2019).

In both cyanobacteria and *Achromatium*, the biochemical formation pathway and function of these intracellular, nonskeletal calcium carbonate inclusions are still not clear. Intracellular carbonates may act as inorganic carbon storage (Head et al. 2000b), control intracellular ion concentrations and buffer intracellular pH (La Rivière and Schmidt 1992; Salman et al. 2015), or regulate buoyancy (Couradeau et al. 2012).

3 Oxides and Hydroxides

Iron is the fourth most abundant element in the Earth's crust. Iron is a redox-sensitive transition element with oxidation states between -II and +VI. Therefore, iron cycling is driven by chemical and microbial oxidation and reduction processes. Additionally, iron is an essential trace element for almost all known organisms. The availability of iron can structure entire microbial communities, and thereby influence the geochemistry of an area. A number of microorganisms are also able to biomineralize iron oxides and hydroxides and play a key role in the biogeochemical cycling of iron.

One of the most interesting and best-studied examples of microbial iron oxide biomineralization (**Table 2**) are the **magnetotactic bacteria (MTB**; for an extended overview, the reader is referred to the **other chapter of this book**). This group of microorganisms produces intracellular magnetic crystals composed of magnetite (Fe_3O_4) and/or greigite (Fe_3S_4) in a specialized, membrane-delineated compartment, the magnetosome (Schüler 2004). The nano-sized, magnetic crystals are usually arranged into chain-like structures which enable the organisms to navigate using the Earth's magnetic field. This magnetotaxis allows MTB to position themselves in their preferred microaerobic oxygen concentration in vertically stratified environments (Frankel and Bazylinski 2009). Magnetotactic bacteria (MTB) are a paragon of biological controlled biomineralization, with their molecular machinery controlled at the gene level (Matsunaga et al. 1992; Schultheiss and Schüler 2003;

Table 2 Iron oxides in microorganisms

	Biomineral	Species	References
BACTERIA	Co- and Cr-containing magnetic inclusions	Different taxonomic groups (genera *Pseudomonas*, *Brevibacterium*, *Rhodopseudomonas*, and *Lactococcus*)	Ariskina (2003)
	Maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$)	Thermophilic iron-reducing bacteria	Zhang et al. (1997)
	Magnetite (Fe_3O_4)		Zhang et al. (1998)
Incertae sedis	MnO_x (and FeO_x)	*Metallogenium*	Zavarzin (1961, 1981), Perfil'ev and Gabe (1965, 1969), Klaveness (1999)
Nitrospirae	Amorphous Fe-oxyhydroxide (FeOOH)	*Leptospirillum ferriphilum*	Yoshida et al. (2008)
	Magnetite (Fe_3O_4) or greigite (Fe_3S_4)	*Cand. Magnetobacterium bavaricum*	Spring et al. (1993), Jogler et al. (2010)
		Cand. Magnetobacterium bremense or strain MHB-1	Flies et al. (2005)
Proteobacteria			
Acidithiobacillia	Amorphous Fe-oxyhydroxide (FeOOH)	*Acidithiobacillus ferrooxidans*	Yoshida et al. (2008)
Alphaproteobacteria			
Caulobacterales	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Caulobacter maris*	Vainshtein et al. (2002)
Rhizobiales	MnO_x and FeO_x	Two *Pedomicrobium*-like bacteria	Ghiorse and Hirsch (1979)
	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Rhodopseudomonas* sp., *R. palustris*, *R. rutilis*	Vainshtein et al. (1997, 2002)
Rhodobacterales	Nano-goethite (α-FeOOH)	*Rhodobacter* sp.	Miot et al. (2009b)
Magnetotactic bacteria	Magnetite (Fe_3O_4)	α-PB: *Magnetospirillum gryphiswaldense*, *Magnetococcus*, *Magnetofaba*, *Magnetovibrio*, *Magnetospira*	Blakemore (1975), Frankel et al. (1979, 1983), Lovley et al. (1987), Bazylinski et al. (1993)
	Amorphous ferrihydrite, magnetite (Fe_3O_4)	*Aquaspirillum magnetotacticum* = *Magnetospirillum magnetotacticum*	Frankel et al. (1985)

(continued)

Table 2 (continued)

	Biomineral	Species	References
Also Delta- and Gammaproteobacteria	Magnetite (Fe_3O_4) or greigite (Fe_3S_4)	*δ*-PB: *Cand. Magnetoglobus multicellularis*, *Cand. Magnetomorum littorale*, *Cand. Magnetananas tsingtaoensis*, *Desulfovibrio magneticus* RS-1 γ-PB: strains BW-2, SS-5, GRS-1	**Reviews**: Bazylinski and Frankel (2003), Bazylinski et al. (2007), Faivre and Schüler (2008)
	Magnetite (Fe_3O_4)	Several species, ≥2 genomic undescribed genera	Monteil et al. (2020)
Betaproteobacteria			
Burkholderiales	MnO_x and FeO_x	*Leptothrix* OUMS1	Sawayama et al. (2011)
		Sphaerotilus discophorus	Rouf and Stokes (1964)
	Magnetite (Fe_3O_4)	*Burkholderia* sp.	Pan et al. (2015)
	Ferrihydrite	*Leptothrix ochracea*	Kennedy et al. (2004)
Nitrosomonadales		and *Gallionella ferruginea*	
	Hematite (Fe_2O_3), ferrihydrite, and goethite (α-FeOOH)		Hallberg and Ferris (2004)
	Fe-oxyhydroxide (FeOOH) and ferrihydrite	Stalk-forming Fe-oxidizing bacteria related to *Gallionella*	Chan et al. (2009)
Gammaproteobacteria			
Enterobacterales	Amorphous Fe(III)	*Escherichia coli*	Bauminger et al. (1980)
	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)		Vainshtein et al. (2002)
	Lepidocrocite [γ-FeO(OH)]	*Bacillus subtilis* and *E. coli*	Châtellier et al. (2001)
Pseudomonadales	Ferritin ("Fe(II) oxide-hydroxide-phosphate core")	*Azotobacter vinelandii*	Stiefel and Watt (1979)
	Ferritin (hydrated FeO_x) and amorphous iron phosphate	*Pseudomonas aeruginosa* *Azotobacter vinelandii*	Harrison et al. (1987)
	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Pseudomonas aeruginosa*	Vainshtein et al. (2002)

Alteromonadales	Membrane-bound intracellular Fe granules and extracellular green rust, magnetite (Fe_3O_4), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], goethite (α-FeOOH)	*Shewanella putrefaciens*	Glasauer et al. (2002, 2003)
	Carbonate green rust [GR*$(CO_3)^{2-}$], vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], and magnetite (Fe_3O_4)		Kukkadapu et al. (2004), O'Loughlin (2008)
	Siderite ($FeCO_3$), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], magnetite (Fe_3O_4), green rust*		Fredrickson et al. (1998)
	Magnetite (Fe_3O_4), ferrous hydroxy carbonate (FHC), carbonate and ferric green rust*		O'Loughlin et al. (2013)
	Magnetite (Fe_3O_4), akaganeite (β-FeOOH), and siderite ($FeCO_3$)	*Shewanella algae*, *Shewanella pealeana*	Roh et al. (2003)
Chromatiales	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Ectothiorhodospira shaposhnikovii*	Vainshtein et al. (1997, 2002)
Deltaproteobacteria			
	Greigite (Fe_3S_4), magnetite (Fe_3O_4)	Unknown group	Lefèvre et al. (2011)
Desulfovibrionales (SRB)	Carbonate green rust [GR*$(CO_3)^{2-}$], vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], and greigite (Fe_3S_4)	*Desulfovibrio alaskensis*	Zegeye et al. (2007)
	Magnetite (Fe_3O_4)	*Desulfovibrio magneticus*	Pósfai et al. (2006)
Desulfuromonadales	Magnetite (Fe_3O_4) and lepidocrocite [γ-FeO(OH)]	*Geobacter metallireducens*	Vali et al. (2004)
Terrabacteria			
Actinobacteria	Maghemite (γ-Fe_2O_3), and greigite (Fe_3S_4)	*Actinobacter* sp.	Bharde et al. (2008)
	Magnetite (Fe_3O_4)		Bharde et al. (2005)

(continued)

Table 2 (continued)

	Biomineral	Species	References
Firmicutes			
Bacilli	Lepidocrocite [γ-FeO(OH)]	*Bacillus subtilis* and *Escherichia coli*	Châtellier et al. (2001)
	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Bacillus cereus*, *B. thuringiensis*, *Lactobacillus plantarum*, *Lactococcus lactis*, *Staphylococcus* sp.	Vainshtein et al. (2002)
Clostridia	Magnetite (Fe_3O_4), akaganeite (β-FeOOH), and siderite ($FeCO_3$)	*Thermoanaerobacter ethanolicus*	Roh et al. (2003)
EUKARYA			
Euryarchaeota			
Stenosarchaea			
Halobacteria	"Amorphous or noncrystalline magnet-sensitive inclusions" (Fe-rich)	*Haloarcula vallismortis*, *Halococcus* sp., *H. morrhuae*, *H. salifodinae*, *Haloferax mediterranei*, *H. volcanii*, *Halorubrum sodomense*	Vainshtein et al. (2002)
EUKARYA			
Cryptophyceae	Magnetite (Fe_3O_4)	2 unspecified species	Bazylinski et al. (2000)
Discoba			
Euglenozoa			
Euglenida	Magnetite (Fe_3O_4)	*Anisonema*	de Araujo et al. (1986)
SAR			
Alveolata			
Ciliophora	Magnetite (Fe_3O_4)	*Cyclidium* sp.	Bazylinski et al. (2000)
Dinophyceae	Magnetite (Fe_3O_4)	1 unspecified species	Bazylinski et al. (2000)
Stramenopiles			
Ochrophyta			
Chrysophyceae	FeO_x and MnO_x	Several species, e.g., *Anthophysa vegetans*, *Siderodendron manganiferum*, *Siphomonas fritschii*, and *Bikosoeca petiolata*	Pringsheim (1946)
Fungi			

Dikarya			
Basidiomycota			
Agaricomycotina			
Tremellomycetes	Magnetite (Fe_3O_4)	*Cryptococcus humicola*	Vainshtein et al. (2014)
Ascomycota			
Saccharomyceta			
Saccharomycotina			
Saccharomycetes			
Saccharomycetales	Magnetite (Fe_3O_4)	*Saccharomyces cerevisiae*	Vainshtein et al. (2014)
Pezizomycotina			
Ieotiomyceta			
Lecanoromycetes	Amorphous FeO_x	*Stereocaulon vulcani*	Jackson and Keller (1970)
	Goethite (α-FeOOH)	*Rhizocarpon geographicum* and 4 lichen species	Ascaso et al. (1976), Galván et al. (1981)
Fungi incertae sedis			
Mucoromycota			
Mucoromycotina	Ferritin (hydrated FeO_x)	*Phycomyces (blakesleeanus)*	Peat and Banbury (1968), David and Easterbrook (1971)
Viridiplantae			
Chlorophyta			
Core chlorophytes			
Chlorophyceae			
Chlamydomonadales	Magnetic mineral, most likely magnetite (Fe_3O_4) or pyrrhotite (Fe_7S_8)	*Chlamydomonas pleichloris "magnetotactica"*	de Barros et al. (1981)

* GR = green rust = $[Fe_{(6-x)}^{II}Fe_x^{III}(OH)_{12}]^{x+}\ [(A^{2-})_{x/2}{\cdot}yH_2O]^{x-}$

Komeili et al. 2004). The genes responsible for the biomineralization of magnetosomes are organized as clusters (Grünberg et al. 2001).

MTB are typically found within the *Alphaproteobacteria*, but have also been affiliated to *Delta-* and *Gammaproteobacteria*, as well as *Nitrospira*. MTB occur ubiquitously in diverse aquatic and sedimentary environments and are believed to contribute significantly to the biogeochemical cycling of iron with contributions reaching up to 10% (Faivre and Schüler 2008).

Many nonmagnetic oxyhydroxides, such as ferrihydrite and goethite, are sequestered by bacteria (cf. Table 2). Amorphous iron hydroxides and ferrihydrite are also considered precursor phases for magnetite formation.

Amorphous intracellular iron-rich inclusions of unclear function (Vainshtein et al. 1998) have been found in nonmagnetotactic *Gammaproteobacteria* (Glasauer et al. 2002; Vainshtein et al. 2002) and magnet-sensitive *Alphaproteobacteria* (Vainshtein et al. 1997).

Despite the fact that **manganese oxides (MnO_x)** are omnipresent, when compared to iron oxide biominerals, manganese biomineralization is way less studied. Manganese oxides occur in almost every terrestrial and marine environment, but they are also important adsorbents, battery materials, and catalysts in industry (Tebo et al. 2004). Manganese oxides are very porous minerals constructed from MnO_6 octahedra that show a high degree of structural variability. Due to their large surface areas, they belong to the most reactive minerals in natural systems. Commonly observed biogenic MnO_x mineral structures (see **Table 3**) are either layered [birnessite or vernadite (δ-MnO_2)] or tunnellike (todorokite) (Post 1999). Vernadite is considered a birnessite which is disordered along the layer stacking. It has to be mentioned that in a lot of cases, the exact structure of microbial MnO_x has not been determined.

A variety of microorganisms, mainly bacteria and fungi, are able to oxidize Mn (II) to the less soluble Mn(IV) through Mn(III) in aerobic environments (Tebo et al. 2004). The formation of Mn(III)/Mn(IV) in solution is a kinetically slow reaction (Morgan 2005), while the biological process is several orders of magnitude faster (Hastings and Emerson 1986; Bargar et al. 2005; Tebo et al. 2019). MnO_x readily precipitates onto microbial extracellular structures, such as EPS, and is commonly observed in association with biofilms and microbial mats. For this reason, natural manganese oxides in aquatic and soil environments are thought to be a result of microbially mediated oxidation (Nealson et al. 1988).

In most cases, **bacteriogenic MnO_x** closely resemble layered structured vernadite or birnessite (Villalobos et al. 2003; Jürgensen et al. 2004; Bargar et al. 2005; Webb et al. 2005; Saratovsky et al. 2006). Recent studies have revealed that bacterially mediated MnOx phases can also have todorokite structure (Kim et al. 2003; Kim and Stair 2004; Feng et al. 2010). Species of the freshwater bacterium *Leptothrix* seem to be able to produce both birnessite (Jürgensen et al. 2004; Saratovsky et al. 2006) and todorokite (Kim et al. 2003; Kim and Stair 2004).

Many **Ascomycete fungi** and some soil lichen (Pentecost et al. 2010) possess the capacity to oxidize Mn(II) and deposit MnO_x. The structure and function of these deposits as well as their role in environmental Mn cycling is currently not known.

Table 3 Manganese oxides in microorganisms

	Biomineral	Species	References
BACTERIA			
Incertae sedis	MnO_x (and FeO_x)	*Metallogenium*	Zavarzin (1961, 1981), Perfil'ev and Gabe (1965, 1969), Klaveness (1999)
	MnO_x	Chemoorganotrophic bacteria	Grote and Krumbein (1992)
Proteobacteria			
Alphaproteobacteria			
Rhizobiales	MnO_x and FeO_x	2 *Pedomicrobium*-like bacteria	Ghiorse and Hirsch (1979)
Betaproteobacteria			
Burkholderiales	MnO_x	*Leptothrix echinata*	Beger (1935)
		Leptothrix discophora	Ghiorse and Chapnick (1983), Adams and Ghiorse (1986), Boogerd and de Vrind (1987), Emerson and Ghiorse (1992), Nelson et al. (1999, 2002), Robbins and Corley (2005)
	Nanocrystalline, todorokite-like MnO_x		Kim et al. (2003), Kim and Stair (2004)
	Single-layer microcrystals of Na-birnessite-like MnO_x		Jürgensen et al. (2004)
	Mixed-valent, layered MnO_x with the chemical formula $M^{n+}{}_yMn^{3+}{}_{0.12}[\square_{0.12}Mn^{4+}{}_{0.88}]O_2{\cdot}zH_2O$ similar to hexagonal birnessites, Zn-chalcophanite, and $Ca_2Mn_3O_8$		Saratovsky et al. (2006)
	MnO_x and FeO_x	*Leptothrix* OUMS1	Sawayama et al. (2011)
		Sphaerotilus discophorus	Rouf and Stokes (1964)
Gammaproteobacteria			
Methylococcales	MnO_x	*Clonothrix*	Perfil'ev and Gabe (1965)
Oceanospirillales	MnO_x	*Oceanospirillum*	Ennever and Summers (1975)

(continued)

Table 3 (continued)

	Biomineral	Species	References
Pseudomonadales	Todorokite $[(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12}\cdot(3\text{-}4)H_2O]$	*Pseudomonas putida*	Feng et al. (2010)
	Vernadite (δ-MnO_2) and poorly crystalline hexagonal birnessite		Villalobos et al. (2003)
	MnO_x	*2 Pseudomonas species*	Zavarzin (1962)
Terrabacteria			
Actinobacteria			
Micrococcales	MnO_x	*Siderocapsa* = *Arthrobacter*	Ehrlich (1966)
Firmicutes			
Bacilli	MnO_x	*Bacillus*	Ehrlich (1966), Nealson and Ford (1980), Rosson and Nealson (1982)
	Layered phyllomanganate and amorphous MnO_x similar to vernadite (δ-MnO_2)	*Bacillus*	Bargar et al. (2005), Webb et al. (2005)
Cyanobacteria/Melainabacteria			
Cyanobacteria			
Nostocales	MnO_x	*Anabaena*	Richardson et al. (1988), Richardson and Stolzenbach (1995)
Oscillatariophycideae	MnO_x	*Microcystis*	Richardson et al. (1988)
FCB group			
Bacteroidetes/Chlorobi group			
Bacteroidetes	MnO_x	*Flavobacterium*	Nealson (1978)
Chlorobi	MnO_x, $CaMnO_3$	*Chlorobium*, *Paludibacter*, *Acholeplasma*, *Geobacter*, *Desulfomicrobium*, *Clostridium*, *Acetobacterium*, and several other bacteria	Daye et al. (2019)

EUKARYA			
Amoebozoa			
Tubulinea	"Amorphous manganese compounds"	*Centropyxis*	Hedley et al. (1976)
SAR			
Stramenopiles			
Ochrophyta			
Chrysophyceae	FeO_x and MnO_x	Several species, e.g., *Anthophysa vegetans*, *Siderodendron manganiferum*, *Siphomonas fritschii*, and *Bikosoeca petiolata*	Pringsheim (1946)
PX clade			
Xanthophyceae	MnO_x	*Vaucheria*	Richardson and Stolzenbach (1995)
Fungi			
Dikarya			
Ascomycota			
Ascomycota incertae sedis	MnO_x, todorokite-like	*Acremonium*	Tani et al. (2004), Miyata et al. (2006), Saratovsky et al. (2009)
	MnO_x	Isolates of the phylum *Deuteromycota*, class *Agonomycetes*	Thompson et al. (2005)
		>10 fungal isolates	Schweisfurth (1971)
Saccharomyceta			
Pezizomycotina			
Ieotiomyceta	MnO_x	*Cladosporium cladosporioides*, *Alternaria alternata*, *Phoma glomerata*, *Penicillium frequentans*, and *P. steckii*	de la Torre and Gomez-Alarcon (1994)
Lecanoromycetes	MnO_x	*Catillaria chalybeia*	Pentecost et al. (2010)
Sordariomyceta	MnO_x	*"Monilicean fungus"= Monilia*	Robbins and Corley (2005)

(continued)

Table 3 (continued)

	Biomineral	Species	References
	MnO_x	*Plectosphaerella cucumerina* and *Acremonium strictum*	Santelli et al. (2011)
Dothideomyceta	MnO_x	*Pyrenochaeta* sp. and *Stagonospora* sp.	
	MnO_x	*Cladosporium sphaerospermum*, *Coniothyrium* sp., *Alternaria tenuis*	Grote and Krumbein (1992)
Eurotiomycetes		*Penicillium brevicompactum*, *P.* cf. *tenuissimum*, *P.* cf. *waksmannii*	
Basidiomycota	MnO_x	Non-specified " arthroconidial anamorph of a basidiomycete"	Emerson et al. (1989)
Viridiplantae			
Chlorophyta			
Core chlorophytes			
Trebouxiophyceae			
Chlorellales	MnO_x	*Chlorella* sp.	Richardson et al. (1988)
Chlorophyceae			
Chlamydomonadales	MnO_x	*Chlamydomonas*	Schulz-Baldes and Lewin (1975)
Sphaeropleales			
Scenedesmaceae	MnO_x	*Scenedesmus subspicatus*	Knauer et al. (1999)
		Scenedesmus	Richardson and Stolzenbach (1995)
Ulvophyceae			
OUU clade			
Ulotrichales	MnO_x	*Ulothrix* sp.	Robbins and Corley (2005)

Extracellular MnO_x precipitation has also been reported for different **algae**. Richardson et al. demonstrated that dense populations of large (>20 μm) photosynthesizing algae generate alkaline microenvironments that induce manganese oxidation (Richardson et al. 1988; Richardson and Stolzenbach 1995). Extracellular MnO_x covers the holdfasts of the green algae *Ulothrix* sp. (Robbins and Corley 2005) and is precipitated by the unicellular algae *Scenedesmus* but also stored intracellularly as Mn^{2+} (Knauer et al. 1999). The significance of phytoplankton on the manganese cycle, especially in freshwater, may be bigger than believed and should be further explored.

Manganese oxides have a large impact on the distribution and availability of other heavy metal cations in natural environments (Post 1999). Due to their porous structure, other divalent metal cations (e.g., Co, Ni, Cu, Pb, and Cd) can be efficiently adsorbed (O'Reilly and Hochella 2003)—an observation with obvious applications in the removal of Mn and other trace metals from contaminated water (Nelson et al. 1999, 2002; Tani et al. 2004; Hallberg and Johnson 2005). Manganese and iron oxides are powerful oxidants that participate in redox reactions of inorganic and organic compounds (Huang and Zhang 2020). Furthermore, mineralization of MnOx can lead to co-dissolution (Crowe et al. 2007) and/or coprecipitation of other elements. Overall, in a biogeochemical context, microbial manganese oxidation (Table 3) is highly significant (Tebo et al. 2004).

4 Phosphates

Microorganisms are key players in phosphorus cycling in nature. Using extracellular enzymes or the secretion of acids, microorganisms convert organic and inorganic phosphorous compounds into soluble and available forms (Tiessen 2008; Barea and Richardson 2015). Microorganisms take up phosphate (Pi) via specific transport systems (Torriani-Gorini et al. 1994) and have adapted to grow at both high and low Pi concentrations. By regulation of the Pi uptake and accumulation of phosphorus reserves, intracellular Pi levels in microorganisms are independent of extracellular concentration and remain rather constant. Phosphorus reserves in microorganisms occur typically in the form of inorganic polyphosphates (polyP) (Kulaev and Vagabov 1983; Kornberg et al. 1999; Kulaev and Kulakovskaya 2000; Kulaev et al. 2005; Schröder and Müller 2012), polymeric orthophosphates, or pyrophosphates (Torriani-Gorini et al. 1994). As part of their phosphorus metabolism, some microorganisms form **insoluble phosphate minerals** (**Table 4**) (Omelon et al. 2013). Their role in the formation of natural phosphate deposits (geological phosphorites) has been recognized since the early twentieth century (Blackwelder 1916; Cayeux 1936).

Understanding the mechanisms involved in the biogenic precipitation of calcium phosphates is particularly relevant to the search for traces of life (Mojzsis et al. 1996; Mojzsis and Arrhenius 1998; Blake et al. 2001) and in medical sciences, where pathological calcium phosphates are responsible for diseases, such as

Table 4 Phosphates in microorganisms

	Biomineral	Species	References
BACTERIA	$KNa_3(Fe_{1,5}Mg_{2,5})(PO_4)_3(OH)_3$	Unspecified SRB (bacteria and archaea)	Hallberg and Wadsten (1980)
	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	Nanobacteria	Kajander and Ciftçioglu (1998)
Proteobacteria			
Alphaproteobacteria			
Rhizobiales	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Brucella abortus* and *B. melitensis*	Huddleson and Winter (1927)
Betaproteobacteria			
Burkholderiales	Amorphous iron phosphate	*Acidovorax* sp.	Miot et al. (2009a)
	Pyromorphite [$Pb_5(PO_4)_3(OH)$]	*Burkholderia cepacia*	Templeton et al. (2003)
	Nanocrystalline hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	*Ramlibacter tataouinensis*	Benzerara et al. (2004)
Gammaproteobacteria			
Pseudomonadales	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*"Bacterium putidum fluorescens"* = *Pseudomonas fluorescens/putida*	Robinson (1889)
		Pseudomonas calciprecipitans	Shinano and Sakai (1975)
	Chlorapatite [$Ca_5(PO_4)_3Cl$]	*Acinetobacter* sp.	Li et al. (2019)
Pseudomonadales/ Enterobacterales	Carbonate-rich fluorapatite [francolite, $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$]	"Gram-negative aerobic pseudomonads or facultatively anaerobic enterobacteria"	O'Brien et al. (1981)
	Struvite ($NH_4MgPO_4{\cdot}6H_2O$) and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Acinetobacter* sp., *Pseudomonas* sp.	Rivadeneyra et al. (1983, 1985)
Enterobacterales	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Proteus mirabilis*	Griffith (1978), McLean et al. (1988), Lerner et al. (1989), Sun et al. (2012)
	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	*Providencia rettgeri and Escherichia coli*	Hirschler et al. (1990a, b)
	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$] and ACP	*Escherichia coli*	Cosmidis et al. (2015)

Alteromonadales	Membrane-bound intracellular Fe granules and extracellular green rust, magnetite (Fe_3O_4), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], goethite (α-FeOOH)	*Shewanella putrefaciens*	Glasauer et al. (2002, 2003)
	Magnetite (Fe_3O_4), carbonate green rust ($[Fe_{(6-x)}^{II}Fe_x^{III}(OH)_{12}]^{x+}(CO_3^{2-})_{0.5x}{\cdot}yH_2O$), and vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]		Kukkadapu et al. (2004)
	Siderite ($FeCO_3$), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], magnetite (Fe_3O_4), green rust*		Fredrickson et al. (1998)
	Vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] and siderite ($FeCO_3$)		Zachara et al. (1998)
Deltaproteobacteria			
Desulfobacterales	Fe-P-rich granules (similar to vivianite)	*Desulfosarcina/Desulfococcus*	Milucka et al. (2012)
Desulfovibrionales	Greigite (Fe_3S_4), pyrite (FeS_2) and intermediates (FeS), sphalerite (ZnS), elemental sulfur, gypsum ($CaSO_4{\cdot}2H_2O$), struvite ($NH_4MgPO_4{\cdot}6H_2O$), magnesite ($MgCO_3$)	*Desulfovibrio desulfuricans*	Hallberg (1972)
	Mackinawite (FeS), vivianite/metavivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]		Ivarson and Hallberg (1976)
	Mackinawite (FeS, tetragonal), pyrite (FeS_2), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], and greigite (Fe_3S_4)		Duverger et al. (2020)
	Hydroxysulfate green rust [$GR_2(SO_4^{2-})$] and vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]	*Desulfovibrio alaskensis*	Zegeye et al. (2007)
	Vivianite ($Fe_3(PO_4)_2.8H_2O$), greigite (Fe_3S_4), pyrite (FeS_2)	*Desulfovibrio* and *Sulfurospirillum*	Berg et al. (2020)
	Mackinawite (FeS), greigite (Fe_3S_4), and vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]	*Desulfovibrio vulgaris*	Zhou et al. (2014)

(continued)

Table 4 (continued)

	Biomineral	Species	References
Myxococcales	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Myxococcus xanthus*	Omar et al. (1994), Da Silva et al. (2000)
	Newberyite [$Mg(PO_3OH){\cdot}3H_2O$], schertelite [$(NH_4)_2MgH_2(PO_4)_2{\cdot}4H_2O$], and taylorite ($K_2SO_4$) in conjunction with struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Myxococcus coralloides*	González-Muñoz et al. (1994)
Terrabacteria			
Actinobacteria			
Micrococcales			
Brevibacteriaceae	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Brevibacterium antiquum*	Smirnov et al. (2005)
Micrococcaceae	Struvite ($NH_4MgPO_4{\cdot}6H_2O$) and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Brevibacterium* sp. *Arthrobacter* sp.	Rivadeneyra et al. (1983, 1985)
Propionibacteriales	Vivianite ($Fe_3(PO_4)_2.8H_2O$) [and siderite ($FeCO_3$)]	*Tessaracoccus lapidicaptus*	Sánchez-Román et al. (2014, 2015)
Streptomycetales	Ni-struvite ($NiNH_4PO_4{\cdot}6H_2O$)	*Streptomyces acidiscabies*	Haferburg et al. (2008)
Corynebacteriales	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	*Bacterionema matruchotii* = *Corynebacterium matruchotii*	Takazoe and Nakamura (1965), Ennever et al. (1971, 1973), Moorer et al. (1993)
	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$] and intracellular Ca-PL-P complexes		Boyan et al. (1984)
	Struvite ($NH_4MgPO_4{\cdot}6H_2O$) and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Corynebacterium* sp.	Rivadeneyra et al. (1983, 1985)
FCB group			
Firmicutes Bacilli		*Bacillus* sp. *Kurthia* sp. *Listeria* sp.	
	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Staphylococcus aureus*	Beavon and Heatley (1963)
		Bacillus pumilus	Nelson et al. (1991)

	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	*Streptococcus mutans*, *S. sanguis*, *and S. sobrinus*	Streckfuss et al. (1974), Moorer et al. (1993)
Clostridia	Vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]	*Alkaliphilus metalliredigens*	Roh et al. (2007)
Tenericutes	Struvite ($NH_4MgPO_4{\cdot}6H_2O$)	*Ureaplasma urealyticum*	Grenabo et al. (1984)
Bacteroidetes/Chlorobi			
Bacteroidetes	Struvite ($NH_4MgPO_4{\cdot}6H_2O$) and monohydrocalcite ($CaCO_3{\cdot}H_2O$)	*Flavobacterium* sp.	Rivadeneyra et al. (1983, 1985)
ARCHAEA			
TACK group			
Crenarchaeota			
Thermoprotei			
Sulfolobales	AFP and lipscombite [$Fe^{II}_xFe^{III}_{3-x}(PO_4)_2(OH)_{3-x}$]	*Sulfolobus acidocaldarius*	Miot et al. (2017)
	Fe- and P-rich globules, goethite (α-FeOOH), and AFP		Kish et al. (2016)
Euryarchaeota			
Stenosarchaea			
Halobacteria	$Mg_2(OH)PO_4{\cdot}4H_2O$	*Halorubrum distributum* and *Halobacterium salinarum*	Smirnov et al. (2005)
EUKARYA			
SAR			
Alveolata			
Ciliophora	Dahllite [carbonate-rich hydroxyapatite, $Ca_5(PO_4)_3(OH)$]	*Spirostomum ambiguum*	Pautard (1970)
	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]		Pautard (1958, 1959), Jones (1967)
	Calcian struvite [$(Mg,Ca)NH_4PO_4 \cdot 6H_2O$] guanine (Creutz et al. 2002)	*Paramecium tetraurelia*	Grover et al. (1997)

(continued)

Table 4 (continued)

	Biomineral	Species	References
Amoebozoa			
Tubulinea			
Elardia	ACP	*Cryptodifflugia oviformis*	Ogden and Hedley (1980)
Opisthokonta			
Metazoa			
Eumetazoa			
Bilateria			
Protosomia			
Ecdysozoa			
Nematoda	Hydroxypyromorphite [$Pb_5(PO_4)_3(OH)$]	*Caenorhabditis elegans*	Jackson et al. (2005)
Fungi			
Dikarya			
Ascomycota			
Saccharomyceta			
Saccharomycotina	Hydroxyapatite [$Ca_5(PO_4)_3(OH)$] and ACP	*Candida albicans*	Ennever and Summers (1975)
Pezizomycotina			
Ieotiomyceta			
Eurotiomycetes	**Uranyl phosphate species**, potassium uranyl phosphate hydrate ($KPUO_6 \cdot 3H_2O$), meta-ankoleite [$(K_{1.7}Ba_{0.2})(UO_2)_2(PO_4)_2 \cdot 6H_2O$], uranyl phosphate hydrate [$(UO_2)_3(PO_4)_2 \cdot 4H_2O$], meta-ankoleite [$K(UO_2)(PO_4) \cdot 3H_2O$], uramphite [$NH_4UO_2PO_4 \cdot 3H_2O$], and chernikovite [$(H_3O)_2(UO_2)_2(PO_4)_2 \cdot 6H_2O$]	*Aspergillus niger* and *Paecilomyces javanicus*	Liang et al. (2015)
Sordariomyceta	Chloropyromorphite [$Pb_5(PO_4)_3Cl$]	*Paecilomyces javanicus* and *Metarhizium anisopliae*	Rhee et al. (2012)

atherosclerosis, calcification of artificial heart valves, or the formation of urinary stones and dental calculus (Dorozhkin and Epple 2002).

In biological systems, calcium phosphates occur mainly in the form of nonstoichiometric sodium-, magnesium-, and carbonate-containing **hydroxyapatite [$Ca_5(PO_4)_3(OH)$]** (often called "biological apatite" or dahllite).

Recently, the formation of oceanic phosphorites has been recognized as occurring in close association with polyphosphate-accumulating bacteria (Omelon et al., 2013). In modern, actively forming phosphorite formations, marine bacteria such as *Pseudomonas* and *Acinetobacter* (Nathan et al. 1993) and the sulfide-oxidizing bacteria *Beggiatoa* (Brüchert et al. 2003; Goldhammer et al. 2010) and *Thiomargarita namibiensis* (Schulz et al. 1999; Schulz and Schulz 2005) have been identified. These bacteria accumulate phosphate as polyP in oxic conditions and release Pi under anoxic conditions, thus creating supersaturation with regard to apatite (Goldhammer et al. 2010; Brock and Schulz-Vogt 2011). Furthermore, it was suggested that polyphosphate granules from abundant diatoms act as mineral templates and contribute to the formation of calcium phosphate minerals in marine sediments (Diaz et al. 2008).

Similarly, many types of oral bacteria are known to contribute to the formation of dental calculus, although their specific role is not clear. Ennever et al. observed apatite mineralization caused by the actions of the dental bacteria *Bacterionema matruchotii* (Takazoe and Nakamura 1965; Ennever et al. 1971, 1973; Boyan et al. 1984). Interestingly, Takazoe and Nakamura noted intracellular polyP granules, which inhibit dental calculus mineralization (Takazoe and Nakamura 1965). Omelon et al. drew a parallel between phosphorite and calculus nucleation, proposing a similar pathway, bacterial Pi release from intracellular polyP storage, for both marine and oral bacteria (Omelon et al. 2013).

Apatite sequestration is mostly considered a biologically induced mineralization. Benzerara et al. demonstrated that the betaproteobacterium *Ramlibacter tataouinensis* crystallizes nanocrystalline hydroxyapatites with their *c* axes oriented perpendicular to the cell surface. This observation suggests one of the few examples of biologically controlled mineralization that results in well-orientated phosphates in bacteria (Benzerara et al. 2004).

Bacterial precipitation of **struvite ($NH_4MgPO_4{\cdot}6H_2O$)** was first described by Robinson in 1889 (Robinson 1889). According to Robinson, struvite was formed as a consequence of the combination of metabolically produced NH^{4+} ions with the magnesium and phosphate ions present in the medium, which could explain the presence of struvite in natural environments.

Since then, the production of struvite by bacteria has been widely documented for a variety of *Proteobacteria* (Robinson 1889; Huddleson and Winter 1927; Hallberg 1972; Shinano and Sakai 1975; Griffith 1978; Rivadeneyra et al. 1983, 1985; McLean et al. 1988; Lerner et al. 1989; Omar et al. 1994; González-Muñoz et al. 1994; Da Silva et al. 2000; Sun et al. 2012) and *Terrabacteria* (Beavon and Heatley 1963; Rivadeneyra et al. 1983, 1985; Grenabo et al. 1984; Nelson et al. 1991; Smirnov et al. 2005).

Struvite is also found in approximately every fifth **kidney stone** (Griffith 1978). To date, the production of this pathological biomineral in kidney stones has been attributed to bacterial action. Bacteria such as *Proteus*, *Pseudomonas*, *Klebsiella*, and *Staphylococcus* are commonly observed in the context of urinary infections. In experimental studies, struvite crystals were shown to form in vitro in the presence *Proteus mirabilis*, a Gammaproteobacterium commonly found in urinary stones of patients suffering from urolithiasis (Griffith 1978; McLean et al. 1988; Lerner et al. 1989; Sun et al. 2012). In this pathological biomineralization process, urea-splitting bacteria such as *Proteus* and some *Staphylococci* convert urea to ammonia, which leads to an increase of pH and the precipitation of struvite.

The production of struvite and other magnesium phosphates by **myxobacteria** is of special interest (Omar et al. 1994; González-Muñoz et al. 1994; Da Silva et al. 2000). Myxobacteria are interesting and common prokaryotic organisms of high ecological importance. These bacteria inhabit various types of soil and play an active role in the degradation of organic materials (Shimkets et al. 2006). According to the experimental studies, they contribute significantly to the formation of struvite in nature. Under certain conditions, magnesium can be replaced by nickel forming the biomineral "nickel struvite" ($NiNH_4PO_4{\cdot}6H_2O$) which has been identified in the nickel-resistant *Actinobacterium Streptomyces acidiscabies* (Haferburg et al. 2008).

Another insoluble magnesium phosphate, $Mg_2(OH)PO_4{\cdot}4H_2O$, was shown to be produced by the halophilic archaeon *Halobacterium salinarum*. It is currently the only repot of this unusual form of phosphorus reserve (Smirnov et al. 2005).

Vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] is commonly observed in reductive environments and occurs in anoxic freshwater sediments where it is often associated with organic matter (Rothe et al. 2016). Under these conditions, with a sufficiently high ortho-phosphate and Fe^{2+} concentration and in the absence of S^{2-} ions, vivianite is stable (Nriagu 1972). Iron (III) oxides are considered an important precursor phase for vivianite formation. The formation of vivianite has been linked to **dissimilatory iron-reducing bacteria** such as *Shewanella putrefaciens* in culture experiments (Fredrickson et al. 1998; Zachara et al. 1998; Glasauer et al. 2002, 2003; Kukkadapu et al. 2004). In dissimilatory iron-reducing bacteria, the oxidation of organic matter is coupled to the reduction of iron oxides (Fredrickson et al. 1998; Zachara et al. 1998; Glasauer et al. 2003; O'Loughlin et al. 2013). The nature of the minerals formed from the reduction of synthetic and natural iron oxides depends on the ions present in culture medium. If enough HCO^{3-} and $HPO_4{}^{2-}$ ions are available, first vivianite and then siderite are formed (Zachara et al. 1998). In the absence of counterions, magnetite or "green rust" is formed as a product of a solid-state conversion (Fredrickson et al. 1998). Green rust is a layered iron hydroxide that acts as a reactive intermediate and slowly converts into vivianite in the presence of phosphate (Hansen and Poulsen 1999).

Extracellular vivianite and siderite nanoglobules have been shown to form on the cell surface of the *Actinobacterium Tessaracoccus lapidicaptus* isolated from sediments in Rio Tinto, Spain. The Fe-rich carbonates and phosphates are found

within the bacterial EPS matrix, which provides nucleation sites for crystal growth. The works of Sánchez-Román link microbial P, C, and Fe cycles and could explain the formation of vivianite and siderite in natural environments (Sánchez-Román et al. 2014, 2015).

There are also indications for **intracellular Fe- and P-rich granules** in microorganisms involved in the anaerobic oxidation of methane coupled to sulfate reduction (AOM). A consortium of methanotrophic archaea and sulfate-reducing *Deltaproteobacteria* mediates this process. Milucka et al. presented evidence for intracellular precipitates rich in iron and phosphorus in the involved *Deltaproteobacteria* species *Desulfosarcina* and *Desulfococcus* (Milucka et al. 2012).

In the hyperthermophilic archaeon *Sulfolobus acidocaldarius*, a passive process of iron phosphate nucleation has been described (Kish et al. 2016). Iron phosphate compounds [Fe- and P-rich globules, goethite (α-FeOOH), and AFP] have been shown to grow within the cell envelope's S-layer independently of metabolic activity. In an artificial maturation experiment, these iron phosphates transformed into **lipscombite** [$Fe^{II}{}_{x}Fe^{III}{}_{3-x}(PO_4)_2(OH)_{3-x}$] under hydrothermal conditions (Miot et al. 2017). With their shape depending on the initial mineral/organics ratio, lipscombite minerals are suggested as proxies for the presence of biogenic matter in iron deposits.

Some microorganisms detoxify Pb through pyromorphite precipitation. Micro X-ray diffraction on intracellular Pb hotspots inside the nematode *Caenorhabditis elegans* showed that crystalline **hydroxypyromorphite [$Pb_5(PO_4)_3(OH)$]** can be formed internally by an organism (Jackson et al. 2005). Nematodes are indigenous soil organisms, and given their high density in soil, biogenic pyromorphite formation may be relevant to Pb cycling in soils.

Rhee et al. observed the formation of **chloropyromorphite [$Pb_5(PO_4)_3(Cl)$]**, the most stable lead mineral that exists, under the influence of the fungal strains *Paecilomyces javanicus* and *Metarhizium anisopliae* (Rhee et al. 2012). The mycogenic chloropyromorphite formation from metallic lead probably demonstrates a microbial survival strategy in lead-contaminated environments.

In a similar manner, fungi have also been shown to precipitate a variety of different **uranium-containing phosphate biominerals** when grown with an organic phosphorus source (Liang et al. 2015). The uranium minerals were located extracellularly, in association with the fungal hyphal matrix. Sequestration of uranium and lead phosphate minerals by fungi demonstrates their role in U, Pb, and P biogeochemistry and their potential application in element recovery or bioremediation.

5 Sulfur-Containing (Sulfates, Sulfides, and Elemental Sulfur)

Sulfates [Gypsum ($CaSO_4{\cdot}2H_2O$), Jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$], Barite ($BaSO_4$), and Celestite ($SrSO_4$)]

Compared to carbonate and silicate, phosphate, or oxide biominerals, detailed information about **sulfate biominerals (Table 5)** is limited (Bosselmann and Epple 2008) on macroscopic observations. Biological formation pathways and molecular control await further elucidation.

Biogenic sulfate crystals were already described by Fischer in the late nineteenth century, when he identified **calcium sulfate crystals** (gypsum) located at the poles of the desmid algae *Closterium* by dissolution experiments (Fischer 1884). This finding was later confirmed by Ondracek in 1936 (Ondracek 1936) and Kopetzky-Rechtperg in 1949 (Kopetzky-Rechtperg 1949). Almost 100 years after their first description, these crystals were shown to consist of barite ($BaSO_4$) with traces of celestite ($SrSO_4$) by means of EDX spectroscopy (Brook et al. 1980). However, some crystalline vacuolar inclusions in the desmid algae *Bambusina* and *Gonatozygon* have been shown to consist of calcium sulfate (Brook 1981).

Gypsum ($CaSO_4{\cdot}2H_2O$) biominerals have also been found to be associated with the surface of bacterial cells in environmental and cultivated samples [for an extended review, see Van Driessche et al. (2019)].

Microbial gypsum deposits have been identified in several nonmarine environments: Extracellular biomineralization of gypsum, calcite, and magnesite was observed in the bacteria *Synechococcus* growing in natural alkaline lake water (Thompson and Ferris 1990). Gypsum was nucleated close to the bacterial cell envelope, whereas calcite was formed secondarily due to the photosynthetic metabolism of *Synechococcus*. Further research suggested the bacterial S-layer as a mineral nucleation site (Schultze-Lam et al. 1992).

Bacteria of the genus *Arthrobacter* isolated from marine evaporite beds have been shown to mineralize gypsum in polar environments (Cockell et al. 2010). Sulfide-oxidizing bacteria have been suggested to take part in gypsum formation in limestone caves (Galdenzi and Maruoka 2003; Mansor et al. 2018). This is supported by gypsum precipitation and Ca isotopic fractionation experiments in the presence of the sulfur-oxidizing bacterium *Acidithiobacillus thiooxidans* (Harouaka et al. 2016). Ca and S isotopic compositions were evaluated as biosignatures that can be utilized to detect subsurface life.

Jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$] is only formed under strong acidic conditions (pH<4) (Bigham et al. 1996b), even in the presence of microorganisms (Bigham et al. 1996a). Therefore, microbial biomineralization of jarosite has been mainly observed in natural acidic environments, such as mines, drainage waters, or acidic rivers. Bacterial formation of jarosite related to their metabolic activity has been demonstrated in culture experiments and natural environments (Ivarson 1973; Lazaroff et al. 1982; Ziegler et al. 2009).

Table 5 Sulfate biominerals in microorganisms

	Biomineral	Species	References
BACTERIA			
Proteobacteria			
Acidithiobacillia	Tooeleite [$Fe_6(AsO_3)_4SO_4(OH)_4{\cdot}4H_2O$], schwertmannite [$Fe_8O_8(OH)_6SO_4$], and jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$]	*Acidithiobacillus ferrooxidans* =*Thiobacillus ferrooxidans* Review: (Yang et al. 2020)	Morin et al. (2003), Egal et al. (2009)
	Jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$]		Ivarson (1973), Lazaroff et al. (1982), Daoud and Karamanev (2006)
	Gypsum ($CaSO_4{\cdot}2H_2O$)	*Acidithiobacillus thiooxidans*	Harouaka et al. (2016)
Betaproteobacteria			
Ferrovales	Jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$]	*Ferrovum*	Ziegler et al. (2009)
Deltaproteobacteria			
Desulfovibrionales	Greigite (Fe_3S_4), pyrite (FeS_2) and intermediates (FeS), sphalerite (ZnS), elemental Sulfur, gypsum ($CaSO_4{\cdot}2H_2O$), struvite ($NH_4MgPO_4{\cdot}6H_2O$), magnesite ($MgCO_3$)	*Desulfovibrio desulfuricans*	Hallberg (1972)
	Schwertmannite [Fe_8O_8 $(OH)_6SO_4$], jarosite [$KFe^{3+}{}_3$ $(SO_4)_2(OH)_6$], and greigite (Fe_3S_4)	*Non-specified SRB*	Gramp et al. (2009)
Myxococcales	Barite ($BaSO_4$)	*Myxococcus xanthus*	González-Muñoz et al. (2003)
Nitrospirae	Jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$]	*Leptospirillum*	Ziegler et al. (2009)
Terrabacteria			
Actinobacteria			
Micrococcales	Gypsum ($CaSO_4{\cdot}2H_2O$)	2 *Arthrobacter* isolates	Cockell et al. (2010)
Cyanobacteria			
Synechococcales	Gypsum ($CaSO_4{\cdot}2H_2O$), Calcite ($CaCO_3$), and magnesite ($MgCO_3$)	*Synechococcus*	Thompson and Ferris (1990), Schultze-Lam et al. (1992)

(continued)

Table 5 (continued)

	Biomineral	Species	References
Firmicutes			
Clostridia	Jarosite [$KFe^{3+}_3(SO_4)_2(OH)_6$]	*Sulfobacillus thermosulfidooxidans*	Ding et al. (2007)
EUKARYA			
Haptista			
Haptophyta			
Pavlovales	Barite ($BaSO_4$)	*Exanthemachrysis gayraliae* *Pavlova* sp.	Fresnel et al. (1979), Gayral and Fresnel (1979)
SAR			
Alveolata			
Dinophyceae	Celestite ($SrSO_4$) with traces of barite ($BaSO_4$)	*Achradina pulchra*	Gómez et al. (2017)
Ciliophora	Barite ($BaSO_4$)	*Loxodes*	Hubert et al. (1975), Neugebauer and Machemer (1997)
		Loxodes and *Remanella*	Rieder et al. (1982)
Rhizaria			
Retaria			
Foraminifera	Barite ($BaSO_4$)	*Stannophyllum zonarium*	Tendal (1972)
Acantharia		*Aschemonella ramuliformis* *Galatheammina* sp.	Gooday and Nott (1982)
		Psammetta erythrocytomorpha	Schulze and Thierfelder (1905), Schulze (1907)
		Agglutinating Foraminifera, two-chambered (Hyperammina-like)	Bertram and Cowen (1998)
	Celestite ($SrSO_4$)	*Podactinelius sessilis* [uncertain taxonomic affinity (Levine et al. 1980)]	Bütschli (1906)
		Acanthometra pellucidum sp.	Odum (1951)
		Phyllostaurus siculus	Wilcock et al. (1988)

Polycystinea			
Collodaria	Celestite ($SrSO_4$)	*Collosphaera huxleyi*	Müller (1858)
		Sphaerozoum neapolitanum (swarmer cells)	Hollande and Martoja (1974)
		Sphaerozoum punctatum	Anderson (1981), Hughes et al. (1989)
		Collozoum and *Collosphaera*	Anderson et al. (1990)
Fungi			
Dikarya			
Ascomycota			
Saccharomyceta	Jarosite [$KFe^{3+}_3(SO_4)_2(OH)_6$]	*Purpureocillium lilacinum*	Oggerin et al. (2013)
Viridiplantae			
Streptophyta			
Streptophytina			
Charophyceae	Barite ($BaSO_4$)	*Chara fragilis*	Schröter et al. (1975)
	Barite ($BaSO_4$)	*Chara*	Sievers and Schmitz (1982)
Zygnemophyceae			
Zygnematales	Barite ($BaSO_4$)	*Spirogyra*	Kreger (1957), Kreger and Boeré (1969)
Desmidiales			
Desmidiaceae	Barite ($BaSO_4$)	*Micrasterias denticulata*	Meindl (1984), Niedermeier et al. (2018)
	Barite ($BaSO_4$)	*Pleurotaenium* and *Micrasterias*	Brook et al. (1980)
	Barite ($BaSO_4$)	*Micrasterias thomasiana*	Wilcock et al. (1989)
	Gypsum ($CaSO_4 \cdot 2H_2O$)	*Pleurotaenium* and *Tetmemorus*	Fischer (1884), Ondracek (1936), Kopetzky-Rechtperg (1949)
Closteriaceae	Gypsum ($CaSO_4 \cdot 2H_2O$) later identified as. . . (see below)	*Closterium*	

(continued)

Table 5 (continued)

	Biomineral	Species	References
	Barite ($BaSO_4$)	Six *Closterium* species	Brook et al. (1980)
	Barite ($BaSO_4$) [and celestite ($SrSO_4$)]	*Closterium littorale*	
	Barite ($BaSO_4$)	*Closterium lunula*	Wilcock et al. 1989)
	Barite ($BaSO_4$) or celestite ($SrSO_4$)	*Closterium moniliferum*	Brook et al. (1988), Krejci et al. (2011a, b)
Gonatozygaceae	Calcium sulfate ($CaSO_4$)	*Bambusina brebissonii* and *Gonatozygon brebissonii*	Brook (1981)
	Barite ($BaSO_4$)	*Gonatozygon kinahani*	
Peniaceae	Gypsum ($CaSO_4 \cdot 2H_2O$)	*Penium*	Fischer (1884)

The formation of jarosite is enhanced by the metabolic activity of iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* (Ivarson 1973; Lazaroff et al. 1982; Daoud and Karamanev 2006). In acidic mine drainages with high arsenic content, *A. ferrooxidans* was shown to promote the formation of tooeleite, an As(III)-Fe(III) sulfate mineral [$Fe_6(AsO_3)_4SO_4\,(OH)_4\cdot 4H_2O$] (Morin et al. 2003; Egal et al. 2009). This offers new possibilities for the removal of As(III) from high-arsenic acid wastewaters.

Biomineralization of jarosite by a fungal isolate, *Purpureocillium lilacinum*, has been shown in the extreme acidic, highly metal-containing environments of Rio Tinto (Oggerin et al. 2013). Nucleation starts on the fungal cell wall, suggesting that extracellular polymeric substances (EPS) act as biomineral nucleation sites.

Sequestration of iron-containing sulfates is suggested to be a strategy for microbial survival and growth, thereby enabling metal resistance and tolerance.

Barite/Celestite

Biomineralization of **barite and celestite** is of special interest, since these organisms have evolved strategies to selectively accumulate Sr and Ba in the presence of up to five orders of magnitude excess calcium. This level of biological control is highly remarkable, taking into account the chemical similarity of Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} ions. Nevertheless, the biological strategies for ion discrimination, uptake, transport, and accumulation are still an enigma to date. The main challenges for these studies remain the high biomineral solubility and the selective quantification of subcellular ion distributions (Krejci et al. 2011b). Answering these questions could be extremely useful for remediation of ^{90}Sr from the environment and nuclear waste.

Furthermore, barite and celestite biominerals quickly dissolve after cell death, because seawater is undersaturated with respect to Ba/Sr. Hence, although Ba/Sr-sequestering organisms belong to the most abundant plankton members, they are very rarely encountered as fossils. Nevertheless, celestite and barite biomineralizations are creating vertical and horizontal concentration gradients, and thereby strongly affect the oceanic cycling of strontium and barium. Barium and strontium depletion in seawater might affect calcification in many marine organisms and restrain the use of Sr/Ca or Ba/Ca ratios as proxies for paleoenvironmental reconstructions (Decelle et al. 2013).

Barite ($BaSO_4$) biominerals are commonly found in desmid and stonewort green algae.

Desmids are unicellular, ubiquitous freshwater green algae that can be easily cultivated and are therefore considered a model system to study Sr/Ba biomineralization. Most intracellular crystalline deposits in desmids are already visible using a light microscope (Brook et al. 1980, 1988; Meindl 1984; Wilcock et al. 1989). $BaSO_4$ crystals are either located in small terminal vacuoles at the tips of the cells, as in *Closterium moniliferum* (Wilcock et al. 1989), or distributed randomly in the cytosol, as in *Micrasterias denticulata* (Meindl 1984).

Barite and celestite have high densities, much higher than the densities of cell constituents or other common biominerals. This is why the specific gravities of barite and celestite facilitate gravitaxis. Surprisingly, in desmids, the $BaSO_4$ crystals appear not to be involved in a gravity-sensing mechanism, and their function remains unclear. But in a variety of other organisms, barite crystals are supposed to have a function in graviperception as so-called statoliths.

In the rhizoids (a kind of roots used for mechanical stabilization) of green algae of the order **Charales** (or "stoneworts") barite accumulations consisting of 7 nm-sized barite spheres were identified (Schröter et al. 1975; Sievers and Schmitz 1982). These particles seem to act as statolith in graviperception, guiding motion of the algae and growth of the rhizoids (Braun 2002).

The **ciliates** *Loxodes* and *Remanella* possess Müller vesicles located at its anterior dorsal margin. These vesicles contain a spherical inclusion, the so-called Müller body, which contains nanometer-sized barite (Hubert et al. 1975) and enables the organism with graviperception (Hemmersbach et al. 1998).

Barite has also been identified in different **microalgae**. Intracellular barite microcrystals occur in at least two planktonic flagellated species of the order Pavlovales (Fresnel et al. 1979; Gayral and Fresnel 1979) and the in the algae *Spirogyra* (Kreger 1957; Kreger and Boeré 1969). The function of these deposits is uncertain.

Bertram and Cowen report barite in the shell of some agglutinated **foraminifera** besides calcium carbonate (Bertram and Cowen 1998). Due to the undersaturation of seawater with respect to barite, the authors conclude a great biological control of barite chamber wall formation. Gooday and Nott describe micrometer-sized barite crystals in the two foraminifera species *Aschemonella ramuliformis* and *Galatheammina* sp. that are found in great depth (Gooday and Nott 1982). Whether these observations describe associated sedimentary barite or controlled barium biomineralization in foraminifera is not clear.

Recently, the marine bacterium *Myxococcus xanthus* has been shown to produce extracellular barite in vitro (González-Muñoz et al. 2003). The authors suggest that **bacterial barite precipitation** occurs on extracellular nucleation sites. Bacterially induced barite precipitation and its role in the oceanic barium cycle have remained largely unexplored.

The most prominent examples of **celestite** ($SrSO_4$) biomineralization can be found in the Rhizaria: The skeleton of Acantharia as well as the central capsules (vegetative stage) (Müller 1858) and membrane-bound vesicles (swarmer cells) of polycystine radiolarians (O. R. Anderson et al. 1990) are known to be built from celestite with a small fraction of barite (Ba/Sr ~ 0.003).

The crystalline inclusions in the polycystine radiolarian *Collosphaera huxleyi* were first described in 1858 by Müller (Müller 1858). Based on the crystal symmetry, he concluded that they were made of celestite. Later on, this observation was supported by Anderson and Hughes (Anderson 1981; Hughes et al. 1989) as well as Hallande and Martoja (Hollande and Martoja 1974). The function of the celestite crystals in polycystine radiolarians is still a matter of debate; they are discussed to help sinking and settling in greater depth during their reproductive cycle.

Acantharia are cosmopolitan, marine unicellular protists that are sister to the silica-secreting polycystine radiolarians. They are well known for their intricately shaped mineral endoskeletons comprised of celestite ($SrSO_4$). Despite their exceptional features, Acantharia biomineralization remains largely unexplored, cultivated isolates are missing, and at the moment, genomic information is unattainable.

Surprisingly, acantharians and polycystine radiolarians are not the only organisms that form this highly unusual biomineral. The endoskeleton of the dinoflagellate *Achradina pulchra* is also composed of celestite with traces of barite as revealed by X-ray microanalysis (Gómez et al. 2017). As in many other cases, the function of this biomineral is unclear.

Sulfides and Elemental Sulfur (Table 6)

Sedimentary sulfides are mainly produced by sulfate-reducing bacteria (SRB). Therefore, microorganisms are assumed to drive the formation of iron sulfides, in particular, **pyrite (FeS_2)**, one of the most common sulfide minerals in the geological record.

Unfortunately, the mechanisms of biogenic pyrite formation by **sulfate-reducing bacteria (SRB)** remain largely unexplored. One of the main reasons for that is probably the difficulty to achieve pyrite formation in microbial cultures. However, there are some indications for its microbial origin: Sedimentary sulfides are generally enriched in light sulfur isotopes (Thode et al. 1953) and have a characteristic morphology, the so-called framboidal pyrite (Rust 1935; Folk 2005). Pyrite "framboids" are raspberry-shaped aggregates (Ø 2–50 μm) composed of microcrystals (typically 0.5–2 μm) commonly found in reducing sediments (Folk 2005). Since the early observations, they seemed to be closely associated with organic matter, which has been demonstrated by means of scanning transmission X-ray microscopy (Maclean et al. 2008) and nano-SIMS (Wacey et al. 2015).

Several in vitro experiments were conducted trying to understand the role of SRB in pyrite formation. Formation of mackinawite (FeS) and greigite (Fe_3S_4), which are both believed to be potential pyrite precursor phases (Wilkin and Barnes 1997; Hunger and Benning 2007), is commonly observed in SRB cultures (Table 6). Pyrite formation in culture was reported only in a few instances (Hallberg 1965, 1972; Rickard 1969; Duverger et al. 2020; Berg et al. 2020). In a recent study, pyrite was shown to form very rapidly in cultures of a consortium of sulfur- and sulfate-reducing bacteria using Fe(III)-phosphate as substrate most likely enhanced polysulfides (Berg et al. 2020). Duverger et al. followed the formation of iron sulfides in *Desulfovibrio desulfuricans* using electron microscopy, X-ray diffraction, and synchrotron-based spectroscopy. The authors demonstrate a strong dependence of the biogenic sulfide composition on the iron source. These studies shed new light on understanding the mechanisms of biogenic pyrite formation, which are essential for the use of biogenic pyrite as paleoenvironmental proxy or as biosignature of early life.

It should be noted that **greigite (Fe_3S_4)**, the ferrimagnetic sulfur equivalent of magnetite, is not only formed as an intermediate in sulfate-reducing bacteria (SRB; see paragraph before) but also formed anaerobically by magnetotactic bacteria (MTB; see paragraph on oxides/hydroxide or other chapter of this book) (Pósfai

Table 6 Sulfide and sulfur biominerals in microorganisms

	Biomineral	Species	References
BACTERIA	Elemental sulfur (S^0)	Sulfur-oxidizing bacteria	Reviews: Kleinjan et al. (2003), Dahl and Prange (2006)
	Framboidal pyrite (FeS_2)	*Non-specified nanobacteria* and bacteria	Schopf et al. (1965), Wilkin and Barnes (1997), Schieber (2002a, b), Folk (2005)
Unclassified bacteria	Elemental sulfur (S^0)	*Thermothrix azorensis* sp.	Odintsova et al. (1996)
Proteobacteria			
Acidithiobacillia			
Acidithiobacillales	Elemental sulfur (S^0), polythionates	*Acidithiobacillus ferrooxidans* = *Thiobacillus ferrooxidans*	Steudel et al. (1987), Prange et al. (2002)
Alphaproteobacteria			
Rhodospirillales	Elemental sulfur (S^0)	*Magnetospirillum*	Kawaguchi et al. (1992), Spring and Bazylinski (2006)
Betaproteobacteria			
Burkholderiales	Elemental sulfur (S^0)	*Spirillum serpens* *Sphaerotilus natans*	Maier and Murray (1965)
		Macromonas	La Rivière and Schmidt (1992)
Deltaproteobacteria			
Desulfovibrionales (SRB = Bacteria and Archaea)	Pyrite and marcasite (FeS_2), greigite (Fe_3S_4), FeS (mackinawite, tetragonal), pyrrhotite ($Fe_{1-x}S$)	*Desulfovibrio desulfuricans*	Rickard (1969)
	Greigite (Fe_3S_4), pyrite (FeS_2) and intermediates (FeS), sphalerite (ZnS), elemental sulfur, gypsum ($CaSO_4 \cdot 2H_2O$), struvite ($NH_4MgPO_4 \cdot 6H_2O$), magnesite ($MgCO_3$)		Hallberg (1972)

	Mackinawite (FeS), vivianite/metavivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$)		Ivarson and Hallberg (1976)
	Mackinawite (FeS), pyrite (FeS_2), vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$), and greigite (Fe_3S_4)		Duverger et al. (2020)
	Pyrrhotite ($Fe_{1-x}S$)		Neal et al. (2001)
	Galena (PbS)		Leleu and Goni (1974)
	Mackinawite (FeS)		Stanley and Southam (2018)
	Vivianite ($Fe_3(PO_4)_2.8H_2O$), greigite (Fe_3S_4), pyrite (FeS_2)	*Desulfovibrio* and *Sulfurospirillum*	Berg et al. (2020)
	Pyrite (FeS_2) and gel-like phase [supposably hydrotroilite ($FeS{\cdot}nH_2O$)]	*Desulfovibrio*	Hallberg (1965)
	Wurtzite (ZnS)	*Desulfovibrio*	Leleu et al. (1975)
	Mixture of sphalerite (ZnS) and mackinawite (FeS)	*Desulfovibrio vulgaris*	Williams et al. (2005)
	Mackinawite (FeS), greigite (Fe_3S_4), and vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$]		Zhou et al. (2014)
	Mackinawite (FeS) and greigite (Fe_3S_4)	*Desulfovibrio hydrothermalis*	Picard et al. (2018)
	Mackinawite (FeS)	*Desulfovibrio capillatus*	Ikogou et al. (2017)
	Sphalerite (ZnS) and heazlewoodite (Ni_3S_2) or vaesite (NiS)	*Non-specified SRB*	Gramp et al. (2007)
	Covellite (CuS)		Gramp et al. (2006)
	Schwertmannite [$Fe_8O_8(OH)_6SO_4$], jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$], and greigite ($Fe_3S_4$)		Gramp et al. (2009)
	Mackinawite (FeS) and greigite (Fe_3S_4)		Gramp et al. (2010)
	Mackinawite (FeS)		Herbert et al. (1998)
	Pyrite (FeS_2)	Mainly *Desulfotomaculum*	Donald and Southam (1999)
	Greigite (Fe_3S_4)	Group *Desulfosarcina/Desulfococcus*	Reitner et al. (2005)
Magnetotactic bacteria	Sphalerite-like FeS, mackinawite (FeS), and greigite (Fe_3S_4)	*Non-specified MTB*	Pósfai et al. (1998)

(continued)

Table 6 (continued)

	Biomineral	Species	References
	Pyrrhotite ($Fe_{1-x}S$)		Farina et al. (1990)
	Pyrite (FeS_2) and greigite (Fe_3S_4)		Mann et al. (1990)
	Greigite (Fe_3S_4)		Heywood et al. (1990)
	Magnetite (Fe_3O_4), pyrite (FeS_2), and greigite (Fe_3S_4)		Bazylinski (1996)
Epsilonproteobacteria			
Campylobacterales			
Helicobacteraceae	Elemental sulfur (S^0)	*Thiovulum*	La Rivière and Schmidt (1992); Lane et al. (1992), Gros (2017)
Gammaproteobacteria	Greigite (Fe_3S_4)	High similarity to *Thiomicrospira* sp. and *Stenotrophomonas maltophilia*	Simmons et al. (2004)
Thiotrichales	Elemental sulfur (S^0)	*Achromatium*	La Rivière and Schmidt (1992), Head et al. (1996, 2000a), Gray et al. (1999, 2004), Gray and Head (2014), Salman et al. (2015)
		Beggiatoa alba	Strohl et al. (1981)
	Elemental sulfur (S^0), cyclooctasulfur	*Beggiatoa alba* and *Thiomargarita namibiensis*	Pasteris et al. (2001), Prange et al. (2002)
	Elemental sulfur (S^0)	*Beggiatoa*	Winogradsky (1887), Teske and Nelson (2006)
		Thiobacterium and Thiospira	La Rivière and Schmidt (1992)
		Thiomargarita	Schulz et al. (1999), Prange et al. (2002)
		Thiomicrospira crunogena	Javor et al. (1990)
		Thioploca	Teske et al. (1995), Otte et al. (1999)
		Thioploca and *Beggiatoa*	Maier and Murray (1965), Larkin and Strohl (1983), Pasteris et al. (2001)
		Thiothrix	Larkin and Strohl (1983), Howarth et al. (1999)

Chromatiales	Elemental sulfur (S^0)	*Chromatium vinosum*	Pattaragulwanit et al. (1998)
		Chromatium vinosum, *Thiocapsa roseopersicina*	Brune (1995)
		Thioalkalivibrio	Sorokin et al. (2001)
Chromatiaceae (purple sulfur bacteria)		*Chromatium*, *Amoebobacter*, *Lamprobacter*, *Lamprocystis*, *Thiocapsa*, *Thiocystis*, *Thiodictyon*, *Thiopedia*, *Thiospirillum*	Pfennig and Trüper (1992)
Chromatiaceae and Ectothiorhodospiraceae	Elemental sulfur (S^0), sulfur chains	*Thiocapsa roseopersicina*, *Chromatium vinosum*, *Marichromatium purpuratum*, *Allochromatium vinosum*, *Halorhodospira halophila*, *H. abdelmalekii*	Prange et al. (2002)
Enterobacterales	Elemental sulfur (S^0)	*Escherichia coli*, *Aerobacter*	Maier and Murray (1965)
Terrabacteria			
Actinobacteria	Maghemite (γ-Fe_2O_3) and greigite (Fe_3S_4)	*Actinobacter* sp.	Bharde et al. (2008)
Firmicutes			
Clostridia			
Clostridiales	FeS unspecified, with NiS	*Desulfotomaculum* sp.	Fortin et al. (1994)
	Mackinawite (FeS)	*Desulfosporosinus orientis*	Stanley and Southam (2018)
FCB group			
Bacteroidetes/Chlorobi			
Chlorobi (green sulfur bacteria)	Elemental sulfur (S^0), sulfur chains	*Chorobium vibrioforme*	Prange et al. (2002)
	Elemental sulfur (S^0)	*Chlorobaculum tepidum*	Marnocha et al. (2016, 2019)

(continued)

Table 6 (continued)

	Biomineral	Species	References
ARCHAEA			
TACK group			
Crenarchaeota			
Thermoprotei			
Sulfolobales			
Desulfurococcales	Elemental sulfur (S^0)	*Acidianus*, *Sulfolobus*, *Pyrodictium*, *Pyrococcus*, and *Thermococcus*	Kletzin et al. (2004)
Euryarchaeota			
Stenosarchaea			
Methanomicrobia	Elemental sulfur (S^0)	Methanotrophic archaea (ANME-2)	Milucka et al. (2012)
EUKARYA			
Viridiplantae			
Chlorophyta			
Core chlorophytes			
Chlorophyceae			
Sphaeropleales	Elemental sulfur (S^0)	*Chlorella fusca* = *Scenedesmus fusca*	Krauss et al. (1984)

et al. 1998), several types of rod-shaped *Gammaproteobacteria* living in sulfidic environments (Simmons et al. 2004), and *Actinobacteria* (Bharde et al. 2008).

Sulfur globules are formed as a metabolic oxidation product of reduced sulfur compounds, such as sulfide, polysulfides, thiosulfate, or polythionates, in diverse groups of prokaryotes.

Sulfur globules are stored within two large groups of **sulfur bacteria**, autotrophic and chemotrophic ("colorless") sulfur-oxidizing bacteria, and some thermophilic *Archaea* (Kletzin et al. 2004). Groundbreaking work on the description of chemotrophic sulfur bacteria *Beggiatoa* and their sulfur globules was published by Winogradsky in the late nineteeth century (Winogradsky 1887). Most chemotrophic sulfur oxidizers, such as *Achromatium* and *Beggiatoa*, belong to the order *Thiotrichales* (see **Table 6**), Gram-negative sulfur bacteria. Autotrophic sulfur oxidizers are mainly found within the purple (*Chromatiaceae* and *Ectothiorhodospiraceae*) (Pfennig and Trüper 1992; Brune 1995; Pattaragulwanit et al. 1998; Sorokin et al. 2001; Prange et al. 2002) and green (*Chlorobi)* sulfur bacteria (Prange et al. 2002; Marnocha et al. 2016, 2019), heliobacteria (*Helicobacteraceae*), and some species of cyanobacteria (Brune 1995). Chemotrophic bacteria use the energy derived from the oxidation of sulfur compounds to fix carbon dioxide, whereas autotrophic bacteria use reduced sulfur compounds as electron donors for photosynthesis (Kleinjan et al. 2003). Some other bacteria, including *Escherichia coli* (Maier and Murray 1965), produce sulfur as part of detoxification from sulfide.

The site of sulfur deposition varies in both groups, i.e., sulfur globules are deposited either intracellularly or extracellularly. Sulfur globule formation is still not fully understood, and a general mechanism for the formation and degradation of sulfur deposits is lacking. In most cases, the chemical nature of the deposited sulfur has also not been resolved yet. Typically, polymeric, water-insoluble sulfur is accumulated as a transient or final metabolic product depending on the organism, the culture conditions, and the sulfur substrate. Transient sulfur deposits have been suggested to act as energy reservoirs (Vetter 1985).

Recently, the speciation of sulfur in the sulfur globules of different groups of sulfur-oxidizing bacteria could be resolved using in situ XANES. The following sulfur species could be identified: In anaerobically grown, phototrophic sulfur bacteria, cyclooctasulfur was present, whereas in aerobically grown bacteria cultures, organic polysulfanes and polythionates dominate (Prange et al. 2002).

Most of today's sulfur deposits are considered biogenic, emphasizing the fundamental role of sulfur bacteria in the biogeochemical sulfur cycle (Dahl 2020).

6 Oxalates and Other Organic Crystals

Probably the most common organic crystals found in nature are oxalate biominerals. Among living organisms, they are widely distributed throughout the three kingdoms of fungi, plantae, and animalia. Out of these, plants and fungi (and lichens) are the major generators of both natural oxalic acid and oxalate biominerals.

Calcium oxalate is by far the most abundant oxalate biomineral, and is commonly found in rocks and soil. Among microorganisms, fungi are the main oxalate biomineral contributors (**Table 7**). Calcium oxalates are widely distributed among fungal classes and appear mostly extracellularly, in close association with the surface of the fungal hyphae. In fungi, the possibility of intracellular oxalate formation is still a matter of debate (Arnott 1995). Fungal calcium oxalate is commonly found in its monohydrate form **whewellite** ($CaC_2O_4 \cdot H_2O$) and its dihydrate form **weddellite** ($CaC_2O_4 \cdot 2H_2O$). Similar to plants, oxalate crystal morphologies in fungi are highly diverse, ranging from needlelike to rhombohedral.

Calcium oxalates have also been found in a great number of **lichens** (Wadsten and Moberg 1985), a complex symbiotic association of a fungal mycobiont (usually an ascomycete) with one or more photosynthetic partners, the photobiont (e.g., green algae or cyanobacteria). These organisms combine to a heterogeneous structure forming the main body of the lichen, the thallus. Oxalate biominerals are commonly found in association with the lichen thallus outside of the protoplasm (Arnott 1995; Burford et al. 2003). In foliose lichens, weddellite crystals are located in proximity to the photobiont layer. It could be possible that the crystal water entrapped in the calcium oxalate crystals is used to maintain photosynthetic photobiont activity during dry periods (Clark et al. 2001).

Calcium oxalates are commonly associated with fungi and lichens in their natural environments, e.g., on mineral substrates and in the rock-lichen interface (Baran and Monje 2010), on plant leaves (Clark et al. 2001), and in soils and leaf litter (Graustein et al. 1977; Dutton and Evans 1996). Fungi and lichens are essential constituents of epi- and endolithic microbial communities and often play an important part in the **rock weathering process**. They contribute to the dissolution of rocks through the excretion of H+ and other organic acids, or through participation in redox reactions with mineral constituents (e.g., Mn or Fe) (Burford et al. 2003; Fomina et al. 2006). Oxalic acid is produced in large quantities by all classes of fungi. In solution, oxalate ions rapidly form complexes with cations. Many of the resulting oxalate salts, especially those of divalent cations, have a very low solubility and precipitate (Baran and Monje 2010). The incorporation of heavy metal ions into oxalates in fungi and lichen is considered a detoxification process and probably contributes to fungal metal tolerance (Gadd 1993).

As a strong leaching agent, oxalic acid contributes significantly to the many metal and mineral transformations mediated by fungi, including the formation of oxalate minerals. For example, the oxalic acid-producing *Aspergillus niger* is able to precipitate calcium oxalate when cultured on calcium carbonate (Sayer and Gadd 1997) or gypsum (Gharieb et al. 1998) by dissolution of the substrate. In ectomycorrhiza, a symbiotic association of fungi with the feeder roots of higher plants, essential plant nutrients are mobilized directly from insoluble mineral sources through excretion of oxalic acid. For instance, apatite dissolution by oxalic acid is linked to phosphorus acquisition and calcium oxalate sequestration (Wallander 2000; Smits et al. 2012; Schmalenberger et al. 2015).

Fungi and lichen also play an important role in mineral formation through the precipitation of various **secondary minerals**, such as calcite (Verrecchia 2000). In

Table 7 Oxalate crystals in microorganisms

	Biomineral	Species	References
EUKARYA			
Fungi			**Reviews:** (Arnott (1995), Khan (1995), Dutton and Evans (1996), Gadd (1999), Verrecchia (2000), Baran and Monje (2010), Gadd et al. (2014)
Dikarya			
Ascomycota			
Saccharomyceta			
Pezizomycotina			
Ieotiomyceta			
Dothideomyceta	Weddellite ($CaC_2O_4 \cdot 2H_2O$)	*Dirina massiliensis*	Edwards et al. (1997)
	Whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot 2H_2O$)		Edwards et al. (1992)
	Whewellite ($CaC_2O_4 \cdot H_2O$)		Edwards et al. (1991)
Eurotiomycetes	Unspecified Ca-oxalate	*Penicillium oxalicum*	Jarvis et al. (1990)
	Lead oxalate [$Pb(C_2O_4)$] and Ca-oxalate (unspecified)	*Aspergillus niger*	Sayer et al. (1999;), Li et al. (2016b)
	Metal oxalates (Zn, Co, Mn, Cu Cd)		Sayer and Gadd (1997)
	Unspecified Ca-oxalate		Gharieb et al. (1998); Li et al. (2019)
Sordariomyceta	Mix of calcite ($CaCO_3$) and whewellite ($CaC_2O_4 \cdot H_2O$)	*Cephalotrichum* sp.	Burford et al. (2006)
	Unspecified Ca-oxalate similar to trihydrate ($CaC_2O_4 \cdot 3H_2O$)	*Cryphonectria parasitica*	Englander and Corden (1971)
	Unspecified Ca-oxalate	*Leucostoma cincta*, *L. persoonii*	Traquair (1987)
	Weddellite ($CaC_2O_4 \cdot 2H_2O$)	*Dasyscyphus capitate/Incrucipulum capitatum*	Horner et al. (1983)
Lecanoromycetes	Glushinskite [$Mg(C_2O_4) \cdot 2H_2O$]	*Lecanora atra*	Wilson et al. (1980)
	Mooloite (hydrated copper oxalate, $CuC_20_4.nH_20$, n ~ 0.1)	*Acarospora rugulosa* and *Lecidea theiodes*	Purvis (1984)

(continued)

Table 7 (continued)

	Biomineral	Species	References
	Moolooite (hydrated copper oxalate, $CuC_20_4.nH_20$, n ~ 0.4–0.7)	4 different lichen species	Chisholm et al. (1987)
	Whewellite ($CaC_2O_4·H_2O$) and Weddellite ($CaC_2O_4·2H_2O$)	*Pertusaria coralline*	Jones et al. (1980)
	Lindbergite ($MnC_2O_4.2H_2O$)		Wilson and Jones (1984)
	Weddellite ($CaC_2O_4·2H_2O$) and whewellite ($CaC_2O_4·H_2O$)	15 different lichen species	Wadsten and Moberg (1985)
	Whewellite ($CaC_2O_4·H_2O$)	*Parmelia chlorochroa*	Erdman et al. (1977)
		Calenia triseptata, *Tricaria carnea*, *Echinoplaca strigulacea*	de Oliveira et al. (2002)
		Circinaria gyrosa	Böttger et al. (2014)
	Weddellite ($CaC_2O_4·2H_2O$)	*Xanthoparmelia chlorochroa*, *X. cumberlandia*, *Rhizoplaca melanophthalma*, *R. chrysoleuca*, *R. haydenii*, and *R. marginalis*	Clark et al. (2001)
	Whewellite ($CaC_2O_4·H_2O$) and anhydrous iron (III) oxalate [$Fe_2(C_2O_4)_3$]	*Caloplaca callopsima* and *Diploschistes ocellatus*	Ascaso et al. (1982)
	Weddellite ($CaC_2O_4·2H_2O$), whewellite ($CaC_2O_4·H_2O$), $ZnC_2O_4·2H_2O$, anhydrous lead oxalate (PbC_2O_4)	*Diploschistes muscorum*	Sarret et al. (1998)
	Whewellite ($CaC_2O_4·H_2O$)	*Xanthoria parietina*	
Basidiomycota			
Agaricomycotina			
Agaricomycetes			
Phallomycetidae	Whewellite ($CaC_2O_4·H_2O$) and weddellite ($CaC_2O_4·2H_2O$)	*Hysterangium crissum*	Graustein et al. (1977)

Agaricomycetidae			
Atheliales	Whewellite ($CaC_2O_4·H_2O$)	*Piloderma fallax*	Tuason and Arocena (2009)
Boletales	Mix of calcite ($CaCO_3$) and whewellite ($CaC_2O_4·H_2O$)	*Serpula himantioides*	Burford et al. (2006)
	Unspecified Ca-oxalate	*Serpula himantioides*	Gharieb et al. (1998)
	Whewellite ($CaC_2O_4·H_2O$)	*Paxillus involutus*	Schmalenberger et al. (2015)
Agaricomycetes inc. sedis			
Polyporales	Ca-oxalate and Cu-oxalate	*Poria placenta* and *Poria vaillantii*	Sutter et al. (1983, 1984)
Fungi incertae sedis			
Mucoromycota			
Mucoromycotina	Weddellite ($CaC_2O_4·2H_2O$)	*Mucor mucedo*	Urbanus et al. (1978)
		Mucor plumbens, *Cunninghamella echinulata*	Jones et al. (1976)
	Unspecified Ca-oxalate	*Mucor heimalis*, *Rhizopus oryzae*	Powell and Arnott (1985)
		Gilbertella persicaria	Whitney and Arnott (1986)
	Weddellite ($CaC_2O_4·2H_2O$), whewellite ($CaC_2O_4·H_2O$), and glushinskite [$Mg(C_2O_4)·2H_2O$]	Unspecified *Mucorales*	Kolo and Claeys (2005)

semiarid regions, fungi biomineralized with both calcite and calcium oxalates have been observed by Verrechia et al. (Verrecchia et al. 1990). It has been proposed that in these climates, calcium oxalate can decompose resulting in calcium carbonate deposits (Verrecchia 2000).

The interaction of oxalic acid secreted by the fungi and lichens with different substrates is believed to be their principal oxalate biomineralization route. For this reason, a variety of other **metal oxalate biominerals** has been identified **in association with rock weathering** by fungi and lichens.

The alkaline-earth oxalate **glushinskite** (magnesium oxalate dihydrate, $Mg(C_2O_4)\cdot 2H_2O$) has been found in the lichen thallus and at the lichen-rock interface of *Lecanora atra* (Wilson et al. 1980). It could be shown in vitro that glushinskite forms together with weddellite and whewellite oxalate biominerals when fungi of the order *Mucorales* interact with carbonate substrates and seawater (Kolo and Claeys 2005).

Early studies of the oxalic-, citric-, and formic acid-producing fungus *Aspergillus niger* showed the transformation of different insoluble inorganic metal compounds into insoluble metal (Cu, Cd, Co, Zn, and Mn) oxalates (Sayer and Gadd 1997). In a similar manner, biogenic **lead oxalate dihydrate** $[Pb(C_2O_4)\cdot 2H_2O]$ was formed by *Aspergillus niger* growing on insoluble lead minerals, such as pyromorphite $[Pb_5(PO_4)_3Cl]$ (Sayer et al. 1999) or fluorapatite $[Ca_5(PO_4)_3F]$ (Li et al. 2016b). These inorganic substrates were solubilized by the lichen's metabolic action, releasing Pb^{2+} ions that were immobilized as lead oxalate. The lichen hyperaccumulator *Diploschistes muscorum* forms extracellular **zinc oxalate dihydrate** ($ZnC_2O_4\cdot 2H_2O$) and **anhydrous lead oxalate** (PbC_2O_4) in Zn^{2+}- and Pb^{2+}-containing solutions (Sarret et al. 1998).

Lindbergite ($MnC_2O_4\cdot 2H_2O$) could be identified in the lichen *Pertusaria corallina* on manganese-rich ores (Wilson and Jones 1984).

Inclusions of **moolooite** (hydrated copper oxalate, $CuC_20_4\cdot nH_20$), a naturally occurring copper oxalate of vivid blue color, were recognized in different whewellite- or weddellite-sequestering lichens growing in extremely rich copper environments (Chisholm et al. 1987).

So far, **non-hydrated Fe(III) oxalate** has only been reported in the lichen *Caloplaca callopsima* in association with an iron-rich dolomite (Ascaso et al. 1982). So far, there is no evidence for Fe(II) oxalate dihydrate biominerals, known as humboldtine ($FeC_2O_4\cdot 2H_2O$).

The accumulation and immobilization of metal ions from the environment through oxalate biomineralization by fungi and lichens offers a variety of potential applications in environmental biotechnology: in detoxification, metal and radionuclide leaching, biorecovery, and bioremediation, or as catalyst. Furthermore, metal oxalates have been suggested as biomarkers for the existence of primitive life forms in extreme or extraterrestrial environments (Frost et al. 2003; Böttger et al. 2014; Cheng et al. 2016).

Besides oxalate biominerals the only organic crystals found in microorganisms are microcrystals of the **purine bases guanine** and **uric acid** (see **Table 8**). Recently, they have been identified in various phytoplankton, such as

Table 8 Organic crystals in microorganisms

	Biomineral	Species	References
EUKARYA			
SAR			
Alveolata			
Colpodellida		*Chromera velia*	Mojzeš et al. (2020)
Dinophyceae	Anhydrous β-guanine	*Gonyaulax polyedra*	DeSa et al. (1963, 1968), Schmitter (1971)
		Gonyaulax, *Prorocentrum*, *Gymnodinium*, *Nocticula*, *Crypthecodinium*, *Gyrodinium*, *Ceratium*, *Glenodinium*	Pokorny and Gold (1973)
		C. operosum aff., *Leonella granifera*	Jantschke et al. (2020)
		Amphidinium carterae *Symbiodiniaceae*	Mojzeš et al. (2020)
		At least three other species including *Symbiodinium voratum*	(Jantschke, unpublished)
	Calcium oxalate	*Symbiodinium*	Doyle and Doyle (1940), Taylor (1968)
	Uric acid		Clode et al. (2009), Kopp et al. (2013)
Ciliophora	Guanine with hypoxanthine and traces of xanthine	*Paramecium tetraurelia*	Creutz et al. (2002)
	Hypoxanthine and guanine	*Parauronema acutum*	Soldo et al. (1978)
Stramenopiles			
Ochrophy			
Eustigmatophyceae			
Goniochloridales	Anhydrous guanine	*Trachydiscus minutus*	Moudříková et al. (2017)
Eustigmatales		*Microchloropsis gaditana*, *Vischeria* sp.	Mojzeš et al. (2020)
Vacuoliviride		*Vacuoliviride crystalliferum*	
Synurophyceae		*Synura petersenii*	

(continued)

Table 8 (continued)

	Biomineral	Species	References
Fungi			
Dikarya			
Ascomycota			
Saccharomyceta			
Saccharomycotina			
Saccharomycetales	Uric acid	*Candida utilis* and *Saccharomyces cerevisiae*	Svihla et al. (1963)
Viridiplantae			
Chlorophyta			
Core chlorophytes			
Chlorophyceae			
Chlamydomonadales	Anhydrous guanine	*Chlamydomonas reinhardtii* *Dunaliella acidophila* *Haematococcus pluvialis*	Mojzeš et al. (2020)
Sphaeropleales			
Scenedesmaceae		*Desmodesmus quadricauda*	(Moudříková et al. 2017)
Trebouxiophyceae			
Trebouxiales		*Lobosphaera incisa*	Mojzeš et al. (2020)
Streptophyta			
Klebsormidiophyceae	Uric acid	*Klebsormidium flaccidum*	Mojzeš et al. (2020)

dinoflagellates, green algae, and eustigmatophytes, as well as ciliates (Creutz et al. 2002; Moudříková et al. 2017; Jantschke et al. 2019; Mojzeš et al. 2020).

Crystalline deposits in **dinoflagellates** are very abundant and are well known from ultrastructural studies, where they are usually referred to as "crystal-like bodies" or "crystal-like particles." Interestingly, these crystalline deposits were first believed to be composed of calcium oxalate (Doyle and Doyle 1940; Taylor 1968). Later on, they were reidentified as **uric acid** crystals using nano-SIMS, EELS, and GC-MS in *Symbiodinium* (Clode et al. 2009; Kopp et al. 2013). DeSa et al. were the first to identify the crystalline material in the dinoflagellate species *Gonyaulax polyedra* (DeSa et al. 1963, 1968) as **guanine**. Recently, deposits of intracellular anhydrous β-guanine were also found in the calcifying species *Leonella granifera* and *Calciodinellum operosum aff.* by means of in situ Raman microscopy and electron diffraction (Jantschke et al. 2019, 2020).

Interestingly, similar Raman data has been obtained from various other dinoflagellate species, including *Symbiodinium* (Mojzeš et al. 2020 and Jantschke, unpublished). Species of the genus *Symbiodinium* are of high ecological importance due to their endosymbiotic relationship with corals. At the moment, contradicting observations about the chemical nature of the crystals in *Symbiodinium* exist. The morphology of the uric acid crystals observed by Clode and Kopp (Clode et al. 2009; Kopp et al. 2013) shows a high resemblance to the guanine crystals observed (Jantschke et al. 2019, 2020). However, uric acid has a distinctively different Raman signature and could not be detected in *Symbiodinium* cells, only in the green freshwater algae *Klebsormidium flaccidum* (Mojzeš et al. 2020). Uric acid and guanine are both part of the cell's purine metabolism, with uric acid being the end product of a series of enzymatic degradation reactions. Whether the organic crystals in *Symbiodinium* are indeed uric acid or guanine, or whether these nitrogen compounds are an expression of different nitrogen accumulation pathways, the status of the symbiotic relationship, and/or environmental conditions, needs to be reexamined.

It is important to note that intracellular guanine crystals were also identified in **other microalgae**, including the chlorophyte *Desmodesmus quadricauda* and the eustigmatophyte *Trachydiscus minutus* (Moudříková et al. 2017), and the ciliate *Paramecium tetraurelia* (Creutz et al. 2002). Therefore, the appearance of intracellular guanine crystals seems to be a trait not unique to dinoflagellates only. Very recently, Mojzes et al. demonstrated the widespread occurrence of guanine reserves among taxonomically distant microalgal species inhabiting different environments. The authors suggest an early evolutionary origin of guanine microcrystals as nitrogen storage and attribute them an important yet unattended role in nitrogen cycling that needs to be further elucidated (Mojzeš et al. 2020).

The **function** of organic crystals (uric acid/guanine) is a matter of discussion. The uric acid deposits in *Symbiodinium* are suggested to be a nitrogen assimilation and exchange product between cnidarian hosts and their dinoflagellate symbionts (Clode et al., 2009; Kopp et al., 2013). Alternatively, they could function as an eyespot and be responsible for the photoreceptive behavior of the cell (Yamashita et al. 2009). DeSa et al. suggested a functional role of guanine in bioluminescence (DeSa et al.

1963, 1968). However, the presence of guanine crystals in nonluminescent dinoflagellate species could not be explained by this idea (Pokorny and Gold, 1973; Schmitter, 1971). Since then, guanine deposits in dinoflagellates are believed to be a nitrogen accumulation product (Schmitter, 1971). Crystalline anhydrous guanine is very interesting because of its extremely high refractive index of 1.83 (W. J. Schmidt 1949). This is the reason why these crystals are very good reflectors and are known to be used by fish and other animals for light manipulation, to produce structural colors, and in vision to build mirrors that reflect light (Gur et al. 2017). It could well be that intracellular guanine crystals also influence light exploitation and photosynthetic performance as suggested by Jantschke et al. (Jantschke et al. 2019).

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Magnetosome Biomineralization by Magnetotactic Bacteria

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Contents

Abstract The magnetosome is an organelle consisting of a magnetic nanocrystal within a biological membrane vesicle. Magnetosomes impart a magnetic moment to the whole microorganism while it swims by flagellar propulsion, leading to alignment of the swimming trajectory to the Earth's magnetic field lines. Thus, the main physiological role of magnetosomes is magnetotaxis, which can be defined as a magnetic-driven behavior working in concert with other sensory systems of the microorganism in order to guide it to suitable microenvironments. Each magnetic

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nanocrystal in magnetosomes is a single-domain particle of magnetite (Fe_3O_4) or greigite (Fe_3S_4), which is biomineralized through precisely controlled processes leading to species-specific size, shape, and location within the cell. Several proteins are involved in magnetosome biomineralization, which includes iron uptake, redox conversion of iron, control on crystal size and shape, and arrangement of magnetosomes in chains properly located within the cell. Magnetosomes occur in microorganisms belonging to several groups scattered through the bacteria domain, as well as in a few protists and microalgae. Biomineralization of magnetosomes is a growing field of research, encompassing fields as diverse as biochemistry and molecular biology, microbial ecology, sediment magnetization, materials science, and biotechnology.

1 Introduction

Magnetotactic bacteria are identified by their passive response to magnetic fields, i.e., they orient their swimming direction to the direction of the local magnetic field lines. This behavior is due to magnetosomes, organelles composed of a magnetic crystal enveloped by a biological membrane (Blakemore 1975). Magnetosomes impart the whole cell a magnetic moment, which interacts with the local magnetic field, generating a magnetic torque that align the cell magnetic moment with the local magnetic field while the bacteria swim propelled by flagella (Klumpp and Faivre 2016). Mature magnetosomes contain either magnetite (Fe_3O_4) or greigite (Fe_3S_4) crystals, both ferrimagnetic minerals (Frankel et al. 1979; Farina et al. 1990; Mann et al. 1990; Pósfai et al. 1998a, b). These magnetic organelles are usually arranged in chains or rows in the cytoplasm, with the magnetic moments aligned parallel to the chain or row axes (Kasama et al. 2006a, b; Pósfai et al. 2006a). Figure 1 shows one example of magnetotactic bacterium and its magnetite magnetosomes.

2 Magnetotaxis at a Glance

Magnetotactic bacteria are either microaerophiles or anaerobes thriving in the chemocline of aquatic environments (Frankel et al. 1997; Frankel et al. 2006; Abreu et al. 2007; Lefèvre et al. 2011a; Lefèvre et al. 2014; Keim et al. 2018). The chemocline comprises gradients of O_2 and other chemicals such as H_2S, NO_3^-, NO_2^-, NH_4^+, and Fe^{2+}, which are generated by the metabolic activities of several distinct guilds of microorganisms in stagnant water or sediments. To form chemical gradients, the rate of consumption must be higher than diffusion rates. In stratified lakes and sediments, the chemical gradients comprising the chemocline form roughly horizontal layers, parallel to the water or the sediment surfaces, respectively. The chemocline is not static; it changes through space and time due to oxygen production by photosynthesis following day/night cycles, bioturbation, and other

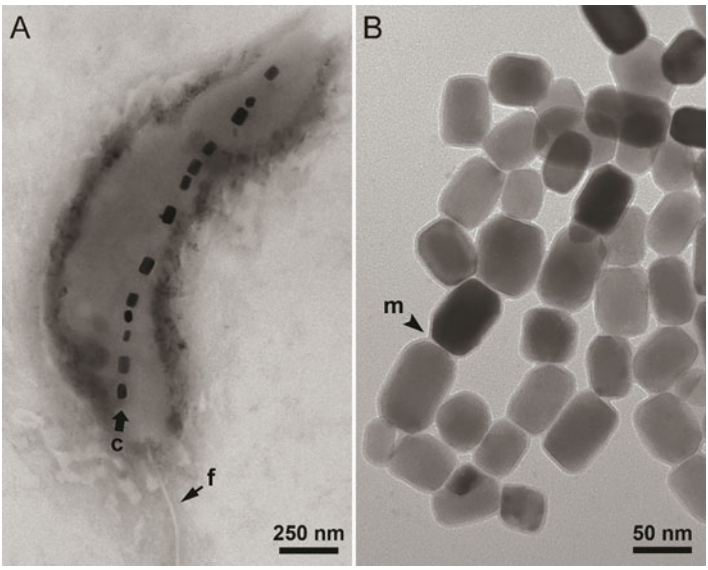

Fig. 1 Magnetotactic bacteria and the magnetosomes. (**a**) Typical cell of the alphaproteobacteria *Magnetovibrio blakemorei* strain MV-1T showing a single chain of prismatic magnetite magnetosomes (c; thick arrow) aligned along the cell's major axis and a flagellum (f; thin arrow). (**b**) Magnetosomes purified after cells lysis. Note the presence of the membrane, which is seen as a translucent coating around each magnetosome (m; arrowhead). Transmission electron microscopy, 80 kV

factors (Nealson 1997; Brune et al. 2000; Fenchel 2002). In such environments, magnetotaxis provides a vertical guideline to swimming microorganisms, facilitating migration through the chemocline, and turning a tridimensional search for optimal conditions into a unidimensional one—since most magnetotactic bacteria are two-way swimmers, they can swim back and forth until finding their preferred conditions within the chemocline (Frankel et al. 1997; Frankel et al. 2006; Lefèvre et al. 2014; Keim et al. 2018). While the cell's magnetic moment provides an axis for swimming, sensory systems for other taxis, such as aero-, photo-, and chemotaxis, drive the choice of the swimming direction (Frankel et al. 1997; Frankel et al. 2006; Wenter et al. 2009; Almeida et al. 2013; Lefèvre et al. 2014; Keim et al. 2018).

3 Magnetosomes Are Tailored for Magnetotaxis

As mentioned above, magnetosomes contain magnetic nanoparticles of magnetite or greigite. Their shape and size determine their magnetic properties. In bulk magnetic materials, magnetic orientation is not evenly distributed throughout the whole material but divided into regions with homogeneous magnetic moment orientations, which mutually cancel each other. Those regions are known as magnetic domains

and show all the atomic magnetic spins parallel to each other, resulting in a greater resultant magnetic moment. The division in magnetic domains is necessary to decrease the magnetic energy of the bulk material. However, if the magnet size decreases, the number of magnetic domains also decreases. Thus, there is a limit in size for any given material to maintain a uniform and stable internal magnetization. When that limit is reached, only one domain is found in the particle, and in this condition the particle is known as a magnetic single domain (SD) (Bean and Livingston 1959).

The size of SD nanoparticles is also limited at the small end size. Particles below a limit size are known as superparamagnetic (SPM), and are recognized because the magnetic moment flips constantly among the stable orientations in the crystalline easy axes separated by the magnetocrystalline anisotropy energy barrier. The thermal energy provides the energy for the magnetic moment to flip the barrier (Bean and Livingston 1959). A SPM particle does not present a stable magnetic moment in the absence of a magnetic field, in contrast to SD nanoparticles, which present a stable magnetic moment.

The size range for SD particles depends on the magnetic material, the magnetocrystalline anisotropy energy, and the shape anisotropy, which depends on its geometrical shape (Butler and Banerjee 1975). For parallelepiped-shaped particles of magnetite, the range of length sizes for SD nanoparticles depends on the axial ratio (width/length). For cubic particles (width = length), the limits to be SD are 50 nm < length < 75 nm. If the axial ratio is 0.8, then 50 nm < length < 110 nm, and if the axial ratio is 0.4, then 50 nm < length < 420 nm. There is a known diagram that consists of the graph of the length versus the axial ratio to show if the magnetite nanoparticles are in the SD region (Butler and Banerjee 1975).

Table 1 shows the values of length and axial ratio for several magnetotactic bacteria, and Fig. 2 shows the corresponding diagram with those data. Most magnetite magnetosomes lie within the single magnetic domain range, suggesting that their main function in the cell is magnetotaxis (Frankel et al. 1979; Dunin-Borkowski et al. 1998; McCartney et al. 2001; Kasama et al. 2006a, b). It is common to observe particles at the beginning or the end of magnetosome chains that are in the size range for SPM magnetite (length < 50 nm). Probably those particles are still growing to reach the SD size range and inherit the magnetic polarity from neighbor crystals in the chain (Kirschvink 1992).

4 The Magnetosome as an Organelle

A recent definition of organelle defines "an organelle as a subcellular structure containing a proteomically distinct interior and a defined boundary layer (whether lipid membrane, lipid monolayer, proteinaceous or phase-defined) that affects cellular physiology" (Greening and Lithgow 2020). According to this definition, magnetosomes can be considered organelles, as (1) they are membrane-coated,

Table 1 Magnetite length and width. Data obtained from magnetosomes of diverse magnetotactic bacteria. Axial ratio = width/length

Microorganism	Length (nm)	Width (nm)	Axial ratio	References
IT-1	90.4 ± 19.6	–	0.74	Araujo et al. (2016)
MWB-1	116	40	0.34	Lin et al. (2012)
ARB-1	82 ± 23	49 ± 15	0.59	Cox et al. (2002)
QHL	101 ± 24	83 ± 21	0.83 ± 0.09	Pan et al. (2008)
MO-1	64 ± 20	57 ± 17	0.89	Lefèvre et al. (2009)
BMC disordered	102 ± 20	60 ± 9	0.6	Zhang et al. (2012)
BMC chains	125 ± 32	99 ± 25	0.8	Zhang et al. (2012)
GRS-1	54.6 ± 4.8	-	0.85	Taoka et al. (2014)
M. magneticum	42	-	0.87	Devouard et al. (1998)
MV-1	48	-	0.68	Devouard et al. (1998)
MC-2	100	-	0.87	Devouard et al. (1998)
UR-1	77.4 ± 11.8	46.2 ± 7.9	0.64 ± 0.09	Koziaeva et al. (2019)
MC-1 acetate grown	83 ± 14	78 ± 11	0.94	Bazylinski et al. (2013a)
MC-1 sulfide grown	72 ± 11	70 ± 13	0.97	Bazylinski et al. (2013a)
Antarctic UII two chains	117 ± 31	67 ± 18	0.6 ± 0.1	Abreu et al. (2016)
Antarctic UII four chains	102 ± 22	72 ± 19	0.7 ± 0.09	Abreu et al. (2016)
Antarctic UII disorganized	83 ± 13	46 ± 7	0.6 ± 0.06	Abreu et al. (2016)
Antarctic Machu Picchu	121 ± 29	59 ± 15	0.5 ± 0.08	Abreu et al. (2016)
Itaipu 3	120	70	0.56	Spring et al. (1998)
Itaipu 4	135	105	0.77	Spring et al. (1998)
Flagellated protist	276.6 ± 61.3	52.7 ± 5.1	0.2 ± 0.04	Leão et al. (2020)
Algae	140	48	0.34	Torres de Araujo et al. (1986)

(2) their content is distinct from the cytoplasm, and (3) they have at least one physiological function (magnetotaxis).

Magnetosomes are the structural signature of magnetotactic bacteria and a few magnetotactic protists (Fig. 1a). Magnetite crystals in the magnetosomes have many features that differ them from magnetic nanocrystals produced by both chemical processes (Vargas et al. 2018) and dissimilatory iron-reducing bacteria (Moskowitz et al. 1989; Sparks et al. 1990). The strict genetic control over biomineralization in magnetosomes allows the identification of relevant phylogenetic characteristics for species description based on the shape, size, composition, and organization within the cell (Table 2; Pósfai et al. 2013).

The lipid composition of the magnetosome and cytoplasmic membranes of *Magnetospirillum magneticum* strain AMB-1 is remarkably similar, showing predominance of the unsaturated fatty acids C16:1 and C18:1 (Nakamura et al. 1991;

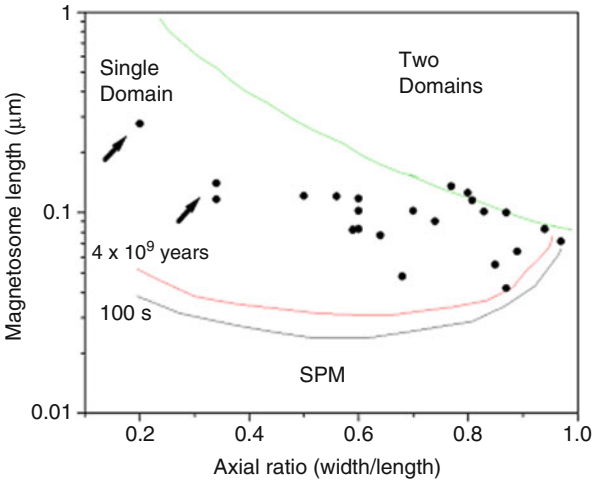

Fig. 2 Diagram of length versus width/length ratio of magnetite magnetosomes, containing the data shown in Table 1. Most magnetosomes lie within the stable single magnetic domain range. Arrows point to data from two magnetotactic eukaryotes, a ciliate (arrow at the left) and an algae (arrow at the right). The lines separate the plot in regions corresponding to two magnetic domain particles, single magnetic domain particles, or superparamagnetic (SPM) particles. The two inferior lines mark two distinct time boundaries for the magnetic moment to flip the magnetocrystalline energy barrier, i.e., the boundaries between permanently magnetic and superparamagnetic

Tanaka et al. 2006). On the other hand, the magnetosome membrane is the site of several proteins specific of magnetosomes, which participate in crucial steps of magnetosome synthesis, such as nucleation and maturation of magnetosomes' mineral core (Uebe and Schüler 2016). After magnetosome maturation, the magnetosome membrane continues to envelop the magnetic crystal. At this stage, the most relevant role of the magnetosome membrane is related to the organization of these structures in one or multiple chain(s) within the cell, maintaining each magnetosome in a defined position along a cytoskeleton-like filament (Komeili et al. 2006).

5 Minerals in the Magnetosomes

As afore mentioned, mature magnetosomes contain either magnetite (Fe_3O_4) or greigite (Fe_3S_4) in their inorganic core (Frankel et al. 1979; Farina et al. 1990; Mann et al. 1990; Kasama et al. 2006a; Pósfai et al. 2006a). Most magnetotactic microorganisms in nature produce magnetite, as well as most cultivated strains. Currently, a single cultivated bacterium produces both magnetite and greigite (Lefèvre et al. 2011a; Descamps et al. 2017). Thus, there is a much larger body of knowledge on magnetite biomineralization in magnetotactic bacteria as compared to greigite.

Table 2 Examples of correlation of magnetite magnetosome features, bacterial morphology, and phylogenetic affiliation

Magnetosome shape	Magnetosome organization	Cellular morphology	Phylogenetic affiliation	References
Cubo-octahedra	Single chain	Spirilla	(MS-1, MSR-1, AMB-1) *Alphaproteobacteria*	Devouard et al. (1998), Faivre et al. (2008), Li et al. (2009)
Elongated octahedra	Single chain	Cocci, rod-shaped	(IT-1) *Ca.* Etaproteobacteria (SS-5) *Gammaproteobacteria*	Lefèvre et al. (2012), Morillo et al. (2014), Araujo et al. (2016)
Prismatic (truncated hexa-octahe-dra/octahedral shape)	Single chain Double chains	Vibrio, cocci, ovoid	MC-1 *Ca.* Etaproteobacteria, (MV-1, MO-1) *Alphaproteobacteria*, *(CLV-1) Betaproteobacteria*	Meldrum et al. (1993a, b), Devouard et al. (1998), Clemett et al. (2002), Lefèvre et al. (2009), Zhang et al. (2012), Bazylinski et al. (2013b), Abreu et al. (2018)
Anisotropic (bullet, tooth, arrowhead, irregular shape)	Multiple chains Single chain	Ovoid cells Vibrio, flagellated protist	(LO-1, HSMV-1) *Nitrospirae*, (RS-1) *Deltaproteobacteria* (SKK-01) *Omnitrophica*	Pósfai et al. (2006b), Lefèvre et al. (2010, 2011b), Kolinko et al. (2012), Leão et al. (2020)

5.1 *Precursor Phases for Magnetite in Magnetotactic Bacteria*

The magnetite magnetosome synthesis pathway is still not deeply understood. It starts at the cytoplasmic membrane with the inward invagination to form a vesicle. After that, with the availability of iron, nucleation and growth of the crystal begins within the vesicle (Komeili et al. 2004; Komeili 2006; Tanaka et al. 2006). The oxygen atoms within magnetite are derived from water instead of molecular O_2 (Mandernack et al. 1999). Magnetotactic bacteria incorporate the iron from the environment, by diffusion as Fe(II), and/or by energy-dependent mechanisms as Fe(III). Interestingly, *Magnetospirillum gryphiswaldense* MSR-1 seem to prefer Fe (III), whereas *Ms. magneticum* AMB-1 prefer Fe(II) (Schüler and Baeuerlein 1996; Schüler and Baeuerlein 1998; Amor et al. 2018). Several iron uptake systems are found in magnetotactic bacteria, such as siderophores (Calugay et al. 2003), copper-dependent iron uptake system (Dubbels et al. 2004), and ferrous iron transport protein B gene (feoB1) (Rong et al. 2008). The iron incorporated remains stored in Fe(III) form, establishing an iron pool in the periplasm and/or in cytoplasm, which would be reduced to Fe^{2+} and transported toward magnetosomes (Amor et al. 2018). Recently, it was detected a pool of noncrystalline Fe(II) species in the cytoplasm and

associated with magnetosomes in *Ms. magneticum* strain AMB-1 (Amor et al. 2020a). Werckmann et al. (2017) showed an iron pool inside magnetosomes, coating the magnetite crystals, in four distinct species of magnetotactic bacteria. They hypothesized that such pool could represent an iron source for magnetite biomineralization (Werckmann et al. 2017).

A series of studies suggested that ferrihydrite, hematite, or high-spin reduced iron complexes could be magnetite precursors after iron transport through the cell outer membrane (Frankel et al. 1979; Frankel et al. 1983; Faivre et al. 2007; Staniland et al. 2007; Fdez-Gubieda et al. 2013; Nagard et al. 2019; Uebe et al. 2019). Baumgartner and colleagues proposed a mechanism involving phase transformations from disordered phosphate-rich iron hydroxide into magnetite via oxidized iron (oxyhydr)oxide intermediates ($Fe_2O_3 \cdot nH_2O$). In this approach, a ferritin-like precursor was localized outside the magnetosome vesicle, while the ferrihydrite-like intermediate was found inside (Baumgartner et al. 2013). Thus, phases corresponding to ferritin-like structures were evidenced in *Magnetospirillum* species strains AMB-1, MSR-1, and MS-1 (Baumgartner et al. 2013; Fdez-Gubieda et al. 2013). However, a recent study using Mössbauer spectroscopy and a *Ms. gryphiswaldense* strain MSR-1 mutant, with deletions in ferritin-like genes, proposed that ferritin and ferritin-like proteins are not required for magnetosome formation in this strain, being more related to oxidative stress resistance (Uebe et al. 2019). In this approach, the mutant strain synthetized magnetite in the same manner as the wild type. Therefore, this finding has raised a new discussion about the biomineralization pathway in magnetotactic bacteria. It is important to point out that most studies still focus on the genus *Magnetospirillum* as a biomineralization model. The mutant specimens obtained by genetic system manipulation of the magnetosome gene cluster are useful tools to understand the process. Nevertheless, the isolation, cultivation, and genetic manipulation of magnetotactic bacteria belonging to other taxa are essential to improve the knowledge on magnetosome biomineralization.

5.2 *Morphology and Crystalline Habits of Magnetite Magnetosomes*

The habits or morphologies of magnetite crystals that occur in magnetosomes vary significantly. However, it is widely accepted that the crystal shape is consistent for a given bacterial species or strain (Bazylinski et al. 1994; Bazylinski and Frankel 2004). Three general crystal morphology classes have been reported for magnetite magnetosomes. The first type is cubic or cubo-octahedral (Fig. 3a) (Balkwill et al. 1980; Mann et al. 1990). This is the simplest type of magnetosome crystal and shows the isotropic cubic geometry characteristic of abiogenic magnetite. The second type is elongated hexa- or octahedral, frequently labeled as “prismatic” (Fig. 3b). This is a type of crystal that assumes the shape of truncated hexagonal prisms, and has been reported in a variety of magnetotactic cells (Lins and Farina 1998; Kopp and

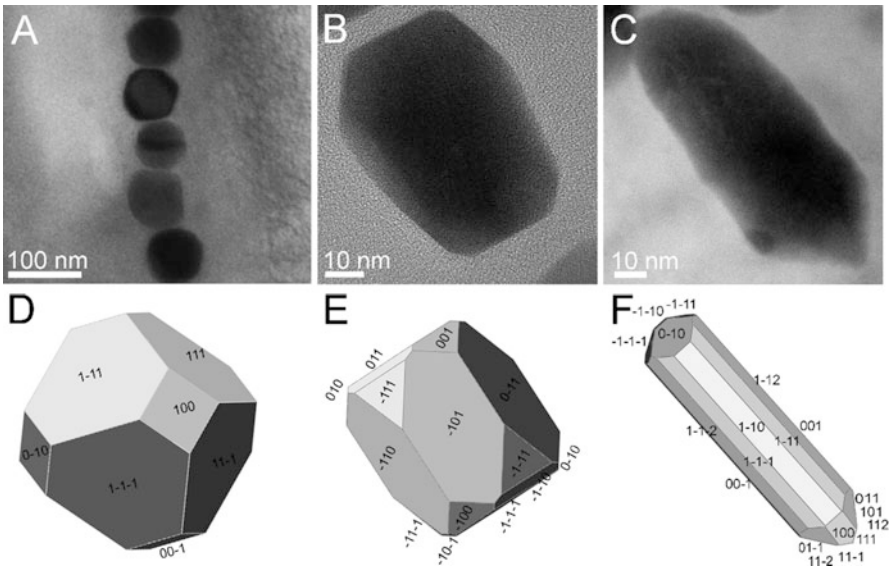

Fig. 3 Conventional and high-resolution transmission electron microscopy images of three general classes of crystal shapes and respective idealized models. (**a**) Chain of cubo-octahedral crystals. (**b**) Elongated prismatic, hexa-, or octahedral crystals. (**c**) An example of anisotropic crystal. (**d–f**) Idealized models for the crystals in (**a**), (**b**), and (**c**), respectively

Kirschvink 2008). The third type comprises more elongated crystals classified as anisotropic, showing tooth, arrowhead, or bullet shapes, with the wider end usually showing larger faces (Fig. 3c). Curved shapes are rather common (Taylor and Barry 2004; Lefèvre et al. 2011b).

The magnetite has a cubic face-centered, inverse-spinel crystalline structure (spatial group Fd3m) (Palache et al. 1944; Faivre and Zuddas 2006). The idealized morphologies of the magnetosomes are based on combinations of faces {100} (of cube), {110} (of dodecahedron), and {111} (of octahedron), with all possible distortions and elongations (Devouard et al. 1998; Pósfai et al. 2006a; Faivre and Schüler 2008). Most elongated magnetite crystals show elongation direction parallel to the [111] direction, which corresponds to the easy axis of magnetization (Mann et al. 1984; Sparks et al. 1990; Taylor et al. 2001; Lins et al. 2005; Pósfai et al. 2006a). The exceptions are mainly the anisotropic crystals, which are elongated along the [112] (Mann et al. 1987; Taylor et al. 2001), [100], (Taylor et al. 2001; Lins et al. 2007; Lefèvre et al. 2011b), or [110] directions (Taylor and Barry 2004; Lefèvre et al. 2011b).

5.3 *Defects and Twin Crystals in Magnetite Magnetosomes*

The magnetite crystals in magnetosomes generally display high structural perfection (Meldrum et al. 1993a, b; Bazylinski et al. 1994). However, some defects and twin crystals are observed in both cultured and uncultured bacterial strains (Devouard et al. 1998; Taylor et al. 2001; Zhang et al. 2017; Abreu et al. 2018). The frequency of these crystalline defects varies from strain to strain, and the proportion of twins appears to be significantly higher in some cells compared to others within the same strain. Besides twinned crystals (Fig. 4), there are defects classified as stacking faults, edge dislocations, irregular edges (Fig. 5), and subgrain boundaries (Taylor et al. 2001; Moisescu et al. 2014).

Whereas in some morphotypes of magnetotactic bacteria about 1% of all magnetite crystals are twins, in others this value reaches approximately 70% (Pósfai et al. 2006a). These imperfections usually occur perpendicular to the chain axis, and the

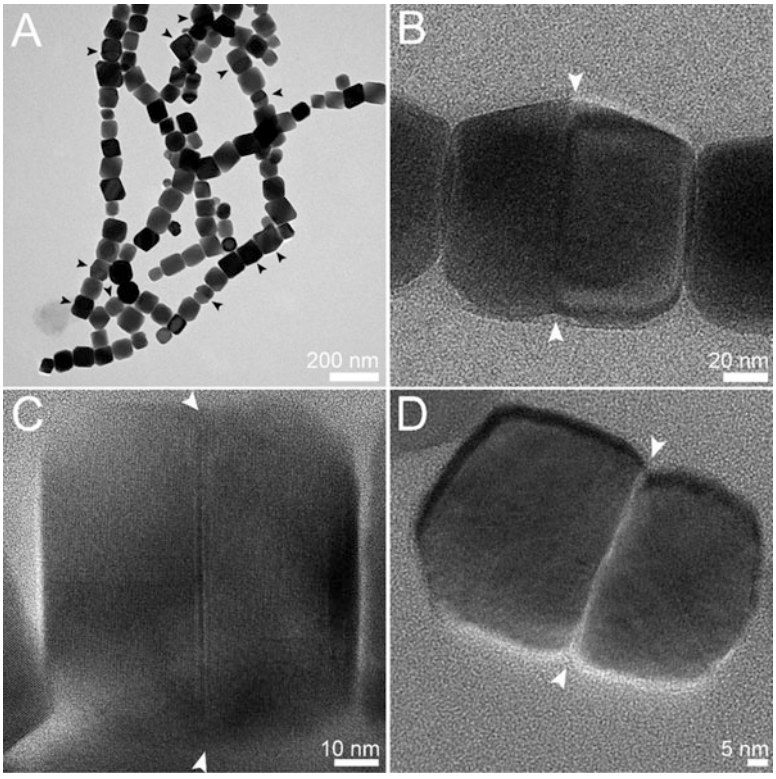

Fig. 4 Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of *Magnetofaba australis* strain IT-1 twin crystals. (**a**) Purified magnetosome chains displaying several twins (arrowheads). (**b–d**) HRTEM images showing twin crystals in detail. The crystals exhibit twin contact planes (arrowheads), all parallel to the (111) planes. Note reentrant angles at the twinning planes (white arrowheads)

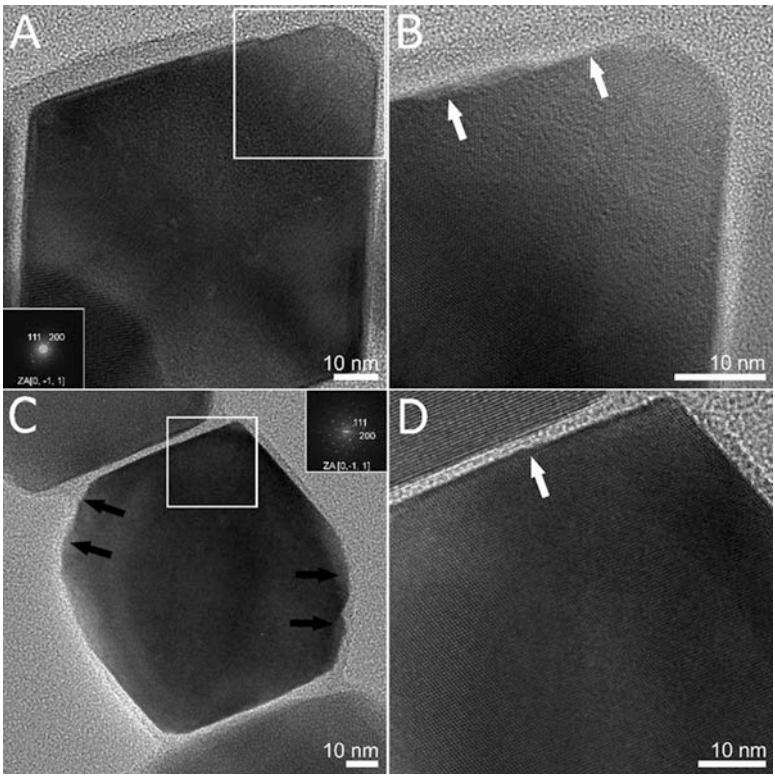

Fig. 5 High-resolution transmission electron microscopy images of cubo-octahedral magnetite from *Magnetofaba australis* strain IT-1 magnetosomes showing some crystalline defects. (**a**) Crystal containing some edge dislocation failures (square). Insert shows the fast Fourier transform (FFT) of the image. (**b**) Higher magnification of the area enclosed in the square in (**a**) showing in detail some edge dislocation failures (arrows). (**c**) Crystal with irregular edges (black arrows) and edge dislocation (square). Insert shows the FFT obtained from this image. (**d**) Higher magnification of the area enclosed in the square in (**c**) showing one edge dislocation (arrow)

twins are rotated by 180° around the [111] direction. Thus, they are not expected to affect the crystal magnetic induction direction, since the magnetite easy axis of magnetization is in the [111] direction (Dunlop and Özdemir 1997; Devouard et al. 1998). Other crystallographic defects, however, can reduce the particle's magnetic moment (Moisescu et al. 2014). It is unknown which physical or chemical parameters govern the formation of twinned crystals in magnetosomes. It is recognized that culture media variations result in different proportions of defective crystals (Moisescu et al. 2014). For example, increasing O_2 concentrations led to enlarged numbers of twin crystals in *Ms. magneticum* AMB-1 (Li and Pan 2012). Changes in some genes can increase twin crystals and defect frequency, for example, the deletion of the *mamZ* in strain AMB-1 mutants promoted reduction in crystal size and an increase in twinning frequency (Raschdorf et al. 2013).

5.4 Chemical Impurities in Magnetite Magnetosomes

In general, magnetite in magnetosomes presents a high chemical purity degree (Amor et al. 2015), as compared to nonbiological natural magnetite, which usually contain trace elements at concentrations >100 ppm, such as Al, Co, Cr, Cu, Ga, Mg, Mn, Ni, Si, Sn, Ti, V, W, and Zn (Clark and Evans 1997; Boutroy et al. 2014). Such chemical purity could indicate a high level of genetic control on magnetite biomineralization in magnetosomes and has been suggested as a biomarker (Thomas-Keprta et al. 2000; Amor et al. 2015). Careful analysis showed that, in fact, most elements were at least 100 times less concentrated in magnetite produced by *Ms. magneticum* AMB-1 than in synthetic crystals. Only Sn and Mo were more concentrated in magnetite magnetosomes than in synthetic magnetite, whereas Ba, Bi, Cd, Ce, Co, Cr, Cu, La, Li, Mn, Ni, Pb, Sr, Ti, Y, and Zn were depleted in magnetosomes. Cs, As, and Ca apparently behave similarly in both biogenic and abiogenic magnetites (Amor et al. 2015).

Supplementation of culture media or microcosms where magnetotactic bacteria grew led to magnetite magnetosomes containing around 1 atom% Co (Staniland et al. 2008; Tanaka et al. 2012; Muñoz et al. 2020), Mn (Keim et al. 2009; Tanaka et al. 2012; Prozorov et al. 2014; Marcano et al. 2020; Muñoz et al. 2020), or Zn (Muñoz et al. 2020) in the crystalline structure of magnetite. Some metals, for example, Ni, Ru, V, and Zn, were added to the culture media at concentrations comparable to those of iron but were not incorporated into the *Magnetospirillum* spp. magnetosome crystal lattice (Tanaka et al. 2012; Prozorov et al. 2014). On the other hand, Sm and Cu were found in presumably amorphous phases associated with magnetosome surfaces (Shimoshige et al. 2017; Muñoz et al. 2020). The thin layer of amorphous Sm_2O_3 layer deposited on the surfaces of magnetosomes led to decrease in saturation magnetization and increase in coercivity, even though the magnetosome cores remained pure magnetite, as confirmed by the Verwey transition temperature, which remained at about 100K (Shimoshige et al. 2017).

Depending on concentration, trace elements such as Co, La, Mn, Ni, Ti, and Zn can change the magnetic properties of synthetic magnetite, including coercivity, the saturation magnetization, and the Verwey transition temperature (Kakol et al. 1994; Saravanan et al. 2002; Lelis et al. 2003; Zélis et al. 2013; Rayan et al. 2019). The saturation magnetization is related to the magnetic moment of magnetosomes and, consequently, to magnetotaxis efficiency. In *Magnetospirillum* spp. magnetosomes, incorporation of Co and Mn to surface layers or the bulk crystal led to changes in coercivity (Staniland et al. 2008; Tanaka et al. 2012; Marcano et al. 2020), whereas Cu and Mn incorporated to the crystal lattice reduced the Verwey transition temperature (Tanaka et al. 2012; Prozorov et al. 2014; Marcano et al. 2020), and both Mn and Sm, either in the bulk crystal or in an surface phase, changed the saturation magnetization (Prozorov et al. 2014; Shimoshige et al. 2017; Marcano et al. 2020).

At concentrations approaching those of iron in the growth media (in the μM/L range), Co(II), Cu(II), Ni(II), and Zn(II) led to decreased cell growth and magnetosome numbers per cell in *Magnetospirillum* spp. (Tanaka et al. 2012;

Muñoz et al. 2020). Muñoz et al. (2020) showed that *Ms. gryphiswaldense* MSR-1 containing magnetosomes were more resistant to Co, Cu, Mn, Ni, and Zn as compared to the same strain that did not produce magnetosomes due to the lack of iron in the growth medium. In their experiments, only Co, Mn, and Zn were incorporated into the crystalline core of magnetosomes, and in small amounts relatively to other cellular structures, indicating that metal incorporation is not the main pathway by which magnetosomes decrease metal toxicity (Muñoz et al. 2020). Maybe metal toxicity increased due to the lack of iron in the growth medium of bacteria without magnetosomes, leading to increased metal/Fe ratios and increased transportation of these metals into the cytoplasm. Accordingly, Tanaka et al. (2012) proposed that Co and Mn entered passively in the cells of *Ms. magneticum* AMB-1 and were inadvertently incorporated in the magnetosome magnetite core.

5.5 Greigite Magnetosomes

Greigite (Fe_3S_4) magnetosomes were described in the 1990s in magnetotactic bacteria from marine environments, estuaries, salt marshes (Farina et al. 1990; Mann et al. 1990; Heywood et al. 1990; Heywood et al. 1991), and, more recently, freshwater (Lefèvre et al. 2011a; Wang et al. 2013). Until this moment, all known greigite-producing microorganisms described are affiliated with the *Deltaproteobacteria* class (DeLong et al. 1993; Abreu et al. 2007; Descamps et al. 2017), although genomic analysis indicates that some members of *Latescibacteria* and *Planctomycetes* may synthetize greigite magnetosomes (Lin and Pan 2014; Lin et al. 2017; Lin et al. 2018). Two general greigite-forming well-studied morphotypes of magnetotactic microorganisms are described: the magnetotactic multicellular prokaryotes (MMPs) and rod-shaped bacteria (Pósfai et al. 1998a, b; Abreu et al. 2007; Lefèvre et al. 2011a; Kolinko et al. 2014). Figure 6 shows some cells of an uncultured MMP and their greigite magnetosomes displaying the characteristic irregular morphologies and blotchy diffraction contrast previously described (Pósfai et al. 1998a).

Greigite is ferrimagnetic and isostructural to magnetite. Currently, it is not known if the greigite easy axis for magnetization is the [111] or the [100] crystallographic direction (Muxworthy et al. 2013; Winklhofer et al. 2014). The size range of greigite crystals from magnetotactic microorganisms lies within the theoretical single-domain size range (Muxworthy et al. 2013). High-resolution images of the crystalline structure of several magnetosomes suggested that greigite crystals form through a series of solid-state transformations, which converts sphalerite-type cubic FeS to mackinawite (tetragonal FeS), and then to greigite (cubic Fe_3S_4). Despite the fact that cubic FeS and mackinawite magnetosomes are not permanent magnets, they are arranged in chains, and their long axis is aligned along the chain axis before they become ferrimagnetic greigite, indicating strict biological control on both chain arrangement and crystallographic alignment relative to the chain axis (Pósfai et al. 1998a, b).

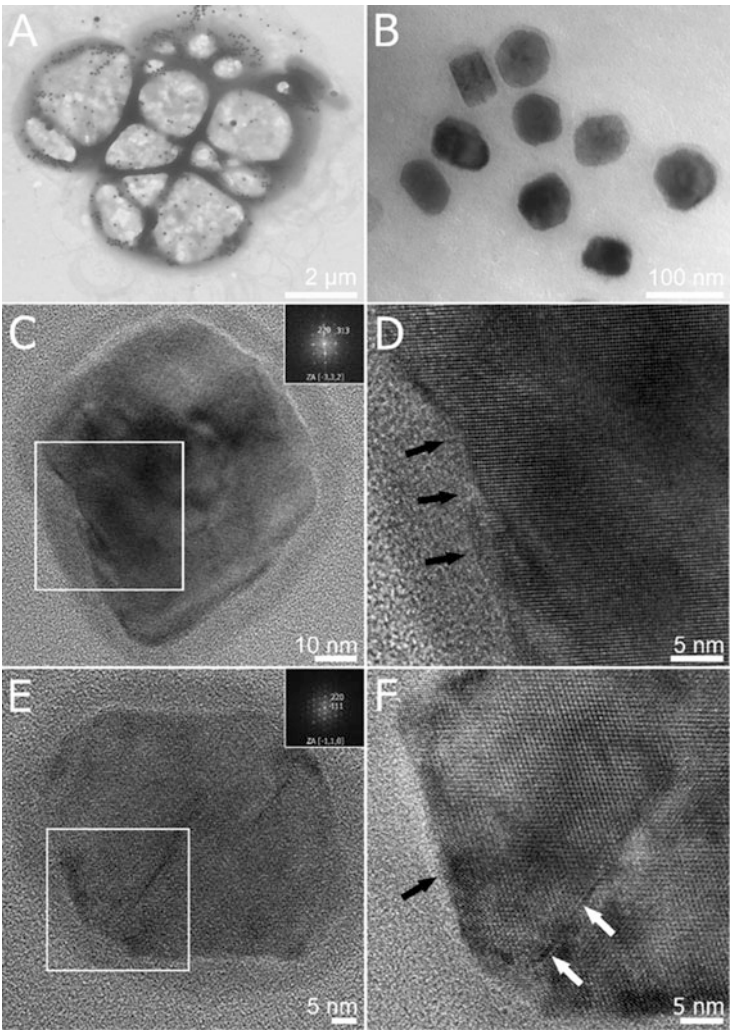

Fig. 6 Uncultured magnetotactic multicellular prokaryote (MMP) and its iron sulfide magnetosomes. (**a–b**) Conventional transmission electron microscopy, whole mounts; (**c–f**) high-resolution transmission electron microscopy. (**a**) Some cells showing magnetosomes (small dark dots), flagella (bottom right), and lipid globules (translucent structures). (**b**) Isolated greigite magnetosomes coated by amorphous layers. Note the irregular shapes, the rough borders, and the blotchy appearance of the crystals. (**c**) Crystal with irregular edges. Insert shows the fast Fourier transform (FFT) of the image. The square delimits the area enlarged in (**d**). (**d**) Higher magnification of the area enclosed in the square in (**c**) showing in detail some irregular edges (black arrows). (**e**) Crystal with irregular edges and stacking faults (square). Insert shows the FFT of the image. (**f**) Higher magnification of the area in the square in (**e**) showing stacking faults (white arrows) and irregular edge contour (black arrow). Note that the frequency of defects in greigite crystals is noticeably higher than usually found in magnetite magnetosomes

An iron-oxygen amorphous phase is frequently observed coating iron sulfide magnetosomes (Farina et al. 1990; Lins and Farina 2001; Kasama et al. 2006b). Kasama et al. (2006b) suggested that this Fe-O amorphous phase results from sample oxidation, but we have observed them also in freshly prepared samples. Lins and Farina (2001) proposed that this Fe-O amorphous phase could be a sink for excess iron atoms resulting from solid-state transformation of mackinawite (FeS) to greigite (Fe_3S_4). During transformation, part of the Fe(II) in mackinawite must be oxidized to Fe(III), and, if the sulfur framework is maintained, some iron atoms must leave the crystal lattice (Lins and Farina 2001).

Two habits of greigite magnetosomes have been identified: (1) equidimensional cubo-octahedral and (2) cubic to parallelepipedal crystals elongated along the [100] direction (Heywood et al. 1990; Heywood et al. 1991; Pósfai et al. 1998a). On the other hand, Kasama et al. (2006b) found variable morphologies and no preferred crystallographic orientation in the greigite crystals of magnetotactic rods. No preferred orientation relative to the chain axis was observed, and magnetosome chains contained some apparently nonmagnetic, misaligned crystals. These rods probably have less control over the crystal biomineralization and chain organization as compared to microorganisms producing magnetite crystals (Kasama et al. 2006b).

High-resolution transmission electron microscopy (HRTEM) analysis identified structural defects like stacking faults, dislocations, undefined faces, thickness variations, and planar defects along (222) planes, along with surface steps and irregularities (Heywood et al. 1991; Pósfai et al. 1998a, b, 2006a; Kasama et al. 2006b). Figure 6 shows greigite crystals containing irregular edges and stacking faults. The defects in the crystalline core are assumed to be associated with the conversion of mackinawite into greigite and would demonstrate the reduced biological control on this step (Pósfai et al. 1998a, b, 2006a; Kasama et al. 2006b). Some greigite magnetosomes appear to be formed by smaller crystals aggregated in the same crystallographic orientation, as a single-crystal-like aggregate (Kasama et al. 2006b; Pósfai et al. 2006a), whereas spinel-type twins are not observed (Pósfai et al. 2006a).

The chemical purity varies depending on the environment where the microorganisms grew, with some magnetosome crystals showing up to ~10 atom% Cu homogeneously distributed in the crystal lattice (Bazylinski et al. 1993; Pósfai et al. 1998a). The precursor phases mackinawite and cubic FeS were also shown to contain Cu, indicating that Cu would be incorporated in the initial cubic FeS crystals and maintained through the solid-state transformation series to mackinawite and greigite (Pósfai et al. 1998a).

Some magnetotactic bacteria are also capable of synthesizing both greigite and magnetite. In these cells, magnetite crystals are always anisotropic, arrowhead, or bullet-shaped (Kasama et al. 2006b; Lins et al. 2007; Lefèvre et al. 2011a; Wang et al. 2013; Descamps et al. 2017). An example of bacteria producing magnetosomes of both greigite and magnetite is *Desulfamplus magnetovallimortis* strain BW-1, the only greigite-producing strain of magnetotactic bacteria available in pure culture (Lefèvre et al. 2011a; Descamps et al. 2017).

6 Characterization of the Magnetic Properties of Magnetosomes

To study the magnetic properties of magnetosomes, the use of magnetometry techniques sensitive enough to detect the magnetization of magnetic nanoparticles is common. Typical studies by magnetometry include the analysis of the curve of magnetization, or magnetic moment, as a function of the magnetic field (Fig. 7). This curve presents hysteresis behavior for single-domain magnetic nanoparticles or for superparamagnetic nanoparticles in a blocked state. It can be considered as a magnetic memory: in the initial state, the magnetization is almost zero for $B = 0$; the magnetization starts to grow with the magnetic field until it reaches a saturation value (the saturation magnetization, M_S). When the magnetic field decreases, the magnetization does not follow the same path to return from saturation, and when $B = 0$, the magnetization gets a value different from zero (the remanence magnetization, M_r). The curve continues to decrease for negative magnetic field values, and the magnetization will be null for a specific magnetic field: the coercive magnetic field (B_C). All these parameters are indicated in Fig. 7.

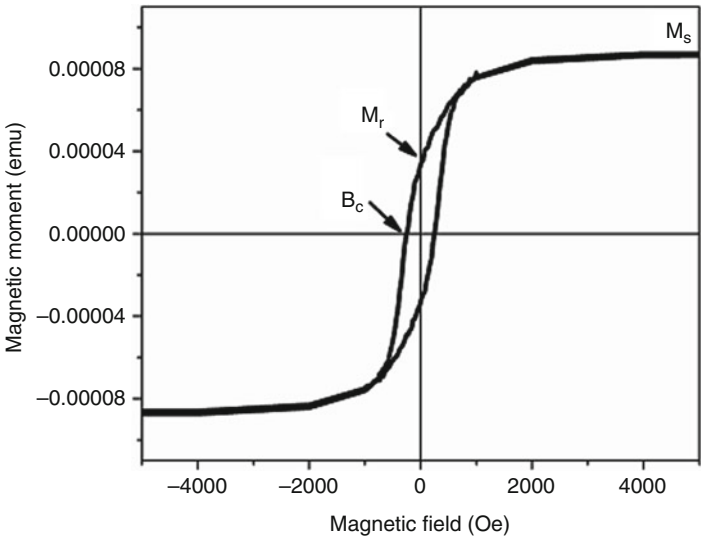

Fig. 7 Magnetic moment versus magnetic field curve showing hysteresis in a sample of magnetosomes from *Magnetovibrio blakemorei* strain MV-1. They were obtained from old culture samples supplied by Dr. Ulysses Lins in 2015. Magnetic nanoparticles were dried on Teflon tape, and the magnetization curve was measured in a SQUID magnetometer (Quantum Design) at ambient temperature. The saturation magnetization (M_S), the remanence magnetization (M_r), and the coercivity or coercive field (B_C) are indicated in the figure. The units of the magnetic moment are electromagnetic units (1 emu $= 10^{-3}$ A m^2), and those of the magnetic field are oersted (1 Oe $= 10^{-4}$ T)

Table 3 Magnetic parameters obtained from the magnetization versus magnetic field curves of magnetosomes

Microorganism strain	M_s	M_r	B_c	B_{cr}	M_r/M_s	B_{cr}/B_c	T_v	References
MSR-1	60	10	7.5	–	0.17	-	-	Han et al. (2008)
MSR-1	0.3	0.11	9.6	15.2	0.37	1.58	-	Zhang and Pan (2018)
MS-1	0.9	-	23	-	0.5	-	97	Yiriletu and Iwasa (2015)
M.g WT	-	-	16.9	18.9	0.54	1.12	102	Katzmann et al. (2013)
A. mag	-	-	26.7	27.6	0.53	1.02	-	Moskowitz et al. (1988)
MV-1a	-	-	-	-	0.49	1.1	110	Moskowitz et al. (1993)
MS-1	-	-	-	-	0.44	1.1	101	Moskowitz et al. (1993)
IT-1	-	-	12.1	26.3	0.18	2.2	110	Personal communication
MV-1b	-	-	25	33.3	0.38	1.3	95	Personal communication
MYR-1	-	-	54.5	61	0.59	1.12	100	Li et al. (2010)
AMB-1	-	-	14.2	18.2	0.45	1.28	104	Li et al. (2009)
RS-1 fum	0.0176	-	46.7	-	0.44	-	86	Pósfai et al. (2006b)
RS-1 sulf	0.0363	-	35.8	-	0.34	-	86	Pósfai et al. (2006b)

M_S = saturation magnetization (Am^2/kg); M_r = remanence magnetization (Am^2/kg); B_c = coercive field (mT); B_{cr} = remanent coercive field (mT); T_V = Verwey temperature (K); data for *Magnetofaba australis* strain IT-1 and *Magnetovibrio blakemorei* strain MV-1 (MV-1b) were obtained by D.A.-A. using a SQUID magnetometer (Quantum Design)

Another characteristic parameter is the remanent coercive field B_{CR}. For randomly oriented noninteracting single-domain particles with uniaxial anisotropy, it is expected that $M_r/M_S \approx 0.5$. Table 3 shows the values for M_r/M_S and B_{CR}/B_C published in the literature for several magnetotactic bacteria. Using those parameters, the Day plot (Kumari et al. 2015) can be constructed to catalog the magnetic material analyzed as magnetic stable single domains, pseudo-single domains, and superparamagnetic or multi-domains. Figure 8 shows the Day plot for the values in Table 3. It is interesting to observe that those magnetic parameters permit the identification of magnetic single domains without the direct observation of the magnetic nanoparticles.

In addition, it is possible to identify the presence of magnetite using magnetic measurements due to a low-temperature phase transition known as the Verwey transition at approximately 124 K (Bohra et al. 2019). The measurement of zero field cooling (ZFC) and field cooling (FC) thermoremanence or magnetization permits the identification of this transition. Table 3 shows the values of the temperature of the Verwey transition in some samples of magnetotactic bacteria, and Fig. 9 shows an example of ZFC and FC magnetization. For magnetotactic bacteria and

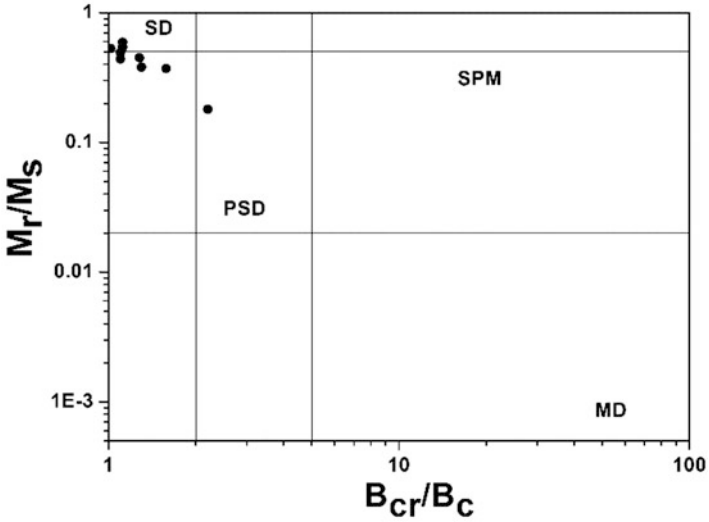

Fig. 8 Day plot (M_r/M_S versus B_{CR}/B_C). Data for different magnetotactic bacteria were obtained in the literature and compiled in Table 3. All points fell the SD region, except for one point in PSD region. This point corresponds to data from *Magnetofaba australis* IT-1. As data were obtained from old samples, the magnetosome chains may be disorganized, leading to magnetic PSD behavior. *SD* single domain, *SPM* superparamagnetic, *PSD* pseudo-single domain, *MD* multi-domain

magnetosomes, the Verwey transition is at approximately 100 K, which is a different value than that temperature measured for bulk magnetite. It has been proposed that a Verwey transition at approximately 100 K is an indication of the presence of magnetosomes in the measured samples (Pan et al. 2005).

Another feature that permits the identification of magnetosomes by magnetic techniques is their organization in chains. Even when the cell envelope of the magnetotactic microorganisms is lysed, the chain organization can be maintained for long time periods. This organization can be observed as a unique feature in first-order reversal curves (FORC) obtained from the hysteresis curves from magnetosomes, and also in ferromagnetic resonance (FMR) spectra.

A FORC is obtained by saturating a sample in a field B_{SAT}, then decreasing the field until a reversal field B_A, and finally sweeping the field back to B_{SAT} in a series of regular steps B_B. This process is repeated for several values of B_A producing several FORCs and yielding the magnetization as a function of B_A and B_B: $M(B_A, B_B)$. The FORC distribution $\rho(B_A,B_B)$ is defined as the mixed partial derivative of $M(B_A,B_B)$, and a FORC diagram is a contour plot of $\rho(B_A,B_B)$ mapped to a different set of coordinates: $B_C = (B_B - B_A)/2$ and $B_U = (B_B + B_A)/2$, where B_C is the distribution of coercive fields, also called switching fields, and B_U is the distribution of interaction fields. Figure 10 shows a typical FORC diagram of magnetosome chains, showing a narrow distribution in the vertical B_U axis and elongation along the horizontal B_C axis and indicating single-domain particles in a chain arrangement

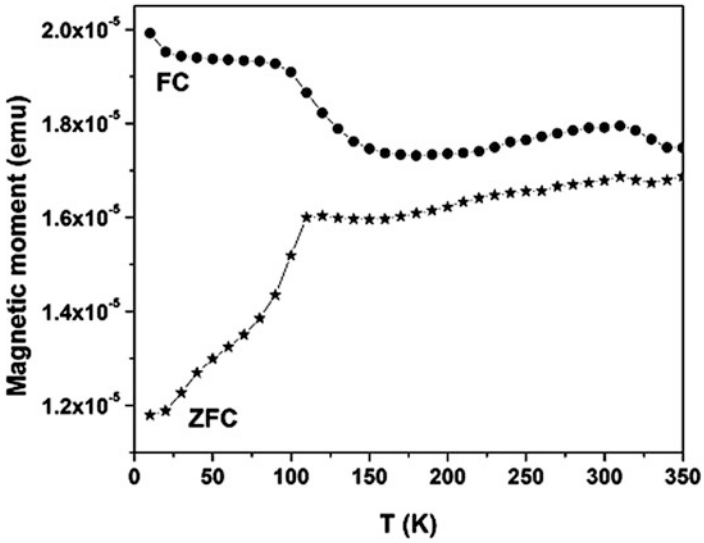

Fig. 9 Zero field cooling (ZFC) and field cooling (FC) magnetization curves as a function of the absolute temperature. Note the changes in the curves at about 100K. Magnetosomes were obtained from an old sample of a culture of *Magnetofaba australis* strain IT-1 supplied by Dr. Ulysses Lins in 2015. Magnetic nanoparticles were dried on Teflon tape, and the magnetization curves were measured in a SQUID magnetometer (*Quantum Design*). For the ZFC curve, the samples were cooled from 300 K to 5 K at zero magnetic field; at 5 K, a magnetic field of 100 Oe was applied, and the magnetization was measured while the temperature increased up to 350 K. For the FC curve, the sample was cooled in the presence of an applied magnetic field of 100 Oe

with weak interactions (Jovane et al. 2012; Katzmann et al. 2013; Zhang and Pan 2018). The mutant ΔmamJ of *M. gryphiswaldense* is not able to organize the magnetosomes in chains, and they organize in clumps, producing a FORC diagram different from that in Fig. 10, showing a region composed of two peaks symmetrical in the B_U axis that has been previously described in pseudo-single-domain PSD magnetite particles (Katzmann et al. 2013).

Ferromagnetic resonance (FMR) is the application of the electron paramagnetic resonance (EPR) technique on permanent magnetic materials. FMR spectroscopy detects coupled spins of a magnetically ordered phase. In that case, the applied magnetic field excites the precession of the total magnetic moment around a local magnetic field. Eventually, the magnetization aligns to the magnetic field direction because of the relaxation process. The resonance condition is fulfilled when the frequency of the microwave radiation coincides with the precessional frequency, and then the microwave power is absorbed by the magnetic material (Faivre et al. 2010). The resonance condition can be written as

$$hf = g_{\text{eff}}\mu_B \cdot B_{\text{App}}$$

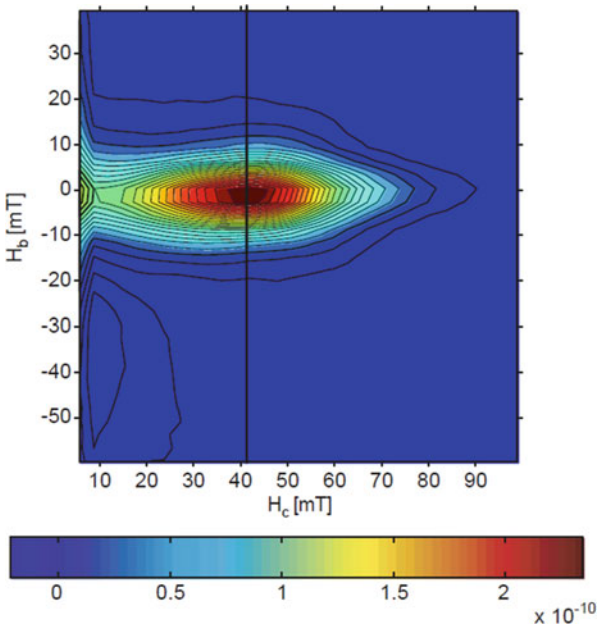

Fig. 10 FORC diagram of magnetotactic bacteria samples collected from Lake Chiemsee, Germany, composed mainly of wild-type cocci, the rod *Magnetobacterium bavaricum*, and a wild-type magnetotactic vibrio. The FORC distribution is bimodal with a broad maximum centered at 42 mT and a sharper peak toward the $Hc = 0$ axis. The sharper peak is attributed to SPM magnetosomes, as they typically occur at the chain ends. Magnetization values are indicated in the color scale bar. Figure reprinted from Earth and Planetary Science Letters Vol. 237, Pan Y, Petersen N, Winklhofer M, et al. "Rock magnetic properties of uncultured magnetotactic bacteria", Pages 311–325, Copyright 2005, with permission from Elsevier

where h is the Planck constant, f is the microwave radiation frequency, g_{eff} is the effective splitting factor, μ_B is the Bohr magneton and B_{App} is the applied magnetic field. Figure 11a shows a typical FMR spectrum. It is common to analyze the derivative of the absorption spectrum. The parameters used to characterize the FMR spectrum are g_{eff}, B_{res}, ΔB, and A (Figure 11a). Regarding the values of g_{eff}, it is observed that $g_{\text{eff}} \approx 2$ is characteristic of superparamagnetic particles showing narrow ΔB, $g_{\text{eff}} > 2$ is characteristic of magnetite samples with a dominant magnetocrystalline anisotropy field, and $g_{\text{eff}} < 2$ is characteristic of samples with a prevalent shape anisotropy field caused by the organization of the particles in chains (Faivre et al. 2010). The values of parameter A are related to the magnetic anisotropy: $A = 1$ corresponds to samples with no significant anisotropy, $A > 1$ is common in magnetite at room temperature having a cubic negative magnetocrystalline anisotropy, and $A < 1$ is related to elongated single-domain magnetite particles or to magnetite particles aligned along their easy axes forming a dominant shape anisotropy, where a positive uniaxial anisotropy can be observed (Faivre et al. 2010). Figure 11b shows an example of an FMR spectrum for magnetosome chains from

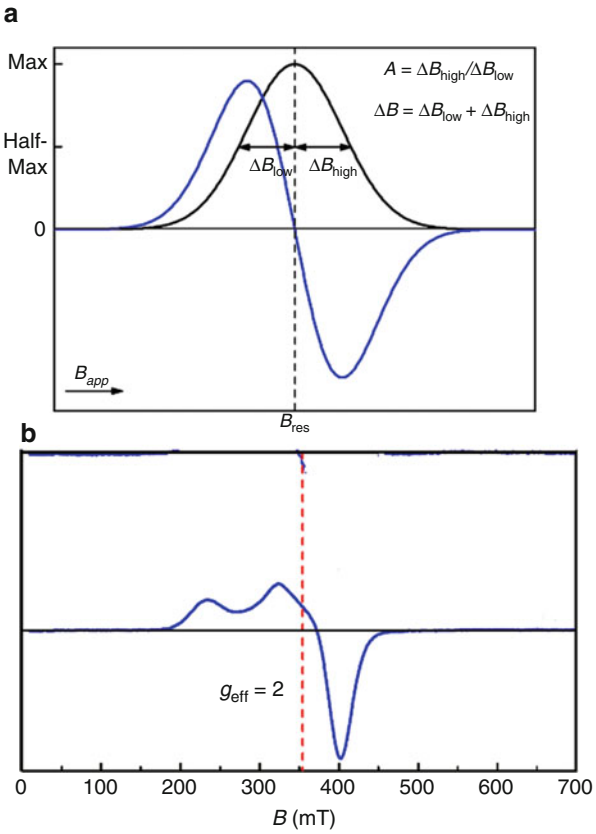

Fig. 11 (**a**) Absorption spectrum (black line) and first derivative spectrum (blue line). The dashed line defines the maximum resonance field (Bres). Parameters ΔB and A are defined in the figure. (**b**) Typical first derivative FMR spectra of magnetosome chains (X band spectra with a microwave frequency of 9.81 GHz). Magnetosomes were obtained from *Magnetospirillum gryphiswaldense* MSR-1. The dashed red line indicates the calculated position of $g_{eff} = 2$. The parameters calculated from the spectrum are $B_{res} = 371.8$ mT, $g_{eff} = 1.89$, $\Delta B = 167.4$ mT, and $A = 0.41$. Figure reprinted from Biophysical Journal Vol. 99 (4), Faivre D, Fischer A, Garcia-Rubio I, et al. "Development of cellular magnetic dipoles in magnetotactic bacteria", Pages 1268–1273, Copyright 2010, with permission from the Biophysical Society

Ms. gryphiswaldense MSR-1. The high-field peak has the following parameters: $g_{eff} = 1.89$, $B_{res} = 372$ mT, $\Delta B = 167.4$ mT, and $A = 0.41$. The low-field peak is related to the assembly of magnetosomes into chains with pronounced uniaxial anisotropy. Magnetosome chains can be identified with FMR spectra similar to those in Fig. 11b obtained from sediments and from different strains of magnetotactic bacteria (Weiss et al. 2004; Kopp et al. 2006; Fischer et al. 2008).

All these techniques together (hysteresis curves, ZFC and FC thermoremanence, FORC curves, FMR spectra) are powerful analytical tools to identify biogenic magnetite nanoparticles organized in chains.

After death of magnetotactic bacteria, magnetosomes may be preserved in suitable environments, contributing to sedimentary magnetism. Magnetofossils (fossil magnetosomes) have been identified in numerous sediments as important magnetic carriers (Chang et al. 1989; Kopp et al. 2006; Kopp and Kirschvink 2008; Zhang and Pan 2018). A study carried out by Mao et al. (2014), where the sedimentation process was simulated in a micro environment with magnetotactic bacteria, showed that natural remanence magnetization in sediments is mainly obtained from magnetosome chains, with the sediment magnetization direction nearly parallel to that of the ambient magnetic field and approximately 90% of the acquired magnetization being due to single-domain magnetite nanoparticles from bacterial origin. The understanding of the ancient geomagnetic field through the study of sediment magnetization is connected to our understanding of the biomineralization of magnetic nanoparticles by magnetotactic bacteria, which are the main providers of magnetic material to natural sediments.

7 Genes and Proteins Associated with the Magnetosomes

Due to the strict genetic control over the magnetosome biomineralization in magnetosomes, the inorganic portion of magnetosomes has very particular properties such as specific shape and a narrow size range for each bacterial species, high chemical purity, and limited crystallographic defects (Matsuda et al. 1983; Mann et al. 1984; Bazylinski et al. 1995; Amor et al. 2015). Controlling the particle size, the magnetotactic microorganisms optimize the magnetic dipole moment of each magnetosome (Bazylinski et al. 1995). Indeed, most crystals are 35–120 nm in diameter, which corresponds to the size range for stable single magnetic domains, meaning that they are permanently magnetic at room temperature (Butler and Banerjee 1975; Moskowitz 1995; Albrecht et al. 2005). A few exceptions were reported, consisting of large crystals that behave as monodomains when arranged in chains, and as two- or multi-domains when the chain arrangement is lost (Spring et al. 1998; McCartney et al. 2001; Lins et al. 2005).

Magnetotactic bacteria have specific genes for the induction and control of the formation of magnetosomes. These genes are collectively known as *mam* (MAgnetosome Membrane) and *mms* (Magnetosome Membrane Specific), which are organized in groups clustered within the genomes of magnetotactic bacteria (Jogler and Schüler 2009). These genes encode several specific proteins involved in magnetosome biomineralization, some of which have been identified as being an integral or peripheral part of the magnetosome membrane (Grünberg et al. 2004; Tanaka et al. 2006; Scheffel et al. 2008; Murat et al. 2010; Quinlan et al. 2011). They control the synthesis of magnetite particles by creating an environment that facilitates the nucleation and growth of immature crystals in a preferential orientation (Bazylinski and Frankel 2004; Tanaka et al. 2006). Other genes called *mtx* (MagneTotaXis-related proteins) and *mad* (Magnetosome-Associated *Deltaproteobacteria*) are also involved in the biomineralization process. However,

the *mtx* genes and some *mam* genes do not synthesize proteins that are part of the membrane magnetosome, and little is known about the mad genes that are specific to *Deltaproteobacteria* and *Nitrospirae* (Richter et al. 2007; Lefèvre et al. 2013a; Rahn-Lee and Komeili 2013).

In the past decade, technological advances led to significant progress in analyzing the molecular aspects of magnetosome biogenesis. Major advances in understanding the role of magnetosome proteins were based on genetic manipulation experiments, in which gene deletion revealed phenotypic changes in magnetosome synthesis (Murat et al. 2010). In addition, location and structure of proteins are also key points to understand their function in magnetosome formation. Various microscopy and molecular techniques were often used to monitor protein localization and structure, to visualize magnetosome membrane, size, morphology, and subcellular arrangement of magnetic particles. There are currently just over 20 species of magnetotactic bacteria in axenic culture. Despite this, the largest number of magnetosome protein studies use *Ms. gryphiswaldense* strain MSR-1 and *Ms. magneticum* strain AMB-1 as models, restricting the understanding of the magnetosomes' biogenesis process to members of *Alphaproteobacteria* (Arakaki et al. 2016; Lang and Schüler 2008; Lefèvre and Bazylinski 2013; McCausland and Komeili 2020; Murat et al. 2010).

Magnetosome biogenesis in magnetotactic bacteria is intrinsically related to the Mam (magnetosome-associated membrane) and Mms (magnetic particle membrane-specific) proteins, coded by *mam* and *mms* genes, respectively, which are clustered in a chromosomal region called the genomic "Magnetosome Island" (MAI) (Uebe and Schüler 2016). More recently, the term "MAI" has been gradually substituted by "magnetosome gene clusters" (MGCs), because some magnetotactic bacteria do not present a real genomic island harboring magnetosome biomineralization genes (Lin et al. 2018). Ten genes (*mamA*, *mamB*, *mamE*, *mamI*, *mamK*, *mamL*, *mamM, mamO*, *mamP*, and *mamQ*) are conserved in all magnetite producers. Nine of them seem to be conserved in greigite producers, and only *mamL* is absent (Uebe and Schüler 2016; Barber-Zucker and Zarivach 2017). In summary, the major operon *mamAB* is conserved in almost all magnetotactic bacteria, and its genes have key roles in magnetosome formation (Murat et al. 2010). There are other small operons, for instance *mamGFDC*, *mamXY*, *mms6*, and *feoAB* in strains MSR-1 and AMB-1, but they are not ubiquitous in magnetotactic bacteria (Uebe and Schüler 2016; Barber-Zucker and Zarivach 2017).

To date, magnetotactic microorganisms have been described in *Proteobacteria*, *Nitrospirae*, and *Omnitrophica* phyla (Lin et al. 2018). In addition, metagenomic approaches suggest the existence of species of magnetotactic bacteria affiliated also to the *Ca. Latescibacteria* and *Planctomycetes* phyla. Despite this large diversity, the magnetosome biomineralization genes are unique, conserved, and shared among all magnetotactic bacteria despite their large phylogenetical distance (Fig. 12).

The magnetosome biogenesis can be divided into four stages: (1) vesicle formation through invagination of the cell membrane; (2) protein sorting; (3) iron transportation and biomineralization; and (4) alignment of magnetosomes in chains. These stages do not necessarily occur in separate moments (Uebe and Schüler 2016). In terms of location, proteins involved in magnetosome formation are usually

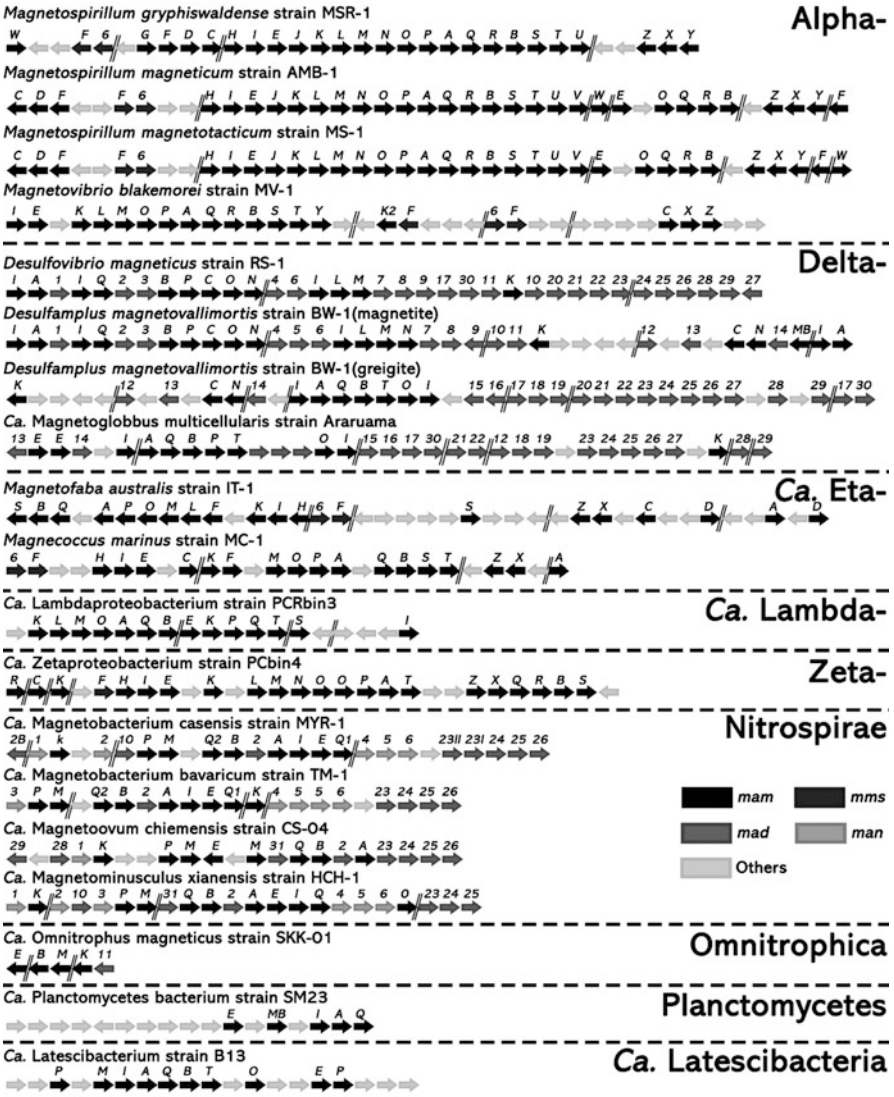

Fig. 12 Magnetosome gene organization in magnetosome gene clusters (MGCs) of cultivated magnetotactic bacteria and metagenome-assembled genomes affiliated to the *Proteobacteria*, *Nitrospirae*, *Omnitrophica*, *Planctomycetes*, and *Ca. Latescibacteria* phyla. Magnetotactic proteobacteria are arranged according to their taxonomic classification. The mam genes are found in all magnetotactic bacteria, whereas the others are restricted to specific taxa, as follows: (i) mms genes, found in proteobacterial genomes (affiliated to the classes *Alpha-*, *Delta-*, *Ca.* Eta-, and *Zetaproteobacteria*); (ii) man genes, observed in genomes affiliated to *Nitrospirae* phylum; and (iii) mad genes, found in genomes affiliated to the *Deltaproteobacteria* class, and to the *Nitrospirae* and *Omnitrophica* phyla. Other genes nonrelated to magnetosome biomineralization also make part of MGCs

classified as belonging to the cytoplasmic membrane (CT), magnetosome membrane (MM), or transmembrane (TM) proteins, although many can be found in different parts of the cell, depending on the biomineralization phase. Their functions are related to vesicle formation from the cell inner membrane, iron trafficking, crystal growth, maturation, and alignment of magnetosome chain. However, dual roles are common, as well as redundant functions (one function performed by more than one protein), making it challenging to describe which protein is essential or not for which function (Amor et al. 2020b; Barber-Zucker et al. 2016; Uebe and Schüler 2016).

Among the genes responsible for the formation of magnetosomes, the *mamAB* operon is preserved in all magnetotactic bacteria described so far and seems to be crucial to magnetosome biomineralization. Some other operons are specific to different taxa, such as the *mamGFDC* and *mms*6 operons, which are only found in magnetotactic bacteria within the *Alphaproteobacteria*. Since this group of magnetotactic bacteria produces cubo-octahedral or elongated prismatic magnetite particles, it is tempting to associate the operons with these crystal morphologies. Size and shape of magnetosome crystals seems to be controlled by the cumulative action of the MamGFDC and Mms proteins in *Ms. gryphiswaldense* MSR-1, although these proteins do not seem to be essential for magnetosome formation (Scheffel et al. 2008). When Mms5, Mms6, Mms7 (MamD), and Mms13 (MamC) were deleted in *Ms. magneticum* AMB-1, the magnetite crystals produced were smaller and defective. This indicates that these proteins probably regulate the size and shape of magnetite in later stages of crystallization and the maturation of magnetite crystals (Arakaki et al. 2014; Uebe and Schüler 2016).

One of the most studied proteins involved in the biomineralization of magnetosomes is MamC (also known as Mms13), which contains two helical transmembrane domains connected by an α-helical loop oriented toward the magnetosome lumen. This loop has structures responsible for a template effect that controls the nucleation and growth of nanoparticles in vitro. Studies with mutants suggested that the connection between the MamC magnetite-interaction loop structure and the charged surfaces of the protein is crucial for magnetite binding, and thus for the size control of the magnetite nanoparticles (Nudelman et al. 2016). Crystals formed by mutants deficient in either *mamC* or the entire *mamGFDC* operon were significantly smaller and less regular with respect to morphology and chain organization (Jogler and Schüler 2009).

MamD, also known as Mms7, contains a LG-repeat motif probably used to bind other proteins, and is tightly attached to the magnetite crystal (Scheffel et al. 2008; Arakaki et al. 2014). The deletion of the gene coding this protein leads to biomineralization of small and elongated magnetite particles, suggesting a function in crystal growth and maturation. Changes in the expression of Mms7 led the magnetosome crystals to change the cubo-octahedral shape to dumbbell or spherical shape (Arakaki et al. 2014), whereas the modulation of Mms7 expression allowed the biomineralization of magnetite crystals with tunable sizes and morphologies (Yamagishi et al. 2016). MamF is another protein associated with the control of crystal size. It is a deeply embedded membrane protein, and, in *Ms. gryphiswaldense* MSR-1 mutants, magnetosome crystals were slightly smaller than in wild type, indicating its role in size control (Scheffel et al. 2008).

Other proteins, such as those encoded by *mamP*, *mamR*, *mamS*, and *mamT* genes, are related to crystal size and shape (Murat et al. 2010). For example, in strain AMB-1 mutants deficient in *mamP*, crystals were mostly small, "flake-like," suggesting that the MamP role in iron redox reactions is also important to control size and shape (Jones et al. 2015; Siponen et al. 2013). Other proteins, like MmsF, Mms5, MamR, and Mms6, seem to participate in crystal maturation (Murat et al. 2010; Lohsse et al. 2014; Rawlings et al. 2014; Arakaki et al. 2014). Indeed, when the gene *mamR* was deleted in *Ms. magneticum* AMB-1, both size and number of magnetosomes were reduced, suggesting a function in magnetite crystal maturation (Murat et al. 2010).

Mms6 is a small acidic protein tightly associated with the surface of bacterial magnetite in *Ms. magneticum* AMB-1 (Amemiya et al. 2007; Arakaki et al. 2010; Staniland and Rawlings 2016). Molecular modelling suggests the existence of specific, multiple sites for binding for ferrous ions in Mms6 (Staniland and Rawlings 2016). In addition, its amphiphilic nature allows it to form aggregates through hydrophobic interactions, forming micelles (Amemiya et al. 2007; Staniland and Rawlings 2016). In vitro experiments showed that Mms6 mediate the formation of cubo-octahedral magnetite crystals, leading to synthesis of uniform magnetic crystals through partial oxidation of ferrous hydroxide (Amemiya et al. 2007; Arakaki et al. 2010). The ability to self-assemble in micelles and to bind ferrous ions makes Mms6 of special interest for synthetic production of biomimetic magnetite crystals (Amemiya et al. 2007; Staniland and Rawlings 2016). In particular, the curvature of Mms6 micelle surfaces would delimit the size of the crystals (Staniland and Rawlings 2016).

The alignment of the magnetosomes into one (or more) chain(s) leads to the sum of the magnetic moments of individual particles. If magnetosome chains are attached to the cell's structural framework, they impart the whole cell a magnetic moment, turning the cell itself into a magnetic dipole, which results in passive alignment of the bacteria to the geomagnetic field. In the cultivated *Magnetospirillum* spp., magnetosome chains are aligned along the long cell axis, based on the interaction of proteins present in the magnetosome membrane (MamJ) with MamK, an actin-like protein that forms dynamic filaments and is required for the magnetosome chain assembly and positioning along the cell long axis (Uebe and Schüler 2016). MamK has also a role in organizing the magnetosome chains during cell division, such that equivalent numbers of magnetosomes are distributed to the two daughter cells (Taoka et al. 2017). Interestingly, MamJ is not conserved in all magnetotactic bacteria, suggesting that there are other mechanisms for magnetosome chain alignment (Bennet et al. 2015).

In addition to the *mam* and *mms* genes, *mad* (magnetosome-associated *Deltaproteobacteria*) and *man* (magnetosome specific to *Nitrospirae*) genes have been described in magnetotactic bacteria affiliated to *Deltaproteobacteria* class or to the *Nitrospirae* and *Omnitrophica* phyla. This suggests that these genes could be associated with greigite and/or bullet-shaped magnetite magnetosome biomineralization (Uebe and Schüler 2016). Studying the proteins involved in the production of bullet shape and greigite magnetosomes has been a great challenge, due to the lack of cultivated strains amenable to molecular manipulations. Despite the diversity described for these organisms, magnetotactic bacteria are microorganisms whose

cultivation is extremely difficult, especially concerning to greigite-producing microorganisms. Therefore, the use of different models that could clarify the role of proteins only seen in *Deltaproteobacteria* and *Nitrospirae* has been delayed by the difficulty of axenic cultivation and genetic manipulation.

Lohsse et al. (2016) showed that the enhanced expression of *mamGFDC*, *mamAB*, *mms6*, and *mamXY* operons in *Ms. gryphiswaldense* strain MSR-1 led to increased magnetosome size and number within the cell. This result is extremely interesting if we consider large-scale production of magnetite nanoparticles for biotechnological approaches. As previously mentioned, magnetosomes are structures that exhibit a narrow size range and characteristic crystal morphology per taxon, which result in stable magnetic single domains (are permanently magnetized at room temperature), and show high chemical purity in standard conditions, but are amenable to doping with Mn and other elements. These characteristics lead to a growing interest in biotechnological applications. Drug delivery, enzyme immobilization, magnetic hyperthermia and contrast enhancement of magnetic resonance imaging, cell separation, DNA recovery or detection, and bioremediation are the most common examples of the current studies in magnetosome application. Size, shape, and composition, especially in medical applications, is of great importance (Kerans et al. 2018; Tanaka et al. 2016; Vargas et al. 2018). Understanding the roles and mechanisms for defining and controlling sizes and shapes can help in the production of "customized" magnetic crystals with the magnetic properties tailored for each application (Peigneux et al. 2016). For this (and other reasons), studies on the diversity, biochemistry, and physiology of magnetotactic bacteria are so essential, not only for the understanding of this diverse group but also for the countless potential biotechnological advances.

Many other *mam* and *mms* genes are involved in the biomineralization process. Here we presented a few studies that shed light on the molecular mechanism for controlled biomineralization of magnetic nanocrystals in magnetotactic bacteria. For detailed information about the genetics of magnetosome biomineralization, as well as organization of magnetosomes in the cell and segregation of magnetosomes during cell division, see Uebe and Schüler (2016).

8 Evolution of Magnetosome Biomineralization

Until recently, the evolution of biomineralization-related genes was completely unknown. The development of DNA sequencing technologies allowed the genomic characterization of both cultured and uncultured species. Initially only magnetite-producing magnetotactic bacteria had their genomes sequenced (Jogler et al. 2009; Schübbe et al. 2009), and genomic comparison of these magnetotactic *Alphaproteobacteria* indicated that horizontal gene transfer played a relevant role in the evolution of magnetite biomineralization (Jogler et al. 2009). However, the genomic sequencing of both uncultured (Abreu et al. 2011) and cultured (Lefèvre et al. 2013a; Lefèvre et al. 2013b) greigite-producing magnetotactic microorganisms brought new insights about the evolution of magnetotactic bacteria.

Nowadays, metagenomic approaches are turning the path of the evolution of magnetosome biomineralization clearer (Lin et al. 2018). According to the recent hypothesis of magnetotactic bacteria gene evolution, we can assume two possible situations: one that the last common ancestor of magnetotactic microorganisms synthesized magnetite magnetosomes and MGC duplication, divergence, loss, or horizontal gene transfer brought up the current scenario of magnetosome biomineralization in the *Bacteria* domain, or that the last common ancestor of all magnetotactic microorganisms produced an unknown mineral and the same events resulted in the current diversity of produced minerals and magnetosome biomineralizing species.

The scarce geological record does not favor any of these hypotheses. The oldest fossil magnetosomes ever found are magnetite crystals 2 billion years old (Chang et al. 1989), when oxygenic photosynthesis was already in place and there were dissolved oxygen in seawater, at least periodically and in certain places, along with anaerobic environments in soils, sediments, and stagnant water (Planavsky et al. 2014).

9 Conclusions

Magnetosome biomineralization is very well-controlled by several proteins working in concert to produce crystals with defined composition, size, shape, and position within the cell. Such strict control results in unique magnetic properties enabling several applications, ranging from sediment paleomagnetism to biotechnology.

Despite the complexity, magnetite biomineralization in magnetosomes is among the best-known examples of biomineralization in prokaryotes. Many advances were attained in the last years due to technical improvements, and much more can be done with further technical advances, particularly in the cultivation of new strains of microorganisms, the use of new molecular tools, and transmission electron microscopy techniques.

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Factors Affecting Biomineralization

S. R. Joshi and Sushmitha Baskar

Contents

Abstract In this chapter we provide an understanding of biominerals and biomineralization processes. The chapter starts with introduction to caves and biominerals. Then precipitation with reference to iron, carbonates, gypsum, calcium nitrate, manganese, and dolomite deposits has been explained with examples. The

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characteristics of biominerals along with the types of biomineralization processes occurring in cave ecosystems have been detailed along with specific examples from Indian caves. Finally, the various factors controlling biomineralization processes such as temperature, pH, nucleation, substrate concentration, and oxygen have been explained in detail. The chapter focuses on the role of microorganisms and their metabolic processes in biomineral formations in cave environments.

1 Introduction

We have often seen protective structures that cover and encapsulate living organisms. The crustaceans and other organisms found on the beach often ignite our interests and of children too. Several organisms such as molluscs, crustaceans, sponges, and corals have biomineralized structures. These structures include shells, cuticles, skeletons, spicules, and so on (Ingalls et al. 2003; Cuif and Dauphin 2005; Kokubo 2007; Märkel et al. 1989; Kopp et al. 2011; Pérez-Huerta et al. 2013; Matsumura et al. 2015). So, what are these protective structures made of? What is their composition? These structures are hard and biomineralized. They are made of biologically produced minerals or in other words known as *biominerals*. Such biominerals can be formed inside the bodies of organisms or outside the bodies of organisms. Structurally when examined under a microscope, these biominerals do not have a specific shape and structure. They vary in size, shape, and structure. Interestingly, the biominerals formed by every organism are different. Now, in the case of minerals that are inorganically formed, for example, sodium chloride (common salt), the mineral has a definite structure. This is one striking difference observed between a biogenically and inorganically formed mineral.

The process by which living organisms form minerals is known as biomineralization. The minerals formed by organisms are influenced by metabolic processes and their products which distinguish them from abiotic mineralization processes. Biominerals vary in mineral characteristics. These include some differences in properties such as shape, size, crystallinity, isotopic, and trace element compositions. Almost 50% of the calcium-bearing minerals are reported as biominerals. The field of biomineralization is highly interdisciplinary and involves the interaction of biologists, geologists, chemists, and physicists. Therefore, "*Biomineralization studies involve scientists who work and focus on the interfaces between earth and life*" (Leadbeater and Riding 1986). Several minerals are known to be formed by living organisms. The biominerals thus formed include silicates, phosphates, nitrates, iron oxides, calcium carbonates, etc.

Biomineralization as a biological process is observed in bacteria producing carbonates; algae and diatoms producing silicates; vertebrates producing phosphates, calcium, and carbonates; invertebrates producing carbonates; etc.

One among the many naturally occurring biomineralization processes is microbiologically induced precipitation of calcium-gypsum carbonate. In this process, microorganisms produce inorganic materials as biominerals through their basic

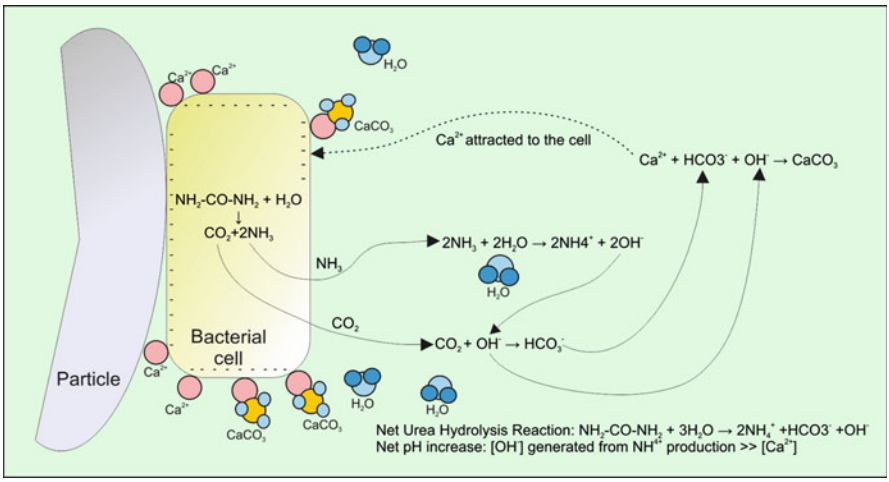

Fig. 1 Calcium carbonate precipitation by bacterial cell in the sand particles (adapted from DeJong et al. 2010)

metabolic activities. This has even developed as a potential technology where biominerals like calcium carbonate are invariably produced by ureolytic bacteria with potential for their application in bioremediation, filler material in rubbers and plastics, CO_2 sequestration, cementation engineering, etc. (Fig. 1).

2 Caves and Biominerals

Caves are subterranean environments and are found in several parts of the world that host diverse microbial life. Researchers working on cave deposits often encounter mineralized living cells. Caves have excellent states of preservation mainly because they have stable conditions (not affected by physical changes or surface weathering) that help in the preservation of biosignatures (Boston et al. 2001). The biosignatures are potentially useful tools in the search for life on other planets (Melim et al. 2009). Most caves are formed in limestone areas and calcareous rocks. But caves are also formed in basaltic rocks, sandstone, granite, quartzite, ice, gypsum, and talus (Northup and Lavoie 2001).

Caves contain novel life forms that can have medicinal and industrial applications. For example, moonmilk also known as *mondmilch* is reported in some caves globally. This creamy, pasty, cheesy deposit observed in different hues has immense medicinal value due to the microbial flora associated with these deposits. In the Indian subcontinent, large deposits of moonmilk were reported from a cave in Meghalaya (Baskar et al. 2016). Such deposits formed by microbe-mineral interactions can be explored for their applications in the pharmaceutical industry for manufacturing novel drugs. Microorganisms and their metabolisms influence

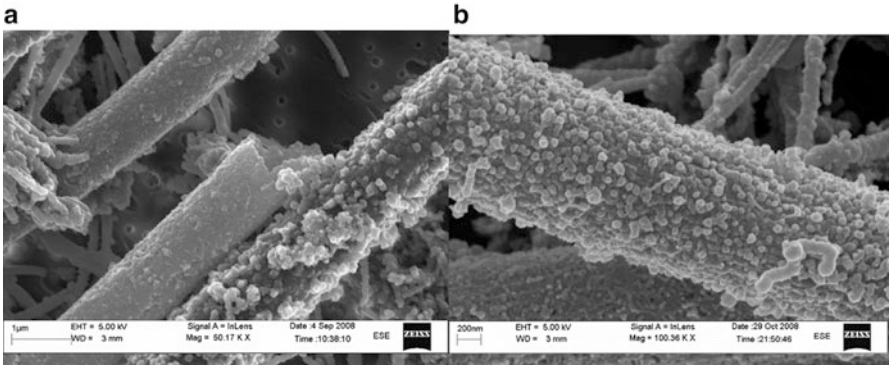

Fig. 2 (**a**, **b**) SEM—critical point dried images of iron biominerals precipitated on bacterial sheaths from biofilms at Borra Cave, India

mineral formations (Ehrlich 1996). Several scientists have extensively researched and noted the presence of microbes and their active role in mineral dissolution and precipitation processes in cave ecosystems. Most caves have different zones that may be well lit, partially lit, or totally aphotic, and each zone has a distinct microbiota. The specific type of cave microbiota observed is often related to the pH, type of mineral, and nutrient present in the specific zone (Barton and Luiszer 2005; Barton and Jurado 2007; Macalady et al. 2008; Engel 2010). In the laboratory microorganisms, microbially mediated precipitation experiments have been done by several workers. The biominerals such as calcite, dolomite, vaterite, and other carbonate minerals have been precipitated in vitro using varied microbial strains and evidenced by several researchers (Boquet et al. 1973; Danielli and Edington 1983; Warthmann et al. 2000; Cacchio et al. 2004, 2012; Baskar et al. 2006, 2016, 2018; Fig. 2a, b).

Caves inhabited by an array of life forms have microbes as an important entity. The microbial community in the subterranean caves which are aphotic derives their energy from minerals and rocks and even adjoining atmosphere being deprived of photosynthetic activity (Banerjee and Joshi 2013). It is these minerals and rock types that make the metabolic substrates for the inhabitant microbes to undertake the microbially induced biomineralization. Organic carbon is available in the caves as allochthonous input. Such carbon comes from soil derived from exterior environment as dissolved organic carbon (Barton 2015). Cultivation of the cave microbes in artificially devised media has always posed a challenge as nutrient-rich media in the laboratory conditions result in reduction of their survivability. The new methodology that is devised to culture the cave microbes has been the use of nutrient-starved media and low temperature conditions (Lavoie 2015). This laboratory growth reduction is correlated to their ability to scavenge the nutrient-deficient cave ecosystems for their adaptability to survive, while the nutrient-enriched synthetic infusions lead the microbial cells getting exposed to osmotic pressure leading to survivability reduction and mostly even death (Ghosh et al. 2017). Thus,

employment of cultivation approach for understanding the factors controlling biomineralization has posed problems to workers as these microbes, most of times, cannot be optimized to their growth under laboratory conditions.

A large number of bacteria undertake a microbially induced process of calcite precipitation called MICP where complicated reactions catalyzed by the urease enzyme occur in Ca^{2+}-rich alkaline environment (Achal and Pan 2011). Such biomineralization is carried out by the specific enzyme, urea amidohydrolase (EC 3.5.1.5) produced by microbially induced calcite-precipitating organisms like *Sporosarcina pasteurii*, a urolytic bacteria (Cuzman et al. 2015; Zhang et al. 2015). MICP has been widely used in geotechnical and civil engineering where the soil quality for improvement of mechanical strength and robustness has been exploited in improvement of environmental processes and construction using microbial products and activities (Ivanov and Chu 2008).

Caves which exist in karst environments are rich in minerals, and about 350 minerals have been reported with few being new addition to science (Onac and Forti 2011). The distinctive speleogenesis characteristic of each cave which is aligned has resulted from its physical, chemical, and biological activities. The kinds of minerals and bedrock like limestone and lava, morphology and shapes, origin with reference to rock, and the nature of its creation with respect to solutional and non-solutional origin have biomineralization linked in each category especially in its geological shape and construction (Engel 2011). The biological transformation forming the biominerals is correlated with biogenic origin of the speleothems and their geometric configurations.

The discovery of chemolithotrophs and chemolithotrophy has made it evident that light is not a driving factor to meet the nutritional needs of an organism. Typical subsurface cave microbes are typical lithotrophs deriving energy from minerals and spring waters rich in solutes (Stevens 1997; Kinkle and Kane 2000).

3 Precipitation, Biominerals, and Caves

3.1 Iron Precipitation

Biogenic iron deposits and their biosignatures in caves can help decipher activities related to past aqueous activity, microbial metabolisms, and sources of energy supporting life forms (Angert et al. 1998). In cave ecosystems iron biominerals are observed on the speleothems, cave walls, ceilings, spring waters, and biofilms. They appear as yellow-, orange-, brown-, or rust-colored minerals. In earlier times descriptive studies focused on the texture and appearance of these precipitates. Later, experimental work in geochemistry, mineralogy, and geomicrobiology has evidenced the involvement of certain groups of bacteria responsible for iron bioprecipitation in cave environments. Minerals such as goethite and hematite are frequently observed and reported from caves (Hill and Forti 1997). Oxidized forms of iron minerals have been noted on bacterial cells and sheaths wherein the microbial

surfaces act as a medium for iron biomineralization (Lowenstam and Weiner 1989; Konhauser 1998; Baskar et al. 2012). Several iron biominerals such as ferrihydrite, iron sulfates, iron phosphates, siderite, and carbonates have been reported in caves by researchers (Luiszer 1992; James 1994; Klimchouk 1994; Konhauser 1997; Maltsev 1997). Emerson and Moyer (1997) reported that abiogenic iron precipitates at a pH above 6 and biogenic iron precipitates at low pH and at circumneutral pH conditions. Iron biominerals have been observed in the Lechuguilla Cave, New Mexico, and scientists suggest a microbial input in their formations (Davis et al. 1990; Polyak and Provencio 2001). In caves, *Gallionella* and *Leptothrix* species often participate in the iron biomineralization process. Microbial species participate in both iron oxidation and reduction. Iron biofilms from an aphotic zone, in the Borra Cave, India, consisted of a dominant group of *Betaproteobacteria* that influenced the formation of biominerals in situ (Baskar et al. 2012). Detailed microbiological investigations revealed several geomicrobially important species that influence microbe-mineral precipitations in situ. The stages of biomineralization were also evident in the electron microscopic studies (Baskar et al. 2012). The iron minerals were precipitated on the bacterial sheaths (Fig. 2a, b).

3.2 Carbonate Precipitation

Microbial metabolism and aerobic carbonate precipitation are the significant roles microorganisms play in the process which have been widely recognized from research studies (Krumbein 1979; Morita 1980; Buczynski and Chafetz 1991; Rivadeneyra et al. 1997). The contribution of enormous amount of extensively distributed and prevalent microbial carbonate in sedimentary system has been hugely understated (Yates and Robbins 1998). Studies done in anoxic environments have provided evidences on the large contribution of microbial metabolic activities to sedimentation of carbonate especially attributed to sulfate reduction (Vasconcelos and McKenzie 1997; Ehrlich 1998; Wright 1999). In vitro experimental results have indicated the role of microbial reduction of sulfate to deposition of carbonates with varying minerals like dolomite or rich content of magnesium-calcite (Vasconcelos et al. 1995; Castanier et al. 1999; Sagemann et al. 1999).

Carbonates are of interest to cave investigators as several forms of biominerals have been reported in these deposits. Several researchers have worked on carbonates such as stalactites, stalagmites, moonmilk, cave pearls, pool fingers, and so on. Microorganisms such as fungi, algae, and bacteria can form biominerals in caves (Went 1969; Cox et al. 1989, 1995). Calcified forms of microbes have been observed in carbonate cave deposits (Jones and Motyka 1987; Polyak and Cokendolpher 1992; Jones and Kahle 1995; Melim et al. 2001; Baskar et al. 2016). The study by Danielli and Edington (1983) was one of the first experimental geomicrobiology studies that demonstrated the ability of microbes to precipitate carbonate biominerals in the laboratory. The involvement of fungi in carbonate mineral formations was reported by Went (1969). Similar studies on

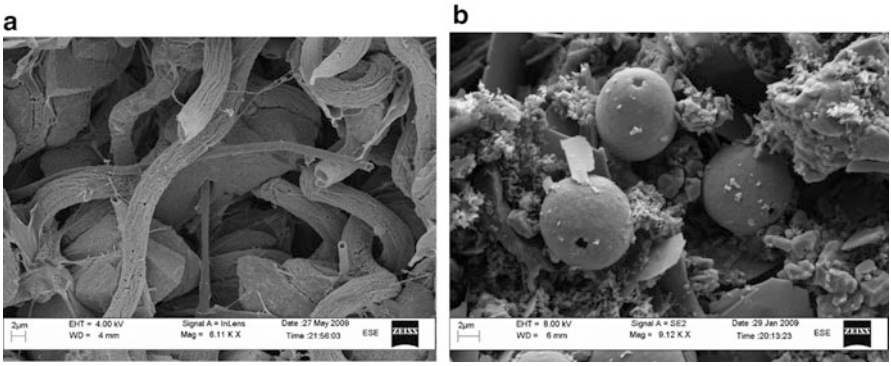

Fig. 3 (**a**) SEM—critical point dried images of moonmilk from Sahastradhara Cave, India. (**b**) SEM of biominerals noted in situ in Krem Syndai, Meghalaya

biomineralization studies by algae were noted by Contos et al. (2001). Jones (1991) reported terrestrial oncoids that were microbially formed from the Grand Cayman Islands. Investigations from caves in Sahastradhara, Krem Syndai, Meghalaya, revealed remarkably interesting biomineralized forms that are thought to be due to microbial metabolisms (Baskar et al. 2014, 2016 Fig. 3a, b).

The metabolic activity of the microbes can create conditions at the microenvironmental level such as increasing alkalinity as localized condition. Increase in alkalinity leads to aqueous phase saturation of calcium carbonate which triggers the mineralization and crystallization of $CaCO_3$ (Danielli and Edington 1983). The size of the calcite crystals in fiber form keeps increasing after the initiation of mineralization even after the stoppage of metabolic activity of bacteria (Cañaveras et al. 2006). The diffusion gradient for movement of ions in the bacterial wall is improved by the capsule of exopolysaccharides and mucus which increases biomineralization and precipitation of biominerals (Warthmann et al. 2000).

3.3 Gypsum Precipitation

It is well known that the caves and the karst structures are formed by dissolution of carbonates rocks by carbonic acid. However, it is also well established that cave structures can also be formed by sulfuric acid dissolution of rocks. Globally, less than 10% of the known caves are represented by caves containing H_2S-rich springs (Palmer 1991). When sulfide-rich waters and oxygen interact at the level of water table or the springs at subterranean level, sulfidic caves are formed in the carbonate rocks (Macalady et al. 2006). These sulfuric acid speleogenic caves pose difficulty in interpreting as it is difficult to identify the mechanism of formation of sulfuric acid. These caves, however, are described by the presence of a large variety of microorganisms which predominantly are sulfur-oxidizing bacteria. These bacteria live in

cave streams and sulfidic springs along with proliferation in surfaces of cave walls designated by production of sulfuric acid and hence are acidophilic in nature (Hose and Pisarowicz 1999; Engel 2000). Thus, presence of sulfur-oxidizing bacteria is a tool to identify and understand the speleogenesis of these caves from sulfuric acid. The prevalent microbial communities in such caves offer information on other sulfidic habitats and biogeochemical cycling of sulfur as well as potential viability and abundance of these microbes at subsurface habitats. The sulfuric acid-speleogenesis model was proposed by Egemeier (1981) which included H_2S volatilization from groundwater to cave environment and oxidation of H_2S by microorganisms or oxidation of sulfur by nonliving factors. This was based on the observations made by Egemeier (1981) on large gypsum deposits, gypsum-replaced limestone cave walls, and H_2S-bearing hot springs in Lower Kan Cave (Egemeier 1981). The carbonate rock gets replaced by gypsum and carbonic acid when sulfuric acid reacts with carbonates (Eqs. 1 and 2):

$$H_2S + 2O_2 \rightarrow H_2SO_4 \quad (1)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3 \quad (2)$$

Gypsum is easily soluble in groundwater and can lead to removal of mass subsequently increasing the void volume.

3.4 Calcium Nitrate Precipitation

Nitrocalcite or calcium nitrate also called cave nitrate is found in dry cave sediments which is the saltpeter which was originally used as an integral component in the manufacture of gunpowder (Faust 1949). These caves are inhabited by a large proportion of nitrifying bacteria specially the *Nitrosomonas* spp. in large densities when compared to their population in surface soils. Their population was found 100 times higher than their presence in the surface soils (Fliermans and Schmidt 1977). Experimental evidences demonstrated that lighter isotopes of nitrogen are abundant in saltpeter (Jameson et al. 1994). This supported the proposition that microbial biogenesis is involved in the generation of cave nitrates. There has been a continuous debate on the origin of nitrogen and the extent to which *Nitrobacter* spp. and *Nitrosomonas* spp. contribute in the formation of saltpeter (Faust 1949).

3.5 Manganese Precipitation

Several studies have indicated the participation of microorganisms in the creation of cave manganese deposits (Jones 1992). A study on Grand Cayman caves by Jones (1992) concluded that many of the manganese deposits prevalent in the cave such as

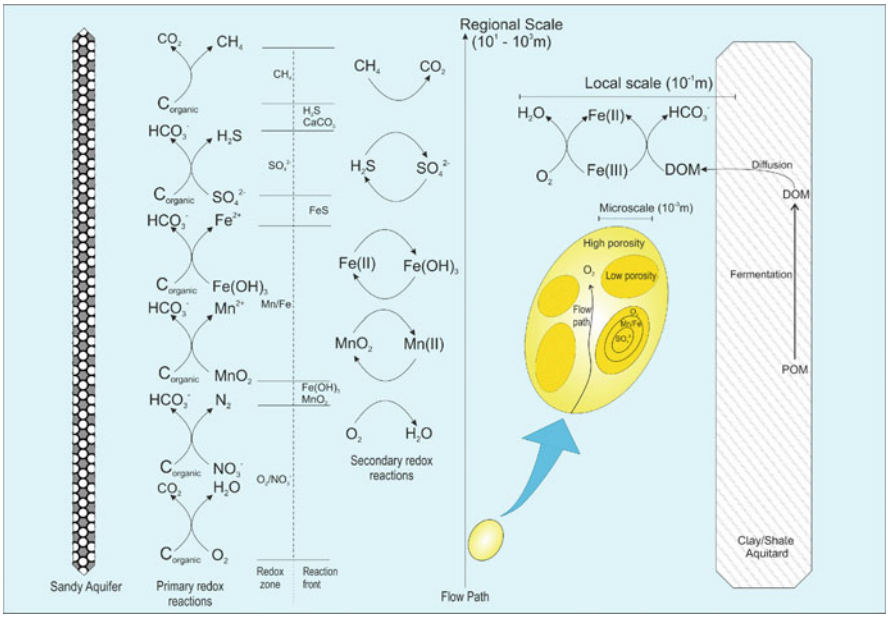

Fig. 4 Schematic view of an aquifer system showing redox reactions and zonations at a variety of spatial scales. POM, particulate organic matter; DOM, dissolved organic matter (adapted from Hunter et al. 1998)

rods, sheets, strands, smooth spheroid in manganese precipitate fossils in stalactites, root calcrete crust, and even karst breccia have biological origin. The deposition of manganese oxides in caves can be increased up to a magnitude of five orders by microbiologically mediated bioreaction (Tebo et al. 1997). Cunningham et al. (1995) reported the involvement of microbes in deposition of ferromanganese in Lechuguilla Cave which indicated biogenic formation of the cave deposits. Crystalline forms of manganese oxides and hydroxides such as romanèchite, todorokite, rhodochrosite, and pyrolusite structures have been reported from various caves (Onac et al. 1997; Northup et al. 2000). There is a sequence of zonal segregation and reduction-oxidation reactions that happen at different spatial scales in these caves to generate various cave formations (Fig. 4).

3.6 Dolomite Precipitation

Dolomite precipitation is rare in the caves. It is calcium magnesium carbonate [$CaMg(CO_3)_2$], a rock-forming mineral commonly known as dolostone in sedimentary rock and dolomitic marble in metamorphic rock. Limestone is known as dolomitic limestone that contains some proportion of dolomite. The original deposition of calcium carbonate muds is known to have altered post-deposition due to

magnesium-rich pore water and became dolomite-rich rocks. Dolomite is a richly present mineral in hydrothermal veins and occurs with barite, fluorite, chalcopyrite, pyrite, galena, and sphalerite. It is highly similar to calcite mineral. A study by Perri and Tucker (2007) reported the Triassic stromatolitic dolomite with preserved mineralized spheroids resembling coccoid and dwarf bacterial forms with differing dimensions occurring in between and within crystals of sedimentary dolomite. The extra polymeric substances present as subpolygonal network were observed as folded sheets several micrometers in length. This suggested that the stromatolites were of biological origin especially the bacterial strains which carried our early precipitation of magnesium carbonates facilitated by metabolic activities of sulfate-reducing bacteria (Perri and Tucker 2007).

The precipitation of calcium dolomite or magnesium calcite prevalent in microbial enriched mats is proposed to be mediated by bacteria which correlates the precipitation of carbonate to involvement of sulfate-reducing bacteria in the environment as well as under laboratory-simulated conditions (Vasconcelos et al. 1995; Lith et al. 2003a; Visscher and Stolz 2005; Wright and Wacey 2005). The carbonate precipitation around the extra polymeric substances of the bacterial cells has driven the mineralization by sulfate-reducing bacteria observed in dolomitic stromatolites (Lith et al. 2003b).

4 Characteristics of Biominerals

Biominerals have some distinct features that can be identified in the laboratory using electron microscopy and isotope studies. The external morphologies of biominerals greatly differ from inorganically formed minerals. For example, they may have grainy outer surfaces and can be irregularly shaped, spherical, or rodlike in their appearances. Mineralogical studies will reveal that they consist of different minerals held together in an organic matrix consisting of exopolysaccharides. Biologically formed minerals are sometimes formed in layers, like in the case of travertine deposits. They have also been observed as coccoid-like forms by scanning electron microscopy with hollow smooth interiors and grainy outer surfaces as in the speleothems from Krem Syndai, Meghalaya (Baskar et al. 2016; Fig. 2a). In the cave deposits from Sahastradhara, the biogenic minerals are intertwined with microbial filaments (Baskar et al. 2014; Fig. 2b).

5 Types of Biomineralization Processes

Biomineralization processes are classified into two important groups based upon their degree of biological control. They include “biologically induced” and “biologically controlled” biomineralization processes, and the nomenclature precedes with “microbial” when biomineralization is “induced” or “controlled” by microorganisms

and hence called as "microbially induced biomineralization" and "microbially controlled biomineralization," respectively.

5.1 Microbially Induced Mineralization

Mineralization induced by organism commonly known as biologically induced mineralization (BIM) is common in open environments as the nature of minerals produced is influenced by the environmental parameters (Brennan et al. 2004). Such biomineralization process is abundantly found in soils, oceans, fresh waters, saline lakes, etc. induced by various bacterial species precipitating mineral carbonates (Douglas and Beveridge 1998; Rivadeneyra et al. 1998; Peckman et al. 1999; Zamarreño et al. 2009). This biomineralization is also related to organismal metabolism and surface structures of the cell. The extracellular polysaccharides along with the associated macromolecules forming the extracellular polymeric substances (EPS) can absorb and bind a substantial quantity of calcium from the surroundings and facilitates precipitation of calcium carbonate. EPS plays a key role not only in $CaCO_3$ precipitation but even in shaping the morphology of the precipitates (Arp et al. 1999; Dupraz and Visscher 2005; Braissant et al. 2007). Microbial metabolism associated with the biomineralization process causes an increase in pH to alkalinity making it possible for calcium carbonate precipitation (Douglas and Beveridge 1998; Castanier et al. 1999). Such an increase in pH is a phenomenon associated with microbially induced mineralization when urea is hydrolyzed by urease-producing carbonate and ammonia. The increased carbonate concentration enables it to combine to the microenvironmental calcium leading to precipitation of calcium carbonate (Hammes et al. 2003; Muynck et al. 2010).

Microbial activities and formation of carbonates of biogenic nature occur widely in soils. Mineralization of carbonate facilitated by the bacterium *Bacillus megaterium* under cultivated conditions was investigated by Lian et al. (2006). The authors used the bacterial culture supernatant, bacteria concentrate, and the unseparated mixture to a calcium carbonate solution and observed the crystallization of calcite. Diffraction and microscopic analysis of the reaction products revealed *Bacillus megaterium* induced biomineralization and formation of calcite as the dominant mineralized phase in the presence of bacteria. Further, crystal morphology indicated the bacteria promoting growth of calcite face under high concentration of bacterial colony. The same phenomenon was found to be reduced with even dissolution of the substrate surfaces when the concentration of bacteria was low. The initial stages of the biomineralization leading to crystallization showed calcite nucleation on the cell walls of bacteria with no obvious morphological features. Carbon isotope measurements indicated that metabolic activity of bacteria may not contribute its carbon for biomineralization. It was concluded that bacterial induced mineralization of calcite leads to epicellular and intercellular growth of calcite controlled mainly by proton pump in respiratory process and sequestration by bacterial cell (Lian et al. 2006).

Ureolytic marine bacteria such as *Sporosarcina* sp., *Bacillus* sp., and *Brevundimonas* sp. were found to induce precipitation of calcium carbonate minerals under cultivation with *Sporosarcina* sp. being the dominant among the cultured isolates though *Bacillus lentus* CP28 facilitated higher calcium carbonate precipitation with maximum urease activity. Enzymatic hydrolysis of urea by urease precipitated calcium crystals, and with an optimal concentration of ammonium ion at 746 mM and pH at 9.6, calcite precipitation was at its maximum with precipitate formed at 96 mg/L demonstrating that precipitation of calcium carbonate was controlled by a variety of marine bacteria (Wei et al. 2015).

5.2 Microbially Controlled Mineralization

The biominerals may be produced within the cell or in the surface of the cell under a particular condition which is known as biologically controlled mineralization (BCM). In case of biologically induced mineralization, the metabolic activities of the organisms result in extracellular formation of these biominerals which has been exploited in bioengineering applications of microbes.

BCM is characterized by the control mechanism where the organism has a control over the nature and occurrence of crystal morphology, crystal growth, composition of the crystals, and location in the microbial cell or cell surface. The process is driven by the cellular processes of a specific microorganism. Such biomineralization is abundant in shells of invertebrate animals especially the molluscs and brachiopods.

In case of mineralization using BCM process, mineralization is controlled using particular metabolic and genetic paths by organisms such as diatoms, magnetotactic bacteria, and coccolithophores (Bazylinski and Moskowitz 1997a, b). A diverse variety of minerals are formed by the mediation of bacteria and archaea, and one such facilitation happens via the biologically controlled formation of biominerals.

There is a great degree of cyrstallochemical control exerted by the organism in BCM on the nucleation sites as well as on the growth of the biominerals. The organism, for the most part of biomineralization, directly synthesizes the minerals within the cell or even on the cell surfaces at designated locations under specific conditions. The biominerals produced by the microorganism (bacteria) bear characteristic narrow size distributed crystals with defined order and consistently specific morphology. These features indicate that biomineralization controlled by organism or BCM is carried out under defined biochemical and genetic control of the host cells. A well-characterized BCM is the formation of magnetosome by a group of bacteria called magnetotactic bacteria where the magnetic crystals produced by BCM process reveal a specific function when compared to other structures in the cells (Bazylinski and Frankel 2000).

Generally iron-oxide or iron-sulfide magnetosomes are biomineralized by the magnetotactic bacteria. Crystals of Fe_3O_4 (magnetite) are contained in iron oxide (Frankel et al. 1979), while the iron-sulfide magnetosomes contain Fe_3S_4 (greigite) crystals (Heywood et al. 1990; Mann et al. 1990). Other minerals such as tetragonal

FeS (mackinawite) and cubic FeS contained in iron-sulfide magnetosomes are likely to be the precursors of greigite (Posfai et al. 1998a, 1998b). Magnetotactic multicellular prokaryotes are reported to produce iron-sulfide magnetosomes magnetic, monoclinic, Fe_7S_8 (pyrrhotite) (Farina et al. 1990), and nonmagnetic FeS_2 (iron pyrite) (Mann et al. 1990). Synthesis of magnetite and not greigite even in the presence of hydrogen sulfide was demonstrated to be a preferred biomineralization process during BCM by cultured magnetotactic bacteria revealing that mineral constituents of magnetosomes are under a strict chemical control of the cells (Meldrum et al. 1993a, 1993b). The magnetite crystals formed during BCM by *Magnetospirillum magnetotacticum* under culture conditions showed that iron could not be replaced by other ions like titanium, chromium, cobalt, copper, nickel, mercury, and lead indicating the preferential utilization iron during the biomineralization process (Gorby et al. 1988). The crystals of magnetite magnetosomes are reported to contain proteins ((Arakaki et al. 2003). A large number of genes coding for the protein Mam have been identified in *Magnetospirillum gryphiswaldense* located in two different regions of the genome (Grünberg et al. 2001). These proteins exhibited typical homology, for example, the protein MamA was homologous to tetratricopeptide repeat proteins, MamB was homologous to cation diffusion facilitators, and MamE was homologous to HtrA-like serine proteases with some of the homologues coding for magnetosome membrane proteins (Matsunaga et al. 2000; Grünberg et al. 2001).

Wahyudi et al. (2001) created an array of mutants of the magnetotactic bacteria *Magnetospirillum magneticum* strain AMB-1 by mutation of transposons and also isolated one of the strains NMA21 which contained a disrupted protein coding gene with similarity to tungsten-containing ferredoxin oxidoreductase of a thermophilic bacterium *Pyrococcus furiosus* (Wahyudi et al. 2003). The protein was synthesized under microaerobic conditions. Analysis of the mutants and the wild type revealed that the bacterial cells of NMA21 had lower uptake rate of iron and did not show formation of magnetosomes when compared with the same parameters of wild-type strain. Further, under cultured conditions, strains that produced magnetosomes formed dark to black-colored colonies, while the mutant strains that did not produce the magnetosomes formed white- to pink-colored, usually light-colored colonies in the Petri plates (Matsunaga et al. 1992).

Higher organisms known to biomineralize magnetic crystals of single magnetic domain contain a similar set of genes responsible for biomineralization of magnetite (Kirschvink and Hagadorn 2000) that have originated in the bacteria. These findings elucidate the fact that BCM involves the metabolic pathways of the organism regulated by a specific set of genes and proteins.

6 Factors Controlling Biomineralization

Some important factors that influence biomineral formations include the abiotic and biotic factors. Most importantly, the metabolism of an organism drives the formation of these protective biomineralized structures which consist of both organic and inorganic matters. Microorganisms including bacteria, actinomycetes, certain algae, and fungi have been reported to be involved in biomineralization processes in several environments (Ehrlich 2002). Scientists have also demonstrated the specific pathways responsible for microbe-mineral precipitation in the laboratory especially for carbonates (Rivadeneyra et al. 1994; Vasconcelos and McKenzie 1997; Baskar et al. 2006; Sánchez-Román et al. 2008).

The occurrence of life on earth seems to have a strong coherence with the first occurrence of sedimentary rocks, and several factors could have influenced the process of biomineralization. Analysis of the contents of organic sediments and isotopes of carbon dating back to as along as 3.6 billion years indicates similar processes as prevalent today in terms of oxygen synthesis, reduction of carbon dioxide, and deposition of carbon. The only difference is that the atmospheric oxygen levels during that age remained low owing to abundance of oxygen sinks. With progressing age of earth, oxidation of metal such as iron, nonmetal like sulfur, and even gases took place. The resultant effect was the increase in the corpus of oxygen like compounds of ferric iron and sulfates paralleled with continuous reduction in oxygen sinks like ferrous compounds in the form of ferrous silicates, ferrous carbonates, and ferrous sulfides. It is proposed that reduction of sulfates by bacterial strains was insignificant until about 2.3 billion years ago as sedimentary systems invariably had irreversible oxidation of sulfides to sulfates. Sufficient research outputs provide evidences pointing to the transitional shift from low oxygen levels in the earth atmosphere happened around 2 billion years ago. The oceanic reduction of sulfate by bacteria and transition of the oxygen sink from an irreversible system to reversible sulfur oxidation/reduction reciprocated to oxidation/reduction of carbon were significant events happening during sedimentary cycling (Garrels 1989).

The formation of biominerals occurs due to the combined action of various factors, such as the availability of nucleation sites, organic matrix, pH, temperature, and so on. Biomineralization occurs in various stages with primary step being the arrangement of organic macromolecules into definite and ordered structures.

6.1 Temperature

Temperature has been implicated as an important factor in bioprecipitation of minerals. In a study by using enrichment culture technique, precipitation mixture of calcium dolomite and magnesium calcite was observed after 3 weeks of incubation with 6% NaCl when 10 mM dissolved sulfate was consumed in totality. The

experiments demonstrated the experimental precipitation of dolomite under anoxic conditions by sulfate-reducing bacteria (SRB) at low temperature under anoxic conditions with hypersaline concentration. The authors proposed that initiation of dolomite precipitation needed sulfate-reducing bacteria as basic requirement. When an uncharacterized SRB was inoculated in another synthetic medium with formate and incubated at 30 °C in static condition, precipitation was observed after approximately 3 weeks with dissolved sulfate diminished to zero. The precipitate contained a mixture of monohydrocalcite and dolomite. The bacterial cells at their polar end showed growth from clear microcrystals to larger crystal structures in about 2 weeks' time, which continued to grow to dumbbell shapes in a maximum of 6 weeks to attain a cauliflower-like shape by coalescing the ends of the dumbbell structure. The control experiments where no bacteria were inoculated in contrast did not form any carbonate biominerals. In case of dolomite precipitation, it was observed to nucleate in colonies of bacteria in an organic matrix which consisted of exopolysaccharides as an extracellular polymer of bacterial origin. With formate as the substrate, the growth of bacteria led to increase in pH along with increase in the concentration of bicarbonate and sulfide. There was simultaneous decrease in the concentration of formate and sulfate (Warthmann et al. 2000).

6.2 pH

Biomineralization, apart from forming minerals by microbes, can be an efficient process to remove metals from solid phase. In a study conducted by Li et al. (2018), the bacterium *Bacillus cereus* cd01 was studied for its biosorption and biomineralization potential under self-mediated effects of pH changes. The organism was found to decrease pH of the culture medium from neutral to acidic range which inhibited the biosorption of Cd^{2+} on bacterial cells. An increase in pH of the cultivation medium to neutral, however, was observed to mediate Cd^{2+} biosorption. The cause for the change in biosorption potential of the bacterial cells was attributed to changes in the membrane fluidity and hydrophobicity of the bacterial cell surface caused by altered pH. Increase in pH of the cultivation medium promoted cadmium biomineralization in bacterial cells revealing higher biosorption and bioaccumulation of the heavy metal on bacterial cells. This was evident from the observations made in EDS, X-ray spectroscopy, and SAED which revealed that Cd^{2+} absorbed on the cells was biomineralized into polycrystalline structure and/or cadmium phosphate and amorphous cadmium sulfide (Li et al. 2018). This indicated that change in pH affected biomineralization of heavy metals like cadmium which was optimum in pH-neutral conditions.

Iron bacteria commonly occur in neutral pH iron seeps whose growth is promoted by the availability of ferrous iron. These bacteria are responsible for majority of the iron oxidation and efficiently precipitate dissolved iron present in aqueous medium (Emerson and Revsbach 1994). These groups of bacteria encounter metabolic problem as ferrous iron acts as electron donor while ferric iron gets precipitated in

the cell wall. Such precipitation of ferric iron hampers the transport of metabolic substances across the cell wall. This problem is solved by the microorganisms as exopolysaccharide slime layer formed as a sheath precipitates iron which leaves the cell wall free of iron precipitation. Such microbes are invariably heterotrophs using organic substances as source of carbon (Hallberg and Ferris 2004). Bacterium like *Gallionella ferruginea* produces extracellular spirally twisted stalk where the precipitation of oxidized iron occurs (Vatter and Wolfe 1956). The iron oxidation occurs at suboxic conditions as the bacteria are microaerophilic autotrophs with carbon dioxide serving as the electron acceptor (Sobolev and Roden 2001). These bacteria prefer to grow and produce stalks for precipitation of metals like iron in natural conditions where the pH of the environment is alkaline or near neutral (Hanert 1981).

Biosorption rate as well as the forms and structure of biomineralized precipitate was found to be affected by pH values in a biosorption study on uranium (VI) by *Saccharomyces cerevisiae* (Zheng et al. 2018). The biosorption reached a maximum at neutral pH, while under alkaline conditions, the ions of uranyl, phosphate, and ammonium generated large quantity of uramphite precipitates evenly distributed on surface of yeast cells (Zheng et al. 2018).

In a study conducted on a diatom *Thalassiosira weissflogii*, external pH was found to influence cell growth modifying the intracellular content of biogenic silica and silicic acid. Modifications of extracellular pH resulted in acidosis in the intracellular compartment of the cell. Silicon metabolism along with theca formation was directly affected by balance in acid and base. The morphogenesis of valve and its formation kinetics during initial stages was dependent of pH. The study demonstrated that acid-base balance is the key in silicon metabolism, thus controlling pattern formation during silicon biomineralization in the studied diatom (Hervé et al. 2012).

6.3 Nucleation

Biominerals are formed because of the nucleation process that occurs during biomineralization although nucleation follows a two-step pathway which may be classical or nonclassical. In classical path, the mineralizing organism undertakes growth by utilizing the crystallizing amorphous nanoparticles on the growing nuclei of the crystal. The other known process is the growth of the crystal nuclei by addition of single ions consistently. Nucleation has been an important process in formation of biominerals where proteins in specific are found to play a key role in nucleation of biominerals. There has been an emergence in knowledge about the nonclassical nucleation process which involves pre-nucleation formation of cluster, assembly of clusters of amorphous mineral along with the maturation, and stabilization schemes. It has been realized that many vital steps in the mentioned processes are regulated efficiently by proteins which precisely control the biogenic crystal development or even stabilization of biominerals of amorphous nature in a variety of organisms. The

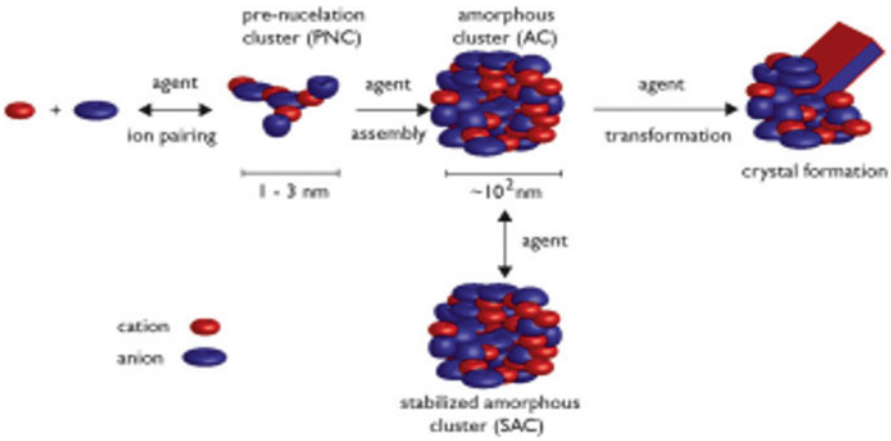

Fig. 5 Nonclassical nucleation scheme involving pre-nucleation clusters formed from constituent cations and anions representing the first step toward mineral formation

involving proteins assemble in such a way which shows compatible properties with the pre-nucleation and amorphous clusters of minerals. This finally creates an environment in the organisms providing favorable conditions for subsequent stabilization or even transformation of these minerals under suitable conditions of sites. These proteins thus act as precursor phases for creation, stabilization, and transformation of minerals of amorphous nature (Fig. 5). Various proteins, lipids, and polysaccharides comprising the extracellular matrix of the organisms in fact form the reaction center for the growth of crystals via nucleation process, thus emerging as the focal point for pre-nucleation crystal cluster formation followed by maturation and transformation of the formed clusters. Proteins are well established to be an important factor in the nucleation process.

With regard to the involvement of proteins in pre-nucleation process, it is proposed that the cross-beta supersecondary domains (red) begin to stabilize the associations of protein chains and strands by interaction with the dynamic disordered (green) domains. This provides mobility and lability within the so formed protein phases. The mineral clusters which are developing get attracted to the polymer-induced liquid precursor phase-like protein phase creating association with the assembled proteins, though the nature and extent of such associations of proteins are not clearly known as yet (Fig. 6).

The classical nucleation theory states that the formation of crystals from the constituent ions in the supersaturated solution needs changes in the concentrations of ions interacting locally. The favorable interaction of these ions at a suitable concentration stabilizes the ion clusters. This results in a situation where the free energy gained by ion dissociation in the surface of the cluster is lower than the free energy gained by subsequent addition of ions to the cluster or the crystals. The entire process is a thermodynamic process involving the difference in free energy between the two phases in crystalline and solution form with kinetics control of the level of

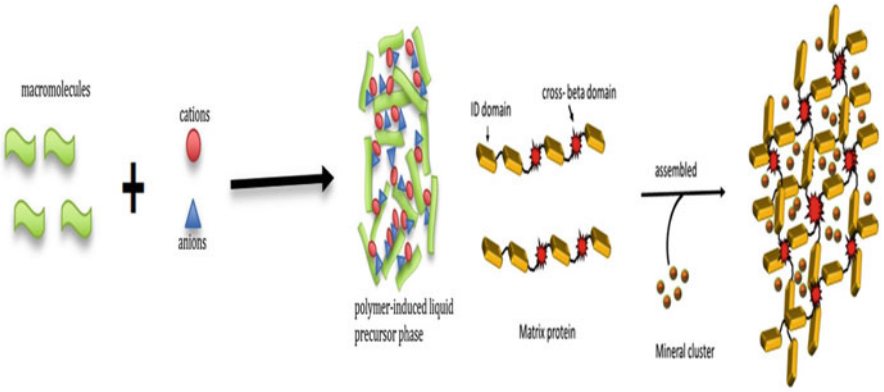

Fig. 6 Polymer-induced liquid precursor organic/inorganic phase formation and scheme of ECM biomineralization, co-assembly of protein chains, and pre-nucleation and/or amorphous mineral clusters

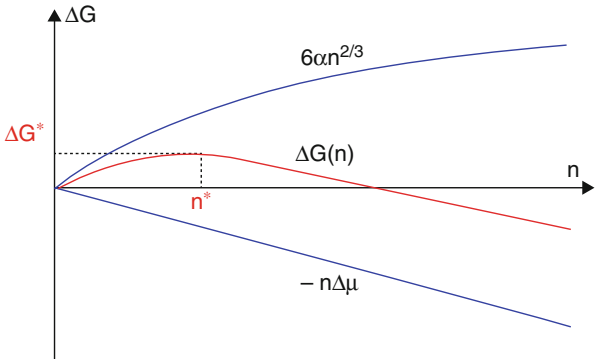

Fig. 7 A generalized presentation of Gibbs free energy formulation in crystal nucleation

energy barrier of cluster formation with a critical size. This also involves the free energy encountered in the formation of new crystal surface. The entire process of crystallization is a reaction of homogenous nature with the reaction free energy that can be represented as the following pathway (Veis and Dorvee 2013):

$$\text{Supersaturated Solution}, G_{ss} <=> \text{Ion Clusters}, G_c <=> \text{Critical Cluster}, G_n \rightarrow \text{Stable Cluster}, G_{crt}$$

A generalized presentation on free energy and Gibbs formulation in terms of crystal nucleation is given in Fig. 7. The uppermost curve represents an unfavorable gain in free energy due to creation of new surface interface. The lowermost curve represents a favorable decrease in free energy as the crystal stabilizes as compared to the initial free energy of the solution. Delta G^* represents the critical free energy in a situation when the cluster size is n^*. At this cluster size, the particles released from

the cluster surface are probably balanced with the growth of the cluster. The cluster will have further growth with greater probability when $n > n^*$.

In case of dolomite precipitation under controlled conditions with formate as the substrate, nucleation as well as growth of the dumbbell-shaped precipitates of dolomite occurred in the presence of sulfate-reducing bacteria in an organic matrix. The bacteria were seen around the surfaces of the mineralized dumbbell which indicated that nucleation and active microbial involvement were necessary for the process of biomineralization as observed in the case of dolomite precipitation (Warthmann et al. 2000).

6.4 Substrate Concentration

Substrate is a key factor in biomineralization process as the metabolic activities of the microorganism are linked directly or indirectly with the availability and concentration of substrate. For example, among various factors that are known to govern the precipitation of calcium carbonate, the significant ones are calcium concentration, amount of inorganic dissolved carbon, pH, and presence of nucleation sites (Muynck et al. 2010). Among these four key factors, bacteria can directly influence the first three by creating alkalinity in the microenvironment. Provision for nucleation of crystals can also be made available by bacteria in the precipitation process (Hammes and Verstraete 2002). Experimental evidences demonstrated that bacteria caused increased calcium carbonate precipitation rates when compared to precipitation by chemical process (Stocks-Fischer et al. 1999). Calcium concentration in the cultivation condition shows a direct bearing on the quantity and nature of calcium carbonate precipitation (Fig. 8).

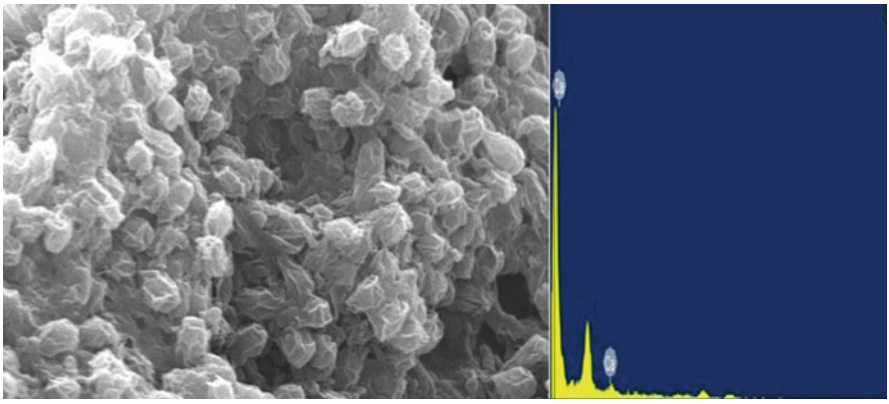

Fig. 8 Calcium carbonate precipitation under cultured conditions by bacteria

Table 1 Factors reported in literature for production of calcium carbonate by urea hydrolysis

Objective	Factors considered		Activity of enzyme urease (mM/min)	Literature cited
	Urea (mM)	Ca^{2+}(mM)		
Removal of Ca^{2+} from wastewater	8	15	0.032	Hammes (2002)
Biocementation	1500	1500	4–18	Whiffin (2004)
Removal of Ca^{2+} from wastewater	16	14	0.293	Hammes et al. (2003)
Plugging of rock pores	333	50	Na	Gollapudi et al. (1995)
Biodeposition	333	340	Na	De Belie and De Muynck (2008)
Carbonate precipitation	606	250	Na	Okwadha and Li (2010)
Stone remediation	66	25	0.041	Bachmeier et al. (2002)
Sr90 sequestration	330	0.025	0.042	Warren et al. (2001)
Cement remediation (Portland cement)	333	50	Na	Ramachandran (2001)
Biocementation	Na	No Ca^{2+} ions	13.33 mM urea hydrolyzed/min.	Omoregie et al. (2016)

na data not available

Urea hydrolysis is a major process of production of calcium carbonate present abundantly in caves, and this biomineralization is influenced by many factors as evident from the work of researchers (Table 1).

6.5 Oxygen

External growth environment involving oxygen concentration influences the biomineralization process. In a study conducted under laboratory conditions on biomineralization of magnetite magnetosomes in the magnetotactic bacteria the *Magnetospirillum magneticum*, Li and Pan (2012) observed that growth conditions like anaerobic static, aerobic static, and aerobic rotating at different rpm affected magnetosome formation. Even increasing the rpm from 80 to 120 under shaking growth condition which changes oxygen availability in the culture medium led to the magnetosomes becoming uniform in dimensions, small in size of the crystal grains, and increase in twinning frequency of the grain. The changes observed in the properties of the crystals such as the magnetic and shapes indicated the effect environmental conditions like oxygen on the behavior of magnetotactic bacteria with regard to biomineralization of magnetite magnetosomes. The study concluded that the prevailing growth environment has a direct implication on the physical as

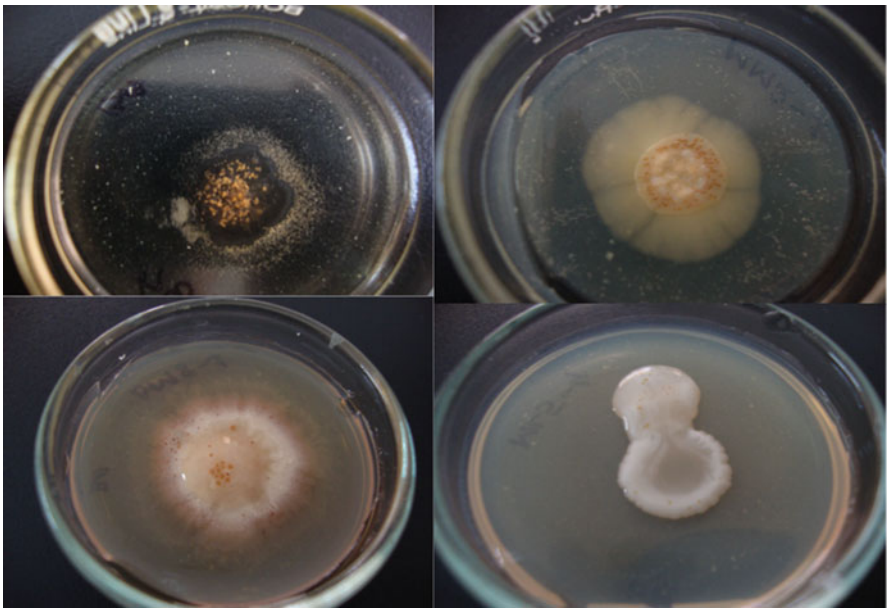

Fig. 9 Bacterial mineralization of $CaCO_3$ in culture media as influenced by growth substrates

well as magnetic properties of such biomineralized magnetite magnetosomes produced by the magnetotactic bacteria (Li and Pan 2012).

It is generally assumed that the dissolved ions in the aqueous solution initiate the formation of crystals by transformation of components. However, there has been increasing evidence that crystallization is mediated by more complex precursors along with the clusters and nanoscale amorphous precipitates (Banfield et al. 2000; Furrer et al. 2002;Yang and Navrotsky 2002). The attachment process of ions to organic or inorganic surfaces is generally considered to be the mechanism of growth of crystals. A study by Banfield et al. (2000) revealed that formation of crystalline structure in iron-oxidizing bacteria depicted an alternative coarsening mechanism with adjacent nanoparticles aggregating and rotating finally adopting three-dimensional parallel orientations.

An organism capable of controlling its growth stops its own growth after reaching a particular dimension of the crystallized structures which is achieved by controlling both nucleation and growth. This is a typical example of biologically controlled mineralization which leads to crystallization and development of spatially controlled crystal faces and orientations. The crystals can grow to produce differently oriented structures like shells, spicules, test of even a defined shaped bone structure. Under laboratory conditions, the speleothemic bacteria when allowed to undertake crystallization in the presence of suitable substrates are observed to be affected temporally and spatially by the nature of media constituents such as the inorganic compound sources and their concentrations (Fig. 9). In a few geomicrobiological studies conducted for some of the longest caves in the subcontinent, bacterial isolates

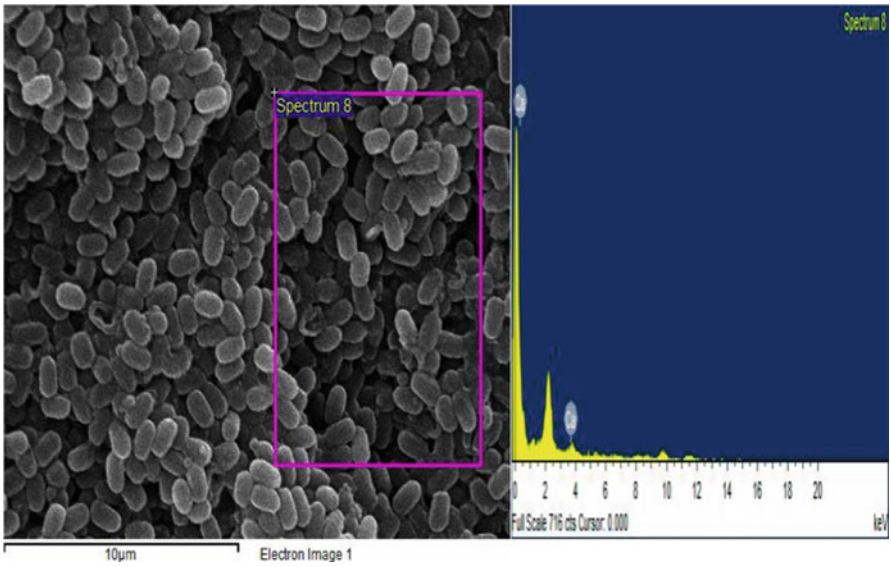

Fig. 10 SEM-EDX of *Bacillus* sp. showing calcium crystallization in calcium-enriched medium

from the caves were investigated for precipitation of calcite under laboratory conditions which revealed evidence of biotic process involved in speleothem formation. Majority of the isolated bacteria belonged to *Bacillus* and *Pseudomonas* which could be manipulated for their optimized growth under laboratory conditions revealing that factors like inorganic compounds, temperature, and calcium salts were vital in biomineralization (Banerjee and Joshi 2014, 2015, 2016).

Bacillus isolated from cave environment were observed to be versatile in terms of carbon utilization in formulated media and showed calcium crystallization even in nutrient-stressed simulated conditions. This revealed that *Bacillus* spp. had higher potential of calcium crystallization indicating them as efficient biomineralizing bacteria involved in biogenic formations of cave structures (Fig. 10).

Small molecules and different proteins actively transport the inorganic molecules and play a role in their assembly. Some of these proteins, involved in condensation synthesis of silica, GeO_2-SiO_2 system, and TiO_2 are called silicatein proteins (Navrotsky 2004).

Studies have investigated and revealed some of the metabolic pathways as factors known to contribute to precipitation of calcium carbonate by microbes (Engel et al. 2004; Baskar et al. 2006, 2007). Biomineralization in the form of extracellular precipitation of calcium carbonate by bacteria and fungi happens through photosynthesis, ammonification, denitrification, anaerobic sulfide oxidation, and sulfate reduction (Riding 2000) (Table 2).

Table 2 Microorganisms involved in major secondary deposits identified in caves

Biomineralization types	Microorganisms involved	Raw materials	Facilitating factors	Contributing factors	References
Calcite precipitation	Bacteria, cyanobacteria, small algae, and fungi	Organic calcium salts	Extracellular polymeric substances	Photosynthesis, ammonification, denitrification, sulfate reduction, anaerobic sulfide oxidation	Riding (2000), Engel et al. (2003), Baskar et al. (2005), Vasconcelos et al. (1995)
Gypsum precipitation	Sulfur-oxidizing bacteria	Sulfuric acid dissolution	Volatilization of H_2S from the groundwater to the cave atmosphere	H2S oxidation to sulfuric acid production in moist subaerial cave wall	Egemeier (1981), Palmer (1991), Engel (2000)
Iron precipitation	Bacteria such as *Leptothrix*-like organisms and *Gallionella*-like organisms	Oxidation of Fe^{2+} to Fe^{3+}	Fe precipitation iron within the cell interior or along the sheaths surrounding microbial cells and filaments	Fe(II) oxidation, Fe(III) hydrolysis and precipitation	Baskar et al. (2008) Singer and Stumm (1970), Konhauser (1998)
Nitrocalcite or calcium nitrate precipitation as saltpeter	Nitrifying bacteria	Nitrification	Nitrogen availability	Na	Faust (1949)
Manganese precipitation as stalactites, karst breccia, and root calcrete crusts	Diverse group of microbes	Oxidization of reduced manganese	Reaction zonation at spatial scales	Various redox reactions	Huntera et al. (1998)
Dolomite precipitation	Coccoid Bacteria	Precipitation of magnesium carbonates	Sulfate-reducing metabolic activities of microbes	Extra polymeric substances of bacteria	Perri and Tucker (2007)

na data not available

7 Conclusions

Biomineralization as a biological process has been gaining newer dimensions and biological sciences and has evolved to a new chemistry that has helped to bring together the synthetic mechanism and construction of structures with functional inorganic-organic materials. The process that produces these structures, small and big, has been the subject of mineralization. The biological synthesis of such inorganic-based structures within the cell or on the surface of the cell is either induced or controlled by the organism itself. These inorganic solids deposited in biological systems can have a wide range of applications ranging from functionalized materials to engineering sciences. Biomineralization has fundamentally changed both life and environment as biological processes were evidenced to have been involved in inorganic biomineralization since as far back as 3.5 billion years ago. The cycling of elements happening over million of years using complex cycles at some critical stage of mineral cycling has intervention of biomineralization process.

Understanding how microbes synthesize crystals using BCM or BIM can have far-reaching impact beyond the conventional lessons of microbiology and geological sciences. Manipulating factors that optimize biomineralization under laboratory conditions and controlling the shape and size of these biocomposite materials will provide multifunctional utility of these complex architectures. Since it's is desirable to have a desirable control over the growth of minerals, it offers wide applicability in materials engineering which warrants to understand and elucidate the biological pathways and mechanisms especially in biologically or microbially controlled biomineralization.

Biomineralization process has even been explored as an efficient mechanism to remediate inorganic contaminants of the environment since mineral precipitation is mediated by microorganisms. This offers scope for technology development in bioremediation approaches. Production of specific organic molecules triggering the nucleation supersaturation by metabolic activity of the organism which impacts the growth of biominerals is an important factor controlling biomineralization. Microbial diversity, mineral precipitation, and sequestration of metal contaminants have been a new field in biomineralogy offering immense potential in ecorestoration and rehabilitation of degraded environment. There is a need to understand in depth the role of external and internal factors that affect biomineralization so that it can be exploited for environmental remediation along with its applications in human welfare.

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Experimental Modeling of Carbonate Mineral Precipitation in the Presence of Cyanobacteria

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Abstract Carbonate mineral precipitation in the presence of cyanobacteria is at the forefront of scientific research due to its importance for understanding paleoenvironments of mineral formation and for optimizing conditions of mineralogical CO_2 sequestration via biological pathway. Stromatolites are among the oldest known biological formations, and they provide insight into early Earth environments and climates. It is therefore essential to understand the processes governing their formation. Numerous field studies were carried out to characterize these bio-formed rocks and their way of formation showing that various parameters could be involved in the processes of formation of carbonate rocks. Thus, reproducing natural environments under laboratory-controlled conditions is an efficient approach to better understand the role of each parameter. The present chapter aims to present the results of various laboratory studies on the biomineralization of Ca, Ca-Mg, and Mg carbonates, via analyzing and discussing mechanisms of mineral formation; providing examples of several case studies; assessing, based on available information, the stoichiometry of inorganic carbon removal in the form of carbonate minerals and organic carbon sequestered in the form of bacterial biomass; and finally recommending future research directions in this actively developing field of science.

1 Introduction

Abiotic and biotic formation of carbonate minerals at the Earth surface environments is one of the major process controlling carbon cycle on both short- and long-term scale. There is a general consensus that microorganisms have been playing the largest role in massive Ca and Mg carbonate deposit formation (Pomar and Hallock 2008). The cyanobacteria are most important organisms involved into calcification since early (Riding 2006; Ries 2010). Actually, cyanobacteria calcification happens almost only in alkaline, freshwater, and hypersaline or brackish water (Merz 1992; Bundeleva 2011).

Even if calcium carbonate organominerals, and probably calcium carbonate biominerals, were present in the Proterozoic, abundant fossil evidence of calcium carbonate biominerals were not found in marine deposits before the Phanerozoic. The saturation state of surface ocean water with respect to $CaCO_3$ has been maintained over almost all Phanerozoic (Raven and Giordano 2009). The crucial role in calcium carbonate formation was played by marine cyanobacterial mats capable of increasing the local supersaturation degree significantly higher than that in the bulk solution.

Calcium ion has a crucial role as a metabolic and morphogenetic messenger for early eukaryotes (Kazmierczak and Degens 1986). The exact microbial processes which were regulating Ω_{CaCO3} in Precambrian oceans are likely to be different from the modern ones and still remain elusive (McCutcheon et al. 2014). Numerical models could help answering these questions (Aloisi 2008).

Microbial carbonate precipitation is responsible for coupling the atmospheric and terrestrial C cycle. Furthermore, the metabolism of underground-inhabiting bacteria is capable of increasing the alkalinity and pH of solution, thus leading to precipitation of carbonate minerals (Ferris et al. 1994). Cyanobacteria possess highly effective single-cell CO_2-concentrating mechanism (CCM), which plays a crucial role in carbonate mineralization (Kamennaya et al. 2012). The CCM comprises four modes of active inorganic carbon uptake, necessary for accumulation of bicarbonate ions in the cell (Badger 2003).

Laboratory experiments and geochemical modeling have shown the importance of the processes of physicochemical mineral nucleation and precipitation together with specific metabolic reactions in carbonate mineral formation in the past (Bosak and Newman 2003). The formation of natural carbonate minerals via microorganisms occurs in multiple environments (Chagas et al. 2016). Thermophilic cyanobacterial community (Orleansky and Gerasimenko 1982) has been shown to efficiently precipitate $CaCO_3$ at 40 °C due to active photosynthesis of *Mastigocladus laminosus* (Nekrasova et al. 1984).

Extracellular microbially driven precipitation of low-Mg calcite appeared to be responsible for ooid formation in a freshwater lake. Although in this lake photosynthetic activity was found to be the main factor of precipitation (Plee et al. 2010), the variety of bacterial communities could result in different precipitation processes. The presence of eukaryotic picoplankton could lead to the formation of small calcite crystals, whereas cyanobacterial picoplankton induced the formation of micritic carbonate (Dittrich et al. 2004). In eutrophic basins, calcite could be produced during daylight via the photosynthesis and partly dissolved at night when dissolved CO_2 concentration decreases due to respiration (Cicerone et al. 1999). The photosynthetic increase of pH is not the sole mechanism of photosynthesis-induced $CaCO_3$ precipitation (Shiraishi 2012). In a UK-travertine deposit stream, other factors such as degassing, water discharge, and temperature, as well as light irradiance, were demonstrated to impact the photosynthesis in the water column and on the submerged supports, thus influencing overall calcification process (Pentecost and Spiro 1990). In such travertine streams, already supersaturated with respect to $CaCO_3$, the annual growth rate of the cyanobacterium *Homoeothrix crustacea* colonies was 1.25 mm y^{-1} (Pentecost 1988), whereas the calcification rate of another cyanobacterium, *Rivularia haematites*, ranged from 12 to 14 μm d^{-1} during the summer to <2 μm d^{-1} during winter (Pentecost 1987). The season exerted the strongest control on mineral precipitation with a maximum in early spring and late summer; both filamentous and coccoid cyanobacteria essentially controlled low-magnesium calcite precipitation (Plee et al. 2008). Recently, the important role of viruses in calcium carbonate precipitation in the presence of bacteria has been demonstrated (De Wit et al. 2015; Lisle and Robbins 2016; Xu et al. 2019; Slowakiewicz et al. 2021).

Biofilms can have an important role in the formation of low-Mg calcite ooid cortex. The formation of algal biofilms in hardwater streams, rivers, and lakes often leads to calcite deposition (Hartley et al. 1996; Merz-Preiβ and Riding 1999). In creeks affected by karst, cyanobacterial biofilms are tightly linked to formation of stromatolite-like structures (Bissett et al. 2008a, 2008b). In these studies, the use of microelectrodes allowed the direct measurement of chemical activity near the surface of biofilms composed of filamentous cyanobacteria (Merz et al. 1995). Calcium carbonate precipitation in the photic zone of a hypersaline microbial mat is primarily controlled by photosynthesis-induced pH and carbonate concentration increase (Ludwig et al. 2005). Biomineralization could also take place under hydrothermal conditions. In this case, high concentrations of pCO_2 generate acidic extracellular polysaccharides (a part of exopolymeric substances or EPS produced by microorganisms). These EPS are capable of adsorbing Ca^{2+}(aq) and Mg^{2+}(aq), thus leading to mineralization and cell aggregation and thus forming solid particles of Ca(Mg)carbonate minerals (Kamennaya et al. 2018). The importance of EPS has been recently demonstrated for dolomite precursor formation in cyanobacteria-dominated microbial mat from a sabkha (Paulo et al. 2020).

The bio-induced formation of Ca carbonate can be useful to artificial applications, such as the restoration of concrete (Zhu et al. 2015; Le Métayer-Levrel et al. 1999; Castanier et al. 2000). Other applications of the biomineralization of Mg carbonate minerals could be the rehabilitation of asbestos mine sites and in situ carbon sequestration (Power et al. 2011; McCutcheon et al. 2016).

The above-considered examples underline the importance of understanding the mechanisms of carbonate mineral precipitation under the influence of microbes. To achieve this understanding, however, well-constrained laboratory approaches are needed. Experimental modeling of naturally occurring processes allows straightforward identification of governing parameters via decreasing the number of freedoms in the system and systematically testing various controlling factors. Below we consider laboratory experiments on Ca and Mg carbonate formation in the presence of cyanobacteria. This is by far the most important process, controlling carbon cycle on the planet since early Proterozoic.

2 Calcium Carbonates

The most efficient microorganisms in Ca and Mg carbonate precipitation are cyanobacteria, due to their capacity to uptake inorganic C via photosynthesis accompanied by rising the pH and saturation degree in the external milieu and in the vicinity of cells. Due to extensive carbonate deposits in the fossil records of the Earth, this process is useful for reconstructing the evolution of cyanobacteria and their role in the carbon cycle of the hydrosphere (Benzerara et al. 2014). In carbonate-rich water, the formation of calcite induced by cyanobacteria is not a simple side effect of photosynthesis. The mechanisms operating behind the

biocalcification are highly variable among the species and strongly depend on the external environment. There is little doubt that the principal physicochemical factor controlling calcite precipitation is the saturation state of water with respect to calcium carbonate. In case of cyanobacteria, $CaCO_3$ precipitation can be a way to mitigate the negative effect of elevated pH in the external environments, notably adjacent to the cell surfaces (Rahman et al. 2019). It can also serve as a protection for the bicarbonate pump, which could possibly be inhibited by carbonate ions. At the same time, even in supersaturated hardwater lakes, the precipitation is not always observed. Quite often, $CaCO_3$ precipitation can be inhibited by various dissolved substances such as magnesium, phosphates, or organic ligands (Pokrovsky and Savenko 1994a, 1994b, 1995). In natural settings, however, carbonate nucleation occurs in specific microniches adjacent to cells and cell aggregates; these microenvironments can be hardly monitored via conventional analyses (Dittrich et al. 2003). It is therefore important to determine the factors leading to the precipitation of calcite under controlled conditions, in order to control and identify their individual importance.

2.1 Mechanisms of Precipitation

According to Jansson and Northern (2010), the precipitation of $CaCO_3$ can occur according to general reactions (Zhong and Mucci 1993; Zuddas and Mucci 1998):

$$Ca^{2+}(aq) + 2HCO_3^-(aq) = CaCO_3(solid) + CO_2(g) + H_2O(l) \quad (1)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) = CaCO_3(solid) \quad (2)$$

The ion HCO_3^- is formed due to dissolution of $CO_2(g)$:

$$CO_2(aq) + H_2O(l) = H_2CO_3(aq) \quad (3)$$

$$H_2CO_3(aq) = HCO_3^-(aq) + H^+(aq) \quad (4)$$

In carbonate mineral-precipitating environments, the concentration of carbonic acid is usually low; as a result, the dissolved CO_2 from reactions (3) and (4) occurs predominantly as HCO_3^-, a part of which dissociates to form carbonate CO_3^{2-}:

$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq) \quad (5)$$

The supersaturation of solution with respect to calcium carbonate (Ω_{CaCO_3}) is defined as

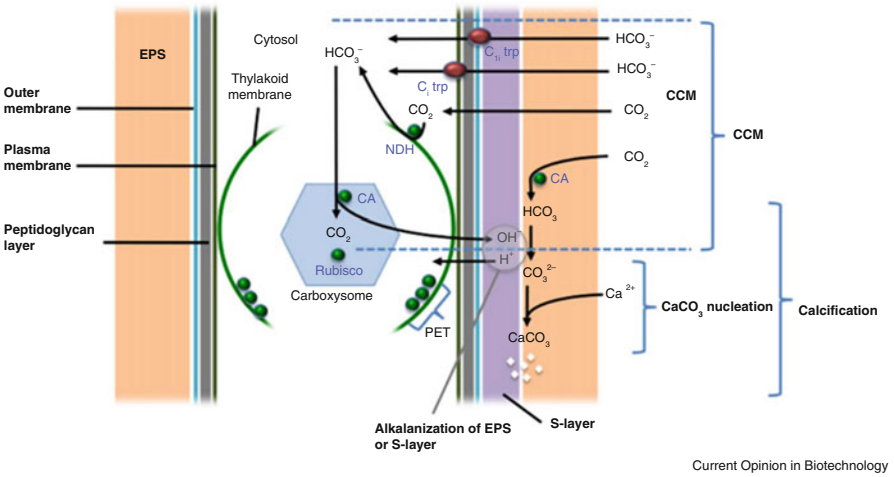

Fig. 1 Schematic operation of the carbon-concentrating mechanism (CCM) leading to calcification in a cyanobacterial cell. CO_2 enters the cells both via active transport of HCO_3^- and through diffusion of CO_2, which is converted to HCO_3^-(aq) whereas cytosolic HCO_3^- is imported to the carboxysome. CA, carbonic anhydrase; Ci, inorganic carbon; EPS, exopolysaccharide sheath; NDH, NADP dehydrogenase; and PET, photosynthetic electron transport. From Jansson and Northern (2010)

$$\Omega_{CaCO_3} = \frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{K_{S_{CaCO_3}}} \tag{6}$$

where $a_{Ca^{2+}}$ and $a_{CO_3^{2-}}$ are activity of free ions Ca^{2+}(aq) and CO_3^{2-}(aq) in solution; $K_{S_{CaCO_3}}$ represents the solubility product of calcium carbonate.

In the world oceans, various kinetic inhibitors preclude spontaneous nucleation of $CaCO_3$ despite sizable supersaturation with respect to calcite and aragonite (Berry et al. 2002); such inhibitors include Mg^{2+}, phosphate ions, and dissolved organic matter (Pokrovsky and Savenko 1994a, 1994b, 1995; Pokrovsky 1998). Cyanobacteria and eukaryotic photosynthesizing algae possess a carbon-concentrating mechanism (CCM). This highly sophisticated metabolic system helps the cells to deliver the CO_2 at the site of Rubisco (the first enzyme in the Calvin cycle that assimilates CO_2 into organic carbon compounds) and enrich CO_2 there up to 1000-fold compared to that in the external milieu (see Fig. 1). Although specific pathways are variable among cyanobacteria, a general setting includes transport of aqueous HCO_3^- across the outer membrane and the plasma membrane, implying symports HCO_3^-/Na^+ or ATP-driven uniports. This is also accompanied by a diffusion of CO_2, into the cell cytosol. The NADP dehydrogenase (NDH) complexes on the thylakoid and plasma membranes are responsible for conversion of cytosolic CO_2. The bicarbonate ion is transformed to CO_2 via carbonic anhydrase (CA)-catalyzed reaction:

$$CO_2(g) + H_2O(l) = H^+(aq) + HCO_3^-(aq) \quad (7)$$

The efficiency of this conversion depends on CA-like concentrations and activities in relevant proteins. The different consecutive and parallel steps of phase nucleation, isomer transition, Ostwald ripening and aging, crystalline mineral formation, and their aggregation in the overall biomineralization processes still need to be understood. The most important cell surface entities involved into biocalcification, the EPS and bacterial S-layer, require detailed structural and functional characterization. For example, some experimental studies demonstrated that the precipitation of $CaCO_3$ is significantly hindered when the function of extracellular carbonic anhydrase in *Synechocystis* sp. was inhibited (i.e., Yang et al. 2016).

Other studies demonstrated that, even if picocyanobacteria were proved to play a key role in the formation of $CaCO_3$, the underlying mechanisms are still unclear (Liang et al. 2013; Obst et al. 2009a, 2009b; Robbins and Blackwelder 1992). A most common hypothesis states that bacterial photosynthesis leads to $CaCO_3$ via modification of calcium-carbonate equilibrium in the surrounding microenvironment, merely via increasing $CaCO_3$ saturation state (Ω_{CaCO_3}) (Kranz et al. 2010). An alternative mechanism of $CaCO_3$ formation involves surfaces of cells as a template for mineral nucleation. The crystallization of CaCO3 further occurs due to supersaturation created in the layer adjacent to the cell surface. In this regard, picocyanobacteria are especially efficient as they exhibit the highest ratio of the surface area to the cell volume (Dittrich et al. 2004; Lee et al. 2004) which can be an optimal template to help the nucleation of crystals. Particular role is attributed to negatively charged surface functional groups able to form strong complexes with divalent cations such as Ca or Mg, thus further promoting the nucleation and crystal growth at the cell surface (Schultze-Lam and Beveridge 1994). Relatively recently, it has been suggested that the first step in biological $CaCO_3$ (calcite, aragonite) formation is precipitation of an amorphous calcium carbonate (ACC), which occurs via condensation of primary surface-adsorbed clusters leading to final generating the crystalline end member (Gebauer et al. 2008; Stephens et al. 2011).

In their study, Liang et al. (2013) showed that each of the three tested *Synechococcus* strains (ARC21, LS0519, and PCC8806) exhibited different impacts on solution chemistry and $CaCO_3$ precipitation; these impacts were primarily linked to the ion-exchange capacity at the interface between the cell surface and the aqueous solution. Results of these authors demonstrated that all *Synechococcus* strains are able to aggregate mineral constituents on their organic templates; this aggregation was strongly promoted by cell surface charge and was possible event at low degrees of solution saturation. The same type of mechanism is proposed by Bundeleva et al. (2014), where cyanobacteria *Gloeocapsa* sp. cells induced the precipitation of $CaCO_3$ via binding of Ca^{2+} with the negatively charged groups of the cell surfaces and cell exopolymeric substances (EPS).

The study of Obst et al. (2009a, 2009b) is also in favor of a heterogeneous nucleation process. Indeed, they performed long-term precipitation experiments in the presence of cyanobacteria *Synechococcus leopoliensis* PCC 7942 with stabilized

CO_2 concentration and externally controlled carbonate equilibrium. This allowed them to differentiate between a direct impact of the photosynthesis on $CaCO_3$ nucleation induced by local oversaturation in the layer adjacent to the cells and an indirect impact of photosynthetic HCO_3^-(aq) uptake leading to increase in solution saturation state. This methodology allowed quantifying the impact of the cyanobacteria in the course of biomineralization via maintaining continuous equilibrium with atmospheric CO_2 and low nutrient concentrations. Obst et al. (2009a, 2009b) demonstrated that, while cyanobacteria can regulate the external chemical environment thus controlling the kinetics of $CaCO_3$ nucleation and precipitation, under nutrient-poor conditions and sufficient CO_2 supply, neither photosynthetic uptake of CO_2 nor active ion-exchange processes across the cell membrane directly influenced kinetics of the mineral nucleation step on the cell surface. These authors concluded that the first nucleation step of $CaCO_3$ on the surface of cyanobacterium *S. leopoliensis* is a passive process, in which both the cell surface moieties and bacterial EPS act as preferential sites for mineral nucleation.

The study of Dittrich et al. (2003) on the precipitation of calcite in the presence of *Synechococcus* sp. cells with two different HCO_3^-(aq): Ca^{2+}(aq) ratios also suggests the importance of cells as nucleation centers in the precipitation mechanisms. These authors studied the role of aqueous solution composition on $CaCO_3$ precipitation at constant saturation state but different ratio of mineral constituents (Ca and DIC). The composition of solutions strongly influenced the calcite precipitation, as the precipitation was higher at HCO_3: Ca >1. However, these laboratory results suggested that the precipitation was mostly controlled by microenvironments around the cells rather than the calcite supersaturation degree of the bulk aqueous solution.

Martinez et al. (2016) used a mixed flow bioreactor consisting of one inorganic Ca stock solution and one cyanobacteria *Synechococcus* sp. PCC 7942 biomass stock solution. Both solutions were pumped at a constant rate to maintain a steady-state condition in the reactor. The inorganic carbon was provided via air bubbling. They observed the precipitation of $CaCO_3$ phase and a gradual pH decrease, thus supporting the following mechanism (reactions (8) and (9)):

$$HCO_3^-(aq) + H_2O(l) = CH_2O(s) + O_2(g) + OH^-(aq) \quad (8)$$

$$HCO_3^-(aq) + OH^-(aq) = CO_3^{2-}(aq) + H_2O(l) \quad (9)$$

Combining reactions (8) and (9) with (2), this mechanism can be summarized by reaction (10):

$$Ca^{2+}(aq) + 2HCO_3^-(aq) = CH_2O(biomass) + O_2(g) + CaCO_3(solid) \quad (10)$$

In their experiments, the mineral precipitation was confirmed by Raman spectroscopy and scanning electron microscopy observations. It was concluded that the photosynthesis of planktonic cyanobacterium may contribute to carbonate biomineralization at the large scale. Martinez et al. (2016) also showed the generation of strongly supersaturated solution using dissolving CO_2 as a sole source of inorganic

carbon provided that cyanobacterial activity maintains sufficiently elevated pH in the bulk solution. Although, in principle, such a system is able to continuously biomineralize CO_2 and store it in the form of calcite, further pilot-level studies are required for a large-scale implementation.

It has to be noted that the role of photosynthesis in the precipitation processes still remains controversial. For example, Kosamu and Obst (2009) studied the precipitation of $CaCO_3$ with *Synechococcus* sp. PCC 7942, with and without a photosynthesis inhibitor (Diuron). With sufficient supply of atmospheric CO_2, precipitation was accelerated when photosystem II was blocked. This calls into question the role of photosynthesis in precipitation mechanisms. These results are in opposition with other studies (e.g., Stipp 1999; Thompson et al. 1997) which suggested that photosynthesis was essential in biomineralization processes.

2.2 *Extracellular Precipitation of Ca Carbonates*

Various cyanobacteria strains have proved to be able to calcify and produce extracellular precipitation of calcium carbonates. For example, Lee et al. (2004) showed that different strains of *Synechococcus* and *Synechocystis* have the calcification ability under microcosm conditions provided that the solution is enriched in HCO_3^- and Ca^{2+} ions. Among various cyanobacterial strains, only two were able to precipitate calcite, thanks to their ability to remove CO_2 and rise the pH. Precipitation of $CaCO_3$ also occurred in the presence of cyanobacteria *Synechococcus* PCC 8806 and PPC 8807 (Lee et al. 2006). Calcium ion adsorption on the outer surface layer of cyanobacterial cells facilitated nuclei formation, necessary for subsequent $CaCO_3$ precipitation (Obst et al. 2006).

Recently, another phenomenon which could impact $CaCO_3$ biomineralization was identified: viral lysis of cyanobacteria. This process could release high amount of intracellular inorganic carbon, thus inducing the homogeneous nucleation of $CaCO_3$. Indeed, Xu et al. (2019) demonstrated that viral lysis of cyanobacteria *Synechococcus* sp. PCC 7177 led to the formation of amorphous calcium carbonate and aragonite, compared with noninfected cultures, where only brucite ($Mg(OH)_2$) precipitated. Suitable conditions for calcification may occur due to viral lysis of cyanobacteria which can liberate inorganic carbon species.

Organic compounds, such as EPS secreted by cyanobacteria, could strongly influence $CaCO_3$ polymorphism. In the study of Kawaguchi and Decho (2002), EPS from the lithified layer of stromatolites led to aragonite precipitation, whereas calcite crystals were formed only in the presence of EPS from the unlithified layer. For marine calcifiers, it has been shown that the chitin-rich skeletal organic matrix of coralline algae is essential for the precipitation of Mg calcite (Rahman et al. 2019). The quantity of phosphorus in the medium is another factor that can impact carbonate precipitation rates and mineral morphology (Paulo et al. 2018).

Experiments with anoxygenic phototrophic bacteria demonstrated that they were able to form $CaCO_3$, whose amount was proportional to that of organic C in the newly formed bacterial biomass (Bundeleva et al. 2012). There was no solid phase at the surface or in the vicinity of the cells, which suggested a cell protection mechanism against carbonate precipitation around the cells. The same protective mechanism was observed with cyanobacteria *Synechococcus* sp. and *Planktothrix* sp. (Martinez et al. 2010). These bacteria were capable of regulating their surface electric potential via decreasing the magnitude of surface charge or even generating positive charges in highly alkaline solutions (Martinez et al. 2008). On the one hand, this helped to electrostatically attract bicarbonate anions required for photosynthesis to the cell surfaces in alkaline solution, where the concentration of HCO_3^-(aq) ions is rather low. On the other hand, maintenance of a positive surface potential in alkaline solutions could protect viable cyanobacteria against Ca^{2+} adsorption and subsequent carbonate precipitation on their surfaces leading to cell entombment.

On the contrary, cyanobacteria *Gloeocapsa* sp. did not show any protection mechanism: experiments demonstrated abundant encrustation of cell surfaces by $CaCO_3$ present in the form of nanospheres (Bundeleva et al. 2014). This difference can be linked to the difference in cellular organization of different cyanobacterial species. The planktonic *Gloeocapsa* sp. is represented by several cells encompassed into one capsule, which probably protect them from the external milieu, and thus no cell surface protection mechanism in alkaline solution is needed. As a result, these species demonstrate very high CO_2-fixing potential making them most suitable cyanobacteria for industrial-scale biomineralization and CO_2 sequestration.

2.3 Intracellular Formation of Ca Carbonates

In the majority of investigated cases of cyanobacterial calcification, extracellular formation of calcium carbonate which is essentially an indirect by-product of cyanobacterial metabolism is the main biocalcification process. However, intracellular Ca carbonate biomineralization can be also performed by many cyanobacterial species which opens new perspectives on the understanding of evolution of cyanobacterial calcification. Indeed, Benzerara et al. (2014) conducted a study of intracellular $CaCO_3$ biomineralization on 68 different cyanobacterial strains. For each strain, they performed scanning electron microscopy (SEM) observations, scanning transmission X-ray microscopy (STXM), and phylogenetic analyses. Among studied species, all but eight showed the formation of intracellular carbonate inclusions. Seven of them contained spherical and poorly crystalline Ca carbonate, located specifically at the poles of the cells (Fig. 2). Other studies, such as Couradeau et al. (2012), Lin et al. (2014), Li et al. (2016), and Cam et al. (2018), showed the same type of intracellular precipitation in various cyanobacteria. Cam et al. (2016) realized an abiotic study of the precipitation of Ca-Sr-Ba-Mg-bearing carbonate, to mimic what happens in intracellularly calcifying cyanobacteria. Similar size and poor crystallinity were observed for most experiments, but the partition of these

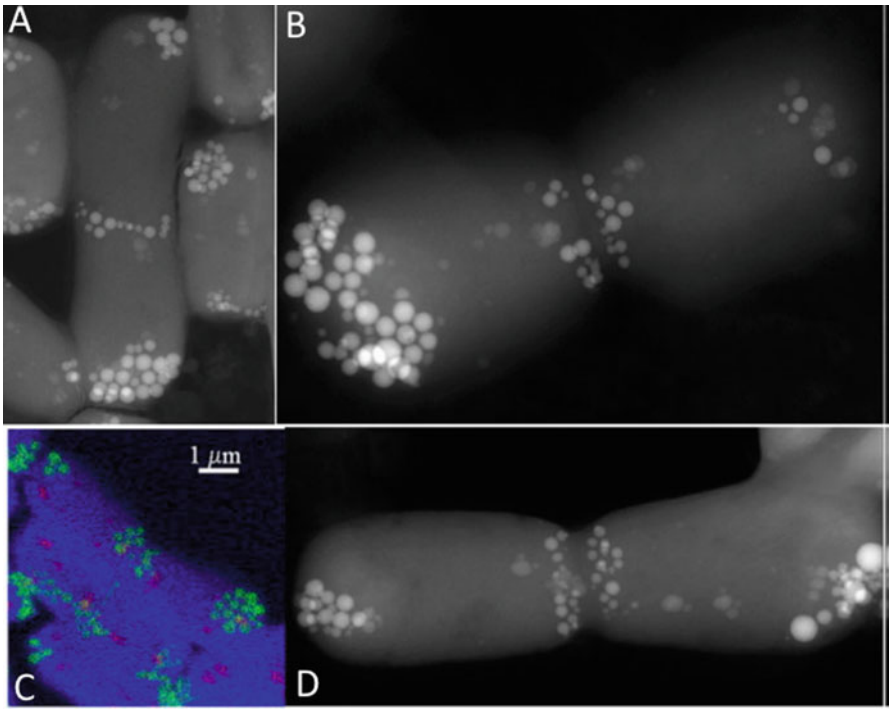

Fig. 2 Group of Karim Benzerara demonstrated multiple cases of intracellular Ca carbonate formation in the cyanobacteria. Significant progress has been achieved, thanks to use of high-resolution in situ techniques such as STEM-HAADF of shown in this figure for *Synechococcus* sp. PCC 6312. Ca carbonate inclusions are distinguished at the poles of the cells and at the sites of septation; the latter are smaller than the ones at the poles. An STEM-EDX map is shown in C: calcium, green; phosphorus, red; carbon, blue. From Benzerara et al. (2014)

elements between aqueous solution and precipitated carbonate solid phase was different from that in cyanobacterial cells.

2.4 Ca Carbonate Precipitation with Heterotrophic Bacteria

It is important to note that other microorganisms than cyanobacteria could allow the precipitation of calcium carbonate minerals. For example, Silva-Castro et al. (2015) studied the precipitation of calcite and aragonite in the presence of cells isolated from seawater and brine in both liquid and solid environments. The cells were identified mostly as heterotrophic bacteria from genera *Bacillus* and *Virgibacillus*. Results showed that precipitation occurred only when organic matter was added in the solution.

Sondi and Matijević (2001) showed that the nature of Ca carbonate whose formation is catalyzed by urease enzyme was strongly dependent on the stirring of the reacting solution and demonstrated that without stirring of solution, there was a formation of an amorphous phase which further crystallized to vaterite and then to calcite. In contrast, under stirring, smaller particles were formed, which recrystallized into vaterite and calcite. The amount of the added enzyme had an influence on the kinetics of reaction: a greater quantity of enzyme leaded to a faster precipitation. However, different enzymes led to different $CaCO_3$ polymorphs. For example, in the study of Sondi and Salopek-Sondi (2005), the presence of *Bacillus* urease induced the formation of spherical and uniform vaterite, whereas only calcite was formed in the presence of *Canavalia* urease. Formation of monohydrocalcite by marine sulfate-reducing bacterium *Desulfovibrio bizertensis* has been recently reported by Bradbury et al. (2020). Barabesi et al. (2007) identified specific genes of *Bacillus subtilis* involved in $CaCO_3$ formation and demonstrated an important role of fatty acid metabolism in the biomineralization process. Ercole et al. (2007) found that proteins of 25–40 kDa and 70 kDa molecular weight located in the capsular polysaccharide fraction of the *Bacillus firmus* and *Bacillus sphaericus* play a major role in Ca^{2+} ion binding necessary for $CaCO_3$ formation.

Generally, both cell surfaces and exopolymeric substances (EPS) excreted by bacteria exhibit a strong ability to complex Ca^{2+}(aq), thus acting as main sites of mineral nucleation. A number of studies attempted directly observing and identifying the nucleation sites involved in Ca carbonate formation in the vicinity of bacterial surfaces. Aloisi et al. (2006) tested the capacity of sulfate-reducing bacteria *Desulfonatronum lacustre* to serve as nucleation centers in solutions strongly supersaturated with calcite and aragonite. Tiny globules were exclusively observed at the surfaces of bacterial cells where they were embedded in a thin film of EPS. Much larger globules were clearly separated from the cells, and they formed independent aggregates. Chemical analyses of cell surfaces and globules indicated that the surface of *D. lacustre* cells could not be a template of $CaCO_3$ precipitation. Despite the fact that some Ca carbonate grains were bound to EPS in the form of very small globules, the large globules exhibited the highest carbonate content and presented the largest contribution to overall $CaCO_3$ precipitation. Specifically, spherical nucleation centers were calcified extensively when released into solution. The initial formation of globules occurred within the EPS layer surrounding the bacterial cell surface. In the study of Bosak and Newman (2005), the uptake of millimolar sulfate and lactate by the sulfate-reducing bacteria *Desulfovibrio desulfuricans* stimulated the formation of calcite crystals. Abundant presence of purified EPS produced by this strain enhanced the formation of round-edge crystals at low supersaturation degree, whereas the effect of these organic substances was strongly reduced at higher supersaturations (Bosak and Newman 2005). These observations indicate that microbes can exert kinetic control by the secretion of exopolymeric substances and by the active uptake or release of primary organic and inorganic metabolites. For example, Ercole et al. (2007) performed $CaCO_3$ precipitation mediated by EPS of *B. firmus* and *B. sphaericus*. Extracellular polysaccharides and capsular polysaccharides extracted from both bacteria were able to mediate $CaCO_3$ precipitation. The shapes of the

crystals were different depending on the capsular and extracellular polysaccharides originated from bacterial surfaces.

The morphology of crystals could also depend on the presence of live or dead cells. Both play a passive role in calcium carbonate precipitation by acting as a template for heterogeneous nucleation, whereas live bacteria additionally play an active role via increasing the pH in the vicinity of their cell surfaces and in certain microenvironments (Chekroun et al. 2004).

Overall, heterotrophic bacterial activity, linked to sulfate reduction, was considered as one of the main mechanisms of carbonate stromatolite buildups (i.e., Vasconcelos et al. 2006; Visscher et al. 1998), although a lot of controversies still remain, given that at relatively low pH of sulfate reduction (6.5–7.0), carbonate saturation might not be sufficient to induce large amount of carbonate mineral formation, especially in alkaline Precambrian ocean.

In addition to aerobic heterotrophic bacteria, anoxygenic phototrophic bacteria (APB) are also able to mediate $CaCO_3$ precipitation in nutrient media (Bundeleva et al. 2012) and form a proto-lamina, necessary for subsequent carbonate stromatolite growth (Bosak et al. 2007). However, unlike cyanobacteria, the APB require initial supersaturation of solution with respect to calcium carbonate and thus cannot be considered as an important factor of global biocalcification processes.

3 Ca-Mg Carbonates

There are different sorts of dolomitic rocks, differing by their quantitative proportions of Ca and Mg: dolomite, its less crystalline and less stoichiometric precursor called "protodolomite," and crystalline high (>5% mol Mg) – and low – (<5% mole Mg) magnesian calcites. The structure of dolomite is similar to that of calcite and exhibit interlayered alterations of Ca and Mg atoms. Protodolomite exhibits elevated Ca content (≤10 molar %) and has various structural distortions and imperfections. High- and low-magnesian calcites can be considered as intermediates between calcite and dolomite. These minerals are abundant in marine settings in the form of skeletal debris and various sediments (Zaitseva et al. 2006). There is little doubt that in natural low temperature systems (<60 °C), dolomite formation occurred via microbially catalyzed reactions (Petrash et al. 2017).

Numerous experiments demonstrated poorly ordered dolomite formation under action of sulfate-reducing bacteria (Baldermann et al. 2015; Vasconcelos et al. 1995; Warthmann et al. 2000), anaerobic microbial consortium (Kenward et al. 2009), methanogens (Kenward et al. 2013), and halophiles (Al Disi et al. 2017; Kenward et al. 2013; Sánchez-Román et al. 2009). Thus, Qiu et al. (2017) demonstrated precipitation of dolomite in the presence of halophilic archaea *Haloferax volcanii* and suggested that under high salinity conditions, the amount of surface carboxylates increases in order to sustain high osmotic pressure, thus promoting dolomite precipitation due to enhanced surface complexation of Ca and Mg ions. Moderately halophilic bacteria *Halobacillus trueperi* were able to produce Mg and Ca

carbonates in both solid (agar) and liquid media of variable salt concentrations, most of the time during the stationary phase of growth. Suggested mechanism involves the adsorption of Ca^{2+}(aq) and Mg^{2+}(aq) and production of CO_2 and NH_4^+ ions. The latter could increase the solution pH, thus leading to a biologically induced biomineralization (Rivadeneyra et al. 2004). Nineteen other moderately halophilic bacteria also formed Mg and Ca carbonates (Sanchez-Roman et al. 2007). In the latter study, with increased calcium concentration in the culture solution, the Mg^{2+} content in calcite decreased, the precipitation time decreased, and the amount of carbonate mineral solid phase increased. Overall, studies of sulfate-reducing heterotrophic bacteria impact on the precipitation of Mg-Ca carbonate minerals demonstrated that the EPS played a dominant role in the nucleation and subsequent precipitation of protodolomite (Bontognali et al. 2008, 2014).

A number of studies addressed Ca isotope fractionation during microbially induced Ca and Mg carbonate formation (Krause et al. 2018; Bradbury et al. 2020). In the presence of sulfate-reducing bacterium *Desulfobulbus mediterraneus*, there was an enrichment in ^{40}Ca in the carbonate minerals precipitated from aqueous solution (Krause et al. 2012). These authors demonstrated that isotope fractionation involves two steps: (1) initial binding of Ca^{2+}(aq) by bacterial biofilm and (2) subsequent fractionation between mineral and aqueous solution due to precipitation of dolomite.

In contrast to relatively good knowledge of heterotrophic bacteria, the role of phototrophic microorganisms such as cyanobacteria on dolomite rock formation is still poorly studied. Zaitseva et al. (2006) demonstrated that cyanobacterium *Microcoleus chthonoplastes* is able to slow down the precipitation of Mg carbonates via producing metal-chelating metabolites. In particular, under active photosynthesis, the huntite ($Mg_3Ca(CO_3)_4$) could be formed, whereas in the darkness, the protodolomite together with various magnesium calcites was observed in carbonate sediments. Other experiments with cyanobacteria *Microcoleus chthonoplastes* reached the same conclusions (Ushatinskaya et al. 2006). A study of Ca-Mg carbonate transformation under soda lake conditions demonstrated that, due to activity of microorganisms inhabiting a cyanobacterial mat, there was a restructuration of the primarily present carbonate minerals (Zaitseva et al. 2007).

A study of Ca and Mg isotope variation in foraminifera carbonate skeletons at variable Mg-Ca ratios (Chang et al. 2004) showed that in reef coral, the controlling factor of carbonate biomineralization was mainly crystal growth. In foraminifera, the nucleation and crystallization produced similar isotope fractionation; therefore, isotopic approach here could not be used for revealing different mechanisms of Ca ion transport in the cells.

4 Mg Carbonates

Precipitation of $CaCO_3$ under microbial activity has been thoroughly studied under variable surface aquatic environments, from the ocean to the groundwater. However, other divalent metal carbonates such as hydrous Mg carbonates (HMC) can be easily precipitated in alkaline aquatic settings provided that there is some biological activity of phototrophic microorganisms such as cyanobacteria or diatoms. Similarly to $CaCO_3$, the HMC precipitation is favored by elevated pH and alkalinity although specific conditions required for such mineral precipitation are insufficiently well known (McCutcheon et al. 2014).

4.1 Formation of Different Mg Carbonates

According to Power et al. (2007), who performed laboratory experiments to compare HMC precipitation under controlled biotic and abiotic conditions, the nature of the precipitated mineral is different depending on whether or not cyanobacteria were present. According to these authors, the formation of Mg carbonate in the presence of cyanobacteria was happening at a faster rate, and with a different mineralogy than in the abiotic systems. The dypingite ($Mg_5(CO_3)_4(OH)_2{\bullet}5(H_2O)$) was the primary precipitate in experimental biofilms, whereas the abiotic controls yielded only nesquehonite ($Mg(HCO_3)(OH){\bullet}2(H_2O)$, Power et al. 2007). In the abiotic control, the addition of NaOH led to formation of dypingite rosettes similar to those produced by microbial biofilms. However, under abiotic conditions, nesquehonite was still the major precipitated mineral, even at higher pH values. Results of these researchers demonstrated a primary role of pH as a factor controlling the identity of bio-precipitated mineral, with more alkaline conditions being more favorable for dypingite.

At the same time, other studies indicate no difference between Mg carbonates formed under biotic or abiotic conditions. As an example, Mavromatis et al. (2012) performed Mg carbonate precipitation in batch reactors with and without cyanobacteria *Gloeocapsa* sp. under various experimental conditions such as stirring and air bubbling, continuous light, darkness, and day/night cycle. In all experiments, similar apparent precipitation rates of HMC (nesquehonite and dypingite) were observed. These authors concluded that the cyanobacteria do not appreciably affect the rates of hydrous magnesium carbonate formation in natural systems. They also performed stable Mg isotope analysis and concluded that Mg isotopic composition of HMC does not allow to discriminate the role of biota or the aqueous solution composition of past aquatic ecosystems.

In addition to the formation of dypingite and nesquehonite, biomineralization of hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\bullet}4(H_2O)$) is also possible. For example, Shirokova et al. (2013) performed batch laboratory experiments in the presence of cyanobacteria *Synechococcus* sp. isolated from stromatolites of Lake Salda

(Turkey), which resulted in the precipitation of dypingite and hydromagnesite similar to the natural hydromagnesite of stromatolites. Rates of precipitation were similar to that reported for dypingite precipitation in the presence of *Gloeocapsa* sp. during stirred, non-bubbled experiments of Mavromatis et al. (2012).

4.2 *Experimental Reactors Used to Reproduce Natural Settings*

Although numerous laboratory experiments were realized in closed (batch) reactors, alternative types of reactors may be used to study the biomineralization in various conditions in order to better approach the natural environments. For instance, McCutcheon et al. (2014) used a plug flow bioreactor constructed from a PVC tubing to study the hydromagnesite precipitation in the presence of sediments covered with a microbial mat, composed mainly of filamentous cyanobacteria and diatoms, extracted from an alkaline wetland (Fig. 3). The large decrease of alkalinity, dissolved magnesium concentration, and conductivity during the carbonation phase strongly supported microbially induced precipitation of HMC. During the first week of the carbonation phase, a drop in dissolved oxygen was observed which may have been caused by the beginning of the carbonate mineral precipitation preventing the sunlight from reaching the mats and thus slowing down the photosynthesis. The precipitated mineral was identified as hydromagnesite. The rate of carbon storage in the precipitated hydromagnesite was determined using empirical mineralization values.

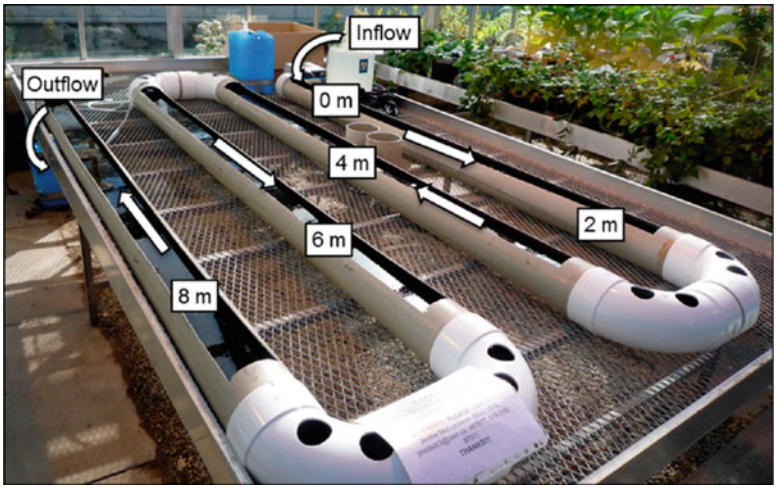

Fig. 3 Example of a bioreactor operating with microbial mats of cyanobacteria and diatoms and producing various hydrous Mg carbonates (McCutcheon et al. 2014). The labels (in meters) represent the sampling points

Overall, such medium-scale laboratory mesocosms operated under controlled external (T, light, pCO_2) and internal (pH, Ω, salts, organic matter) parameters, ideally in a flow-through biofilm-bearing system, are best suited to study the governing factors and mineral precipitation rates at the environments that can be reasonably well extrapolated to contemporary natural settings. In order to use these laboratory facilities to reproduce Precambrian environments (high water temperature and high pCO_2), a number of adjustments have to be implemented. The main shortcoming of any biofilm-like cyanobacterial culture is that sizable gradients of pH, Ca(Mg), and Ω in the vicinity of biofilm surface, at the scale of μm to mm, have to be monitored; ideally, this monitoring should include a diel pattern with high temporal resolution.

4.3 Mg Carbonate Precipitation with Fermentative Bacteria and in Microbial Consortium

Similar to Ca carbonates, the biomineralization of Mg carbonates can occur in the presence of other microorganisms than cyanobacteria. For example, Sanz-Montero et al. (2019) demonstrated that fermentative bacterium *Desemzia incerta* can induce the Mg carbonate precipitation in both solid and liquid media. During their experiments, the culture medium was undersaturated with respect to most carbonate minerals except dolomite and magnesite so that hydromagnesite and nesquehonite were not expected to precipitate from this fluid. However, after 15 days of experimental incubations at 30 °C, some mineral precipitation was observed in both solid and liquid cultures. In all the samples, the mineralogical analysis of the precipitates indicated various high Mg carbonates, dominated by a dypingite-hydromagnesite assemblage that also comprised some dolomite, Mg calcite, and magnesite. In the solid culture experiment, mostly nesquehonite was formed where as in liquid medium, only huntite was observed. The EPS that surrounded the microorganisms embedded various carbonate crystals which contained magnesium and some amount of calcium. The lysis of biomass yielded sizable amount of Mg^{2+}(aq) and Ca^{2+}(-aq) which strongly increased the saturation state of solution and favored precipitation of Mg-rich carbonate minerals (Cabestrero and Sanz-Montero 2018). Similar to Ca carbonate system, a general belief is that the microniches of locally high alkalinity and Mg^{2+} concentration in the vicinity of bacteria provide necessary nucleation sites of Mg-rich carbonate mineral precipitation (Pontoizeau et al. 1997; García Del Cura et al. 2014). The key process of Mg incorporation in the solid structure is Mg^{2+}(aq)-organic ligand complexation leading to partial dehydration of $Mg(H_2O)_6^{2+}$ (Power et al. 2009, 2017).

Another experiments with microbial consortium involved a combination of primary silicate mineral dissolution in the presence of heterotrophic bacteria and relevant HMC precipitation by photosynthetic activity of cyanobacteria (Lamerand et al. 2020). In a concerted study of olivine (Mg_2SiO_4) dissolution and relevant

HMC precipitation, we demonstrated that heterotrophic bacterium *P. reactans* and their organic exometabolites enhanced the release of Mg and Si from olivine structure whereas *Synechococcus* sp. cyanobacterial photosynthesis raised the pH and favored precipitation of hydrous Mg carbonates and silicates in the vicinity of the cells (Lamerand et al. 2020). Cyanobacterial activity increased the pH above 10, thus inducing the precipitation of brucite, hydromagnesite, and nesquehonite, together with Mg silicates such as sepiolite. Interestingly the decrease of pH following cyanobacterial cell lysis brought about the dissolution of earlier precipitated HMC minerals. Overall, the impact of bacterial consortium on primary mineral dissolution and secondary carbonate mineral precipitation was higher than that of individual species and may represent important and understudied biotically controlled mechanism of CO_2 sequestration in natural waters.

5 Efficiency of Phototrophic Bacteria to Precipitate Calcium and Magnesium Carbonates for Ex Situ Carbon Sequestration

Based on batch laboratory experiments performed by our group on cyanobacterially induced precipitation of Mg and Ca carbonates (Bundeleva et al. 2012, 2014; Mavromatis et al. 2012; Shirokova et al. 2013), we analyzed the ratio between sequestered metal cation or inorganic carbon (precipitated in the form of carbonate minerals) and the amount of sequestered organic carbon, via an increase in microbial biomass due to cell growth. This allowed assessing the efficiency of biological C sequestration via cyanobacterial biomineralization under controlled laboratory conditions.

5.1 *Mg Hydrous Carbonate Precipitation in the Presence of* Gloeocapsa *sp. Cyanobacteria*

Mavromatis et al. (2012) studied the precipitation of hydrous Mg carbonate in the presence of cyanobacteria *Gloeocapsa* sp. The amount of HMC increased with an increase in the amount of biomass produced during experiment (Fig. 4) and can be approximated by

$$\mathrm{Mg}_{\mathrm{precipitated}}(\mathrm{mmol}) = k \times \mathrm{Biomass}_{\mathrm{produced}}(\mathrm{g}_{\mathrm{wet}}), \quad r^2 = 0.96 - 0.88 \qquad (11)$$

where k is an empirical coefficient ranging from 2.7 to 7.0. Taking into account the ratio of wet to dry biomass of *Gloeocapsa* sp. (10 ± 2), this yields the molar inorganic Mg to organic C ratio in the reaction product of 0.54–1.4 depending on stirring/bubbling regime and the status of *Gloeocapsa* sp. bacteria (alive, dead, or

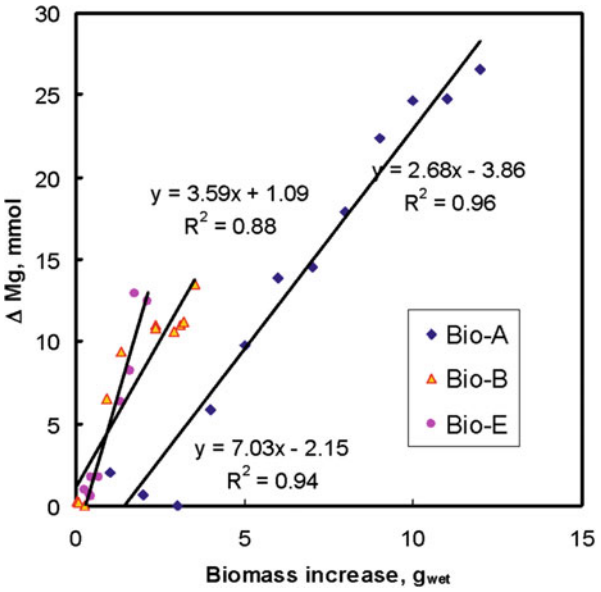

Fig. 4 Plot of Mg removed (mmol) as a function of absolute biomass increase during *Gloeocapsa* sp. growth and hydrous Mg carbonate precipitation. Data from Mavromatis et al. (2012)

inactivated). This value is generally consistent with a theoretical (stoichiometric) Mg:C_{org} ratio of 1 for nesquehonite bearing in mind that the nesquehonite is a first precipitating phase during cyanobacterial photosynthesis:

$$\begin{aligned} Mg^{2+}(aq) + 2HCO_3^-(aq) + 3H_2O = \quad & MgCO_3 \bullet 3H_2O(s) \\ \downarrow + & CH_2O(org) + O_2 \uparrow \end{aligned} \qquad (12)$$

Note that the theoretical value Mg:C_{org} in case of dypingite or hydromagnesite formation is equal to 1.25.

5.2 *Mg Hydrous Carbonate Precipitation in the Presence of Cyanobacteria Isolated from the Lake Salda (Turkey) Hydromagnesite Stromatolites*

Another HMC precipitation experiments involved cyanobacterial culture isolated from live stromatolites of an alkaline, Mg-rich lake (Shirokova et al. 2013). The amount of hydrous magnesium carbonate precipitated as a function of the *Synechococcus* sp. cyanobacterial biomass produced in the reactor is shown in Fig. 5. A straight line that fits all the experimental results is represented by

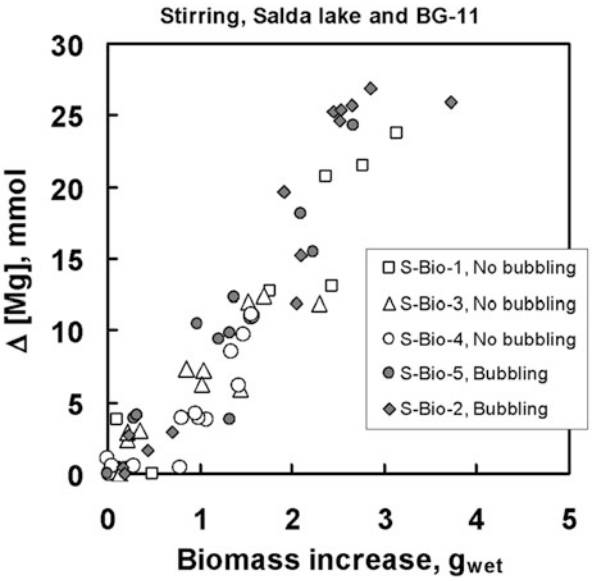

Fig. 5 Experimental dependences ($r^2 = 0.84$–0.93) of moles of Mg precipitated in the form of HMC and the cyanobacterial biomass produced during various biotic performed by Shirokova et al. (2013)

$$\mathrm{Mg}_{\mathrm{precipitated}}(\mathrm{mmol}) = k \times \mathrm{Biomass}_{\mathrm{produced}}(g_{\mathrm{wet}}), \quad r^2 = 0.93 - 0.84 \qquad (13)$$

with k equals to 7.1 ± 0.9. Taking into account that the ratio of wet to dry biomass of *Synechococcus* sp. is 8 ± 2 yields the inorganic Mg to organic C ratio of 1.4 ± 0.2 (molar scale). This value is consistent with stoichiometric Mg:C_{org} value of 1 for nesquehonite (Eq. 12), although closer to the value 1.25 of hydromagnesite and dypingite. Considering all experimental conditions together (air bubbling or not, stirring of solution), there was a good correlation ($R^2 > 0.84$) between the concentration of precipitated Mg and biomass produced in the reactor (Fig. 5). It is noteworthy that both total yield of HMC and apparent rates of HMC precipitation were highly similar among experiments regardless of aqueous solution composition, elapsed time, cell concentration, and bubbling mode. Linear relationships according to Eq. 13 are useful for first-order (with an uncertainty of 25%) prediction of the amount of HMC formed due to photosynthesis of cyanobacteria.

5.3 *Calcium Carbonate Precipitation in the Presence of* Gloeocapsa *sp. Cyanobacteria*

Based on a thorough study of Bundeleva et al. (2014), a linear dependence between the concentration of Ca ion and the cyanobacterial biomass yield has been established (Fig. 6). The slope of this relationship is close to 2 according to

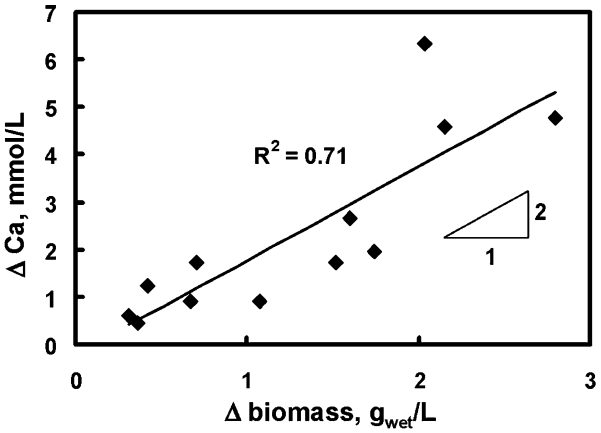

Fig. 6 Linear dependence of the change of Ca concentration due to $CaCO_3$ precipitation and the amount of cyanobacterial biomass produced during biocalcification experiments with *Gloeocapsa* sp. in nutrient (phosphate-free BG-11) solution. The initial supersaturation degree is from 15 to 150 and the pH ranges from 8.6 to 9.6. Data from Bundeleva et al. (2014)

$$\mathrm{Ca\ (mmol)} = (2.0 \pm 0.2) \times \mathrm{Biomass_{cyanobacteria}}(g_{\mathrm{humid}}) \tag{14}$$

Based on this equation, the molar ratio of precipitated Ca to carbon produced by bacterial photosynthesis is equal to 0.48 ± 0.12. This value is two times lower than the theoretical ratio $Ca:C_{org}$ according to $CaCO_3$ precipitation during photosynthesis:

$$Ca^{2+} + 2HCO_3^- = CaCO_3 \downarrow + CH_2O + O_2 \uparrow \tag{15}$$

As a tentative explanation of this deviation from theoretical value, one can cite:

1. Kinetic inhibition of $CaCO_3$ nucleation by the bacteria-produced EPS which led to preserving high supersaturation degree and lowering Ca carbonate yield
2. Inhibition of crystallization on already-present seeds due to passivation by DOM and bacterial metabolites
3. Excess release of cyanobacterial EPS into solution which is not accounted to by measuring biomass concentration (Bundeleva et al. 2014)

It is noteworthy that the measured rate of photosynthetically induced $CaCO_3$ precipitation (range from 0.01 to 0.10 mmol L^{-1} $hr.^{-1}$; Bundeleva et al. 2014) is comparable to those observed for non-capsular planktonic *Synechococcus* sp. and *Planktothrix* sp. cyanobacteria (from 0.03 to 0.04 mM $h.^{-1}$; Martinez et al. 2010), aerobic ureolithic bacteria (0.01 mmol L^{-1} $h.^{-1}$), and anoxygenic phototrophic bacteria (from 0.005 to 0.13 mmol L^{-1} h^{-1}; Bundeleva et al. 2012). Much higher rates of calcification have been reported for unicellular green algae *Nannochloris atomus*: 0.345 mmol L^{-1} h^{-1} at 33 °C (Yates and Robbins 1998).

5.4 Calcium Carbonate Precipitation in the Presence of Anoxygenic Phototrophic Bacteria (APB)

For APB, there was a linear ($R^2 = 0.70–0.99$, $p < 0.01$) relationship between the amount of precipitated Ca and the biomass yield during experimental incubations as reported by Bundeleva et al. (2012). This dependence for *Rhodovulum steppense* A-20s and *Rhodovulum* sp. S-17-65, two anoxygenic phototrophic bacteria isolated from alkaline lakes in south of Siberia (Kompantseva et al. 2010), can be represented by linear Eqs. (16) and (17), respectively:

$$\begin{aligned} \mathrm{Ca_{precipitated}(mol)} &= (1.5 \pm 0.5) \times \mathrm{Biomass_{produced}(g_{humid})}, \quad r^2 \\ &= 0.80 \pm 0.10 \end{aligned} \tag{16}$$

$$\begin{aligned} \mathrm{Ca_{precipitated}(mol)} &= (0.5 \pm 0.3) \times \mathrm{Biomass_{produced}(g_{humid})}, \quad r^2 \\ &= 0.85 \pm 0.15 \end{aligned} \tag{17}$$

The slopes of these dependences varied between 1 and 2 and 0.2 and 0.8 for *Rhodovulum steppense* A-20s and *Rhodovulum* sp. S-17-65, respectively, and depended on initial Ca^{2+}(aq) and HCO_3^-(aq) concentrations (Fig. 7). Converting humid to dry biomass (11.7 and 16.1 for *R. steppense* A-20s and *Rhodovulum* sp. S-17-65, respectively) yields the ratio of sequestered Ca to organically produced carbon of 0.45 ± 0.15 and 0.2 ± 0.1 for A-20s and S-17-65 bacteria, respectively.

Several case studies described in this section demonstrate high potential of photosynthesizing microorganisms to effectively remove C in both organic (biomass) and inorganic (mineral) forms during their metabolic activity.

The molar ratio of $C_{inorganic}$ to $C_{organic}$ removed from solution during biologically induced Ca and Mg carbonate precipitation in the presence of cyanobacteria and anoxygenic phototrophic bacteria ranges from 0.2 to 1.4. The highest value (1–1.4), compatible with theoretical ratio of 1, is associated with Mg hydrous carbonate precipitation in the presence of *Synechococcus* sp. cyanobacteria.

We noted a remarkable similarity of the amount of inorganic carbon biomineralized by phototrophic bacteria per gram of organic carbon (in the form of bacterial biomass) produced (0.5 for *Gloeocapsa* sp.; 1.1 for *Synechococcus* sp.; 0.3–0.6 for anoxygenic phototrophs). This suggests some universal features of C sequestration by aquatic phototrophic bacteria. It follows that photosynthesizing microorganisms are capable of sequestering approximately equal amount of organic and inorganic carbon during their growth in Ca(Mg), HCO_3-bearing media.

The ratios of carbonate C to organic C obtained for bacterially driven mineralization can be compared to those produced by marine plankton coccolithophorids which ranges from 0.8 to 0.9 and sizably decreases with an increase in pCO_2 (Riebesel et al. 2000). This value should be explicitly considered during (1) paleobiogeochemical reconstructions and assessment of biota response to ocean acidification (Beaufort et al. 2011) and (2) quantitative modeling of ex situ C sequestration (Gwenzi 2019).

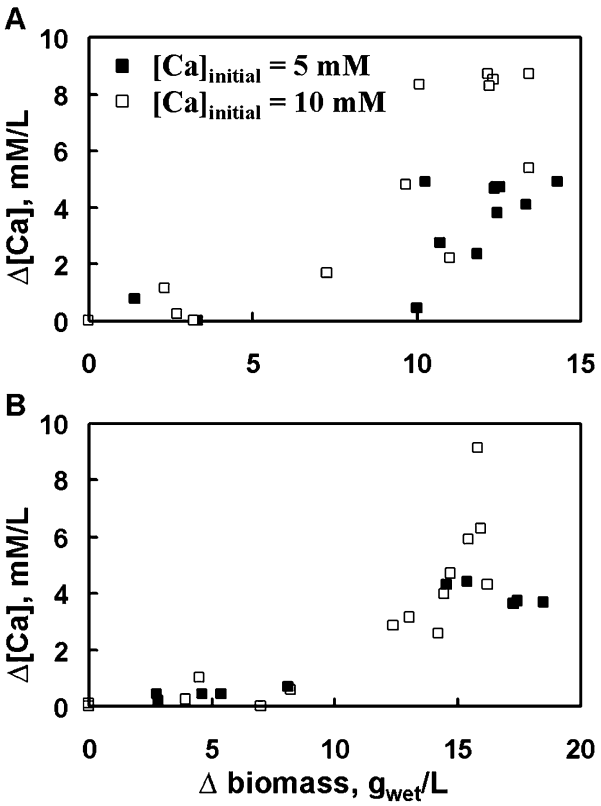

Fig. 7 Increase of sequestered Ca concentration (in the form of $CaCO_3$) with an increase in the biomass of anoxygenic phototrophic bacteria *Rhodovulum steppense* A-20s (**a**) and *Rhodovulum* sp. S-17-65 (**b**) in nutrient-rich, phosphate-free solution. Ca concentration in the initial solution ranges from 5 to 10 mmol L^{-1}, and HCO_3 concentration ranges between 5 and 20 mmol L^{-1}. Data from Bundeleva et al. (2012)

On a broader scale, the obtained results for microbial biocalcification are consistent with well-known ratios of organic carbon to inorganic carbon production (R_{OI}) for marine and freshwater organisms, which allows to determine whether an ecosystems is a net sink or net source of atmospheric CO_2 (Suzuki et al. 1995; Suzuki 1998). The latter author recommended the ratio 1:0.6 of calcification to photosynthesis in seawater. A 1:1 R_{OI} ratio has been suggested for freshwater environments (McConnaugbey 1994). It is interesting that the autotrophs of coral reefs exhibited a photosynthesis that was higher than calcification by 2–9 times (Kinsey 1985; Barnes and Chalker 1990), although the ratio of C_{inorg} to C_{org} in calcifying autotrophs of coral reefs was close to theoretical value (Zimmerman et al. 1996). However, it remains unknown how the ratio of inorganically sequestered C (in the form of $CaCO_3$ of skeletons) to organic C of the organism biomass ranges across different phyla of calcifying eukaryotes including phyto-and zooplankton, sponges, and mollusks, and how it is related (for the same species) to environmental conditions including temperature, nutrient regime, and atmospheric CO_2. Moreover, given that some organisms are capable of precipitating dolomite and magnesite, as it is the case of crustose coralline algae *Hydrolithon onkodes* (i.e., Nash et al. 2011), discrimination between forms of inorganic C becomes an important issue.

As further perspectives of this research, we foresee a need of systematic assessment, using well-elaborated experimental techniques, of the ratio between organic carbon produced by cells and inorganic carbon sequestered in the form of minerals, for a wide variety of photosynthesizing organisms of marine and freshwater environments. One should also consider combining a double culture of primary producers with heterotrophic bacteria. The coupled cyanobacteria-heterotrophic bacteria metabolism should allow a possibility of photosynthetically produced C_{org} degradation by heterotrophic bacteria into dissolved HCO_3^- and CO_2 that can be potentially transformed into mineral form, thus doubling the efficiency of atmospheric CO_2 sequestration by microorganisms.

An important step toward resolving a mystery of Mg-rich carbonate (dolomite, magnesite) formation in the past sedimentary environments in view of difficulties in production of such carbonates in the laboratory has been achieved via experimental modeling of nonequilibrium cyclic growth and replacement mechanism through precipitation and dissolution steps, reproducing possible lagoonal/playa environments (Hobbs and Xu 2020). In this regard, it is important to note that both photosynthetically induced pH and CO_3^{2-} concentration rise (during day time) and organic matter degradation by heterotrophs, thus maintaining high DIC concentration (especially during nighttime), are recognized as driving factors of calcification in microbial mats (i.e., Ludwig et al. 2005). It is therefore possible that alternating day/night cycles of microbial activity involving the dominance of cyanobacteria and heterotrophs may provide necessary cycling of solution saturation degree, thus favoring anhydrous Mg-rich carbonate precipitation at ambient conditions.

6 Conclusion

Experimental studies on the precipitation of calcium and magnesium carbonates in the presence of aquatic phototrophs (cyanobacteria) and heterotrophic bacteria allow a better understanding of the processes of formation of these minerals in natural environments. These processes are controlled by various parameters such as pH, concentrations of elements in solution, the presence of organic compounds, living or dead cells, and their EPS. Studies under controlled laboratory conditions allow constraining the role of each of these parameters in the overall mechanisms. Subsequently, the use of reactors able to mimic the natural environments and elaboration of more realistic models through the joint use of different strains of cyanobacteria should allow a better understanding of these mechanisms as a whole. The best type of reactors to study microbial bio-carbonation is flow-through (open system) biofilm plug flow reactors; however, these require high-resolution spatial and temporal monitoring. Quantitative biomineralization process is essential for understanding the formation of stromatolites in the past and also allows important applications for the society such as CO_2 sequestration, mine rehabilitation, or building restoration.

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Key Applications of Biomineralization

Arda Akyel, Micah Coburn, Adrienne J. Phillips, and Robin Gerlach

Contents

Abstract Biomineralization is a natural process with significant potential for use in various engineering applications. Engineered biomineralization has been researched intensively, primarily to develop methods to control mineral formation by microorganisms to enable various technologies. Engineered microbial mineral formation processes have developed from theory and a proof-of-principle vision to a technology being applied in the marketplace. Biological manufacturing methods, such as engineered mineral precipitation, can significantly reduce energy-intensive cement manufacturing activities and contribute to resource and climate conservation.

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This chapter provides an overview of key applications of biomineralization, already realized or currently under development, categorized as aboveground, near-ground, or belowground. Aboveground applications consist of biological building products with potential to replace energy-intensive materials, such as cement. Ground-level applications consist of surface and near-surface stabilization applications which can increase soil stability or treat toxic chemical contamination. Belowground applications include enhanced oil recovery as well as the sealing of leakage pathways around wells. Applications in construction, soil stabilization, and the sealing of leaky wells have advanced the furthest, and some of them have been commercialized; other technologies are on the verge to commercialization. Also described in this chapter are the many metabolic pathways used by microorganisms, which can result in mineral precipitation, where urea hydrolysis-induced calcium carbonate precipitation is the technology likely used most frequently in full-scale applications. Much research and development work remains to be performed in this field, and additional applications for biomineralization will be developed in the construction, environmental, biotechnology, and medical fields. This chapter reviews in some detail existing research and development activities with a focus on parameters important for engineered biomineralization applications.

1 Introduction

Engineered biomineralization has been researched intensively for approximately two decades with a significant uptick in the past 10 years. The controlled mineral formation by microorganisms has enabled technologies which were not available previously. As a result, numerous research articles and literature reviews have been written over the past decade, which summarize the research along with established or potential applications (Bang et al. 2010; Cunningham et al. 2011; El Mountassir et al. 2018; Krajewska 2018; Phillips et al. 2013a; Phillips et al. 2018; Stocks-Fischer et al. 1999). The prior chapters of this book mostly focused on fundamental science and modeling related to understanding mineral formation by microorganisms. This chapter reviews key applications that have been realized or are currently under development. Key applications are categorized as (1) aboveground, (2) near-ground, and (3) belowground in this chapter. Aboveground applications consist of biological building products with potential to reduce energy-intensive materials. Ground-level applications consist of surface and near-surface stabilization applications which can increase soil stability or treat toxic chemical contamination. Belowground applications include enhanced oil recovery as well as the sealing of leakage pathways around wells.

1.1 Chemistry and Pathways

Biomineralization reactions can generally be classified into three categories: biologically controlled mineralization, biologically induced mineralization, and biologically influenced mineralization (Dupraz et al. 2009a; Phillips et al. 2013a). Biologically induced mineralization, the precipitation of minerals as by-products of microbial metabolism, is the most frequently used approach in application development; specifically, ureolysis-induced (aka ureolytic) biomineralization of calcium carbonates (explained in detail below) has been used most frequently in research and application development.

There are various types of minerals that can be produced by microorganisms, e.g., carbonates, iron oxides, silicates, and gypsum (Cecchi et al. 2018; Miot et al. 2009a, b; Skorupa et al. 2019). At this point carbonate minerals, such as calcium carbonate, appear to be the most frequently used minerals produced for engineered biomineralization applications. A prerequisite for the formation of minerals is that saturation for the mineral of interest is exceeded locally and at least temporally, and microbiological activities can influence saturation and promote mineral precipitation. For calcium carbonate ($CaCO_3$) mineralization, the saturation state (S) depends on Ca^{2+} and CO_3^{2-} concentrations as well as temperature, ionic strength, and other parameters that affect the solubility "constants" (K_{SO}) (Eq. 1) (Phillips et al. 2013a). When S is greater than 1, a system is considered supersaturated and precipitation is thermodynamically favorable (Stumm and Morgan 2013). Supersaturation is required for precipitation, but supersaturation does not guarantee precipitation (Connolly and Gerlach 2015) because compounds such as organics (proteins, organic acids, chelators, etc.) can inhibit precipitation reactions (Aggarwal et al. 2013; Arp et al. 2001; Bentov et al. 2010):

$$S = \frac{\left\{Ca^{2+}\right\}\left\{CO_3^{2-}\right\}}{K_{SO}} \tag{1}$$

Microbially catalyzed reactions that increase alkalinity and thus usually carbonate and bicarbonate concentrations are summarized in Table 1. Microorganisms can be responsible for carbonate generation using urea hydrolysis, nitrate reduction, sulfate reduction, photosynthesis, asparaginase hydrolysis, and iron reduction among other mechanisms. In the presence of certain cations, such as calcium (Ca^{2+}), this increase in carbonate alkalinity can induce the precipitation of carbonate minerals such as calcium carbonate ($CaCO_3$) (Eq. 2) (Connolly and Gerlach 2015; Phillips et al. 2013a):

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \tag{2}$$

For each of the reactions listed in Table 1, microorganisms generate, directly or indirectly, inorganic carbon in the form of HCO_3^- or CO_3^{2-}, thus increasing alkalinity (Eq. 3). Depending on the prevailing pH, bicarbonate (HCO_3^-), and/or

Table 1 Microbially catalyzed reactions that increase alkalinity and thus carbonate and bicarbonate concentrations with potential for engineered biomineralization applications

Biomineralization type	Reaction	Microorganisms	References
Urea hydrolysis	$CO(NH_2)_2$ (urea) + $H_2O \rightarrow NH_2COOH + NH_3$ NH_2COOH (carbamic acid) + $H_2O \rightarrow NH_3 + H_2CO_3$ $2NH_3 + H_2O + H_2CO_3 \leftrightarrow 2NH_4^+ + OH^- + \mathbf{HCO_3^-}$	*Sporosarcina pasteurii*, *Bacillus sphaericus*	Connolly and Gerlach (2015), De Muynck et al. (2011), Phillips et al. (2013a)
Asparaginase hydrolysis	$C_4H_8N_2O_3$ (asparagine) + $H_2O \rightarrow C_4H_6NO_4^- + NH_4^+$ $C_4H_6NO_4^-$ (aspartate) + $H_2O \rightarrow C_3H_7NO_2$ (alanine) + $\mathbf{HCO_3^-}$	*Bacillus megaterium*	Lee and Park (2018), Li et al. (2015)
Iron reduction	$8FeO(OH) + CH_3COO^- + 15H^+ \rightarrow 8Fe^{2+} + 2\mathbf{HCO_3^-} + 12H_2O$	*Geobacter* sp., *Shewanella* sp.	Connolly and Gerlach (2015), Li et al. (2019)
Photosynthesis	$\mathbf{HCO_3^-} \rightarrow CO_2 + OH^-$ (CO_2 fixation) $\mathbf{HCO_3^-} + OH^- \leftrightarrow \mathbf{CO_3^{2-}}$	Cyanobacteria, algae	Arp et al. (2001)
Oxidation of organic Ca-salts (e.g., Ca-acetate)	$Ca(C_4H_6O_4) + 4O_2 \rightarrow Ca\mathbf{CO_3} + 3CO_2 + 3H_2O$	*Bacillus pseudofirmus*	Jonkers et al. (2010), Sharma et al. (2017), van Paassen et al. (2010b)
Nitrate reduction (e.g., with acetate as electron donor)	$5CH_3COO^- + 8NO_3^- + 3H^+ \rightarrow 10\mathbf{HCO_3^-} + 4\ N_2 + 4H_2O$	*Pseudomonas calcis*	Boquet et al. (1973), Connolly and Gerlach (2015), van Paassen et al. (2010b)
Sulfate reduction (e.g., with acetate as electron donor)	$CH_3COO^- + SO_4^{2-} \rightarrow 2\mathbf{HCO_3^-} + HS^-$	Sulfate-reducing bacteria (SRB)	Connolly and Gerlach (2015), Van Lith et al. (2003), van Paassen et al. (2010b)

carbonate (CO_3^{2-}) ion concentrations increase while hydroxyl ion (OH^-) production and proton (H^+) consumption occurs:

$$\text{Alkalinity} \approx HCO_3^- + 2CO_3^{2-} + OH^- - H^+ \quad (3)$$

Calcium carbonate can precipitate in various forms, with calcite, aragonite, and vaterite being the most common forms observed (Krajewska 2018; Mitchell and Ferris 2006a). Transition from less crystalline phases, such as vaterite, to more crystalline phases, such as calcite, occurs through Ostwald ripening during which more thermodynamically stable mineral phases form from less stable intermediates (Connolly and Gerlach 2015; Tourney and Ngwenya 2009; Xiao et al. 2010).

There are many metabolic pathways used by microorganisms, which can result in calcium carbonate formation. Urea hydrolysis is likely the most frequently used pathway in engineering research and development, followed by nitrate reduction, but other metabolisms such as sulfate reduction, iron reduction, photosynthesis, and asparagine hydrolysis are also possible pathways (Connolly and Gerlach 2015; Phillips et al. 2013a). Ureolytic biomineralization is somewhat unique among these metabolisms since it can act independently of growth and thus provides engineers with the opportunity to control mineral formation by adjusting urea and calcium concentrations and amounts while being able to rely on a fairly easily controlled catalyst: the enzyme urease. Urease is a ubiquitous enzyme, essential in nitrogen metabolism, and has functions in nitrogen provision, detoxification, and organismal defense (Feder et al. 2020; Krajewska 2009a; Lauchnor et al. 2015). Urease is found in many different organisms, including bacteria, plants, and fungi (Feder et al. 2020; Krajewska 2009a; Lauchnor et al. 2015).

1.2 Parameters Affecting Mineral Formation by Microorganisms

Environmental parameters, such as temperature and pH, as well as the chemical environment influence microbial growth and activity (Mortensen et al. 2011; Qabany et al. 2012); the same factors can also influence mineral formation. Hence, each biomineralization application at each location will require a certain level of optimization to successfully adapt to the existing conditions and control saturation. In this section we focus on describing the influence of temperature and pH value on microbial activity, saturation conditions, and thus mineral formation since these two parameters are some of the most important in the development and application of engineering applications.

Temperature is important since it affects microbial and enzyme activity; temperature can also affect the saturation state of a solution since solubility "constants" are indeed temperature-dependent; temperature can also affect mineralogy and morphology of precipitates (Feder et al. 2020; Ferris et al. 2004; Skorupa et al. 2019). As

Table 2 Carbonic acid diprotic dissociation and calcium carbonate precipitation

Reaction	Equation	pKa[a]
Carbonic acid dissociation	$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O$	6.3
Bicarbonate dissociation	$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$	10.3
Calcium carbonate precipitation	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ (biocement)	–

[a]Note that pKa values are also dependent on temperatures and ionic strength; here the pKa values are provided for ~20 °C and low ionic strength

outlined in Table 1, there are several metabolisms that can promote carbonate mineral precipitation. Some of these reactions are microbial growth-dependent, while others simply rely on the activity of enzymes produced by microbes but might not be essential for growth. Microbial growth and enzyme activity usually increase with temperature until they peak and decrease again with further increasing temperature because enzymes and other essential cell components become damaged at higher temperatures. In general, the temperature range for effective microbial growth is narrower than the temperature range for acceptable enzyme activity. For example, the ureolytic bacterium, *Sporosarcina pasteurii*, can grow at temperatures from >0 °C to around 40 °C, while the enzyme urease produced by *S. pasteurii* or derived from plants is capable of hydrolyzing urea at temperatures of up to ~75 °C for at least several minutes (Feder et al. 2020; Skorupa et al. 2019).

Appropriate pH values are also critical; microbial and enzymatic activities, for instance, are sensitive to pH since both high and low pH values can inhibit or permanently denature enzymes, and other essential microbial functions (Dupraz et al. 2009b; Fidaleo and Lavecchia 2003; Krajewska 2016; Lauchnor et al. 2015; Qin and Cabral 1994). With regard to calcium carbonate precipitates, pH values indirectly influence the saturation state since carbonate concentrations are strongly dependent on pH values with increasing fractions of the dissolved inorganic carbon being present as carbonate (CO_3^{2-}) at higher pH values (Table 2).

Negatively charged bacterial surfaces or extracellular polymeric substances (EPS) can act as nucleation sites for mineral formation by accumulating calcium or other multivalent cations in close proximity to each other, thus effectively increasing their local concentrations (Mitchell and Ferris 2006b). In addition, bacterial cell wall functional groups such as hydroxyl and phosphate groups can become negatively charged at high pH values (Phillips et al. 2013a; Rodriguez-Navarro et al. 2003; Sharma et al. 2017). The resulting, increased number of nucleation points could enable more and/or larger crystal formation events (Rivadeneyra et al. 1996; Sharma et al. 2017). Indeed, when mineral formation was examined microscopically, minerals were observed mainly associated with the bacteria initially, and bacteria were observed inside mineral precipitates later on, indicating that bacteria acted as nucleation sites (Zambare et al. 2020).

2 Key Applications

In the remainder of this chapter, current and envisioned biomineralization technologies are summarized. The most mature technologies can be separated roughly into three categories: (1) aboveground, building, and construction materials, (2) near ground-surface and stabilization applications, and (3) subsurface applications (Fig. 1).

The building and construction materials section covers the possibility of using biomineralization to create building materials, to remediate existing structures and the possibility of adding self-healing properties to existing or new building materials. The stabilization applications section discusses the expanding research and field demonstrations of utilizing microorganisms and enzymes to stabilize or immobilize soil, dust, and toxic mine tailings as an alternative to more traditional methods. Finally, engineering applications related to the deeper subsurface are highlighted. Biomineralization technologies for deeper subsurface applications, e.g., leaky well sealing, have been developed over the past decades and have reached commercial sector application.

Different applications have different requirements with respect to time available for implementation, desired permeability, strength, toughness, etc. Thus, depending on the application, implementation strategies are likely to be different. Some applications may require the relatively rapid formation of strong bonds, e.g., for building materials (bricks, foundations, etc.), while other applications, like self-healing concrete, require long-lasting biomineralization potential that can ramp up rapidly when needed to fill cracks in a structure once present (Seifan et al. 2016). Hence, it is important to understand how to control biomineralization to address the requirements inherent in these different applications.

Economics are one of the greatest hurdles in enabling the widespread use of biomineralization as an alternative to materials, such as cement which is well-established and relatively inexpensive. While biomineralization technologies are at

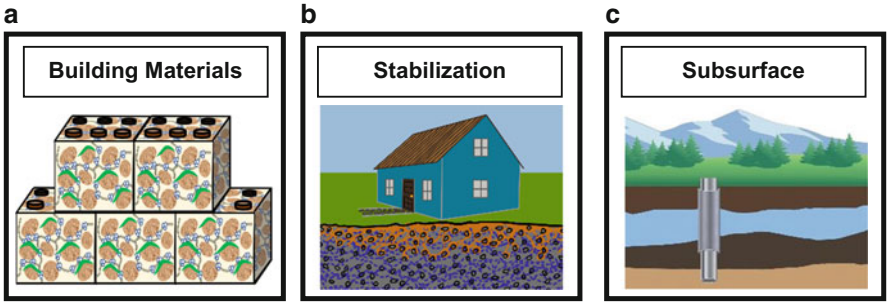

Fig. 1 Schematic overview of the most technologically advanced applications of microbial biomineralization. The remainder of this chapter summarizes the state of the technology as well as recent research and development activities in these three main topic areas: (**a**) building and construction materials, (**b**) ground stabilization applications, and (**c**) subsurface applications

this point more expensive, they have proven to be competitive due to their success rate, reliability, and relative ease of implementation. Ureolytic biocementation could indeed prove to be a greener (i.e., lower carbon emission) alternative since it largely avoids high-temperature processes with exception of the production of urea, which is often produced through the combination of the Haber-Bosch process (Haber 1905) for ammonia production and the Bosch-Meiser process for ammonia to urea conversion (Bosch and Meiser 1922). Depending on the source of ammonia and CO_2 for these processes, a significant amount of energy for heat and pressurization might be necessary. Other mineralization mechanisms, as outlined above, are also providing possible strategies, but ureolysis-induced calcium carbonate precipitation is currently the most commonly used strategy for larger-scale applications.

2.1 Building and Construction Materials

Cement production requires extensive, though well-established, high-temperature processing and currently contributes 6–7% of the annual anthropogenic carbon emissions (Abdul-Wahab et al. 2016; Achal et al. 2015). Portland cement is used to produce concrete, likely the most commonly used building material in the world. Concrete is a mixture of cement, aggregate (e.g., sand or gravel) and water, and overall, concrete is a durable, low-cost construction material with more than 10 billion tons used annually around the globe (Abdul-Wahab et al. 2016; Brown et al. 2014). Concrete is known for its high compressive strength but is characterized by a relatively low tensile strength. Thus, in many applications steel must be used to reinforce concrete. Under ideal conditions concrete prevents steel reinforcements from corrosion. However, cracks can form when concrete structures age or are mechanically damaged and experience freeze-thaw cycles or other environmental stresses. The cracking of concrete is a worldwide problem, and, in a 2006 report, it was estimated that the annual cost for repair, protection, and strengthening of concrete structures amounts to between $18 and $21 billion in the USA alone (Emmons and Sordy 2006). Indeed, some large concrete structures such as bridges could be impractical to replace or will be extremely costly to repair (Gardner et al. 2018). Specifically, cracks in cement can provide pathways for corrosive substances, such as oxygen and water into the structures, which can lead to corrosion of the steel reinforcements. These damages can affect mechanical properties and durability of the concrete structure, consequently reducing the useful life of concrete (Achal et al. 2015).

Biological building materials are considered an alternative to concrete, and biocementation is considered a viable strategy for maintenance and repair of existing concrete structures (Khodadadi et al. 2017; Van Tittelboom et al. 2010). These potentially more environmentally friendly and sustainable technologies do not require energy-intensive Portland cement production. Instead, biocement requires two main constituents: (1) microorganisms (or enzymes) to initiate the biomineralization reactions and (2) aqueous solutions that provide the ingredients and proper

conditions to enable the mineral precipitation. Biocement can be produced in place, using low-energy methods while using local materials such as existing sand and gravel; however, a need still exists for somewhat energy-intensive raw materials, such as $CaCl_2$ (ice-melt) and urea (fertilizer) if ureolysis-induced biomineralization is used. Both urea and $CaCl_2$, productions require energy, and comprehensive life cycle analyses and techno-economic analyses (LCAs and TEAs) comparing traditional Portland cement and biocement are, at this point, not available.

2.1.1 Biological Bricks, Grout, and Mortar

2.1.1.1 Biomineralized Bricks

Bricks and precast concrete parts are the most-used building materials in the world (Brown et al. 2014; Wong et al. 2018). They are part of our everyday world (Fig. 2) and are designed to have great compressive strength, which is achieved through extensive manufacturing at temperatures above 1000 °C. The company, bioMASON, is one of the first to produce biologically produced masonry products. Their current products can be used for exterior cladding, paving, flooring, and on walls. These products contain approximately 85% by-product from granite quarrying and 15% calcium carbonate which is produced using ureolysis-induced calcium carbonate precipitation, thus decreasing the overall energy consumption. bioMASON's bioLITH tiles can be manufactured within approximately 72 h and

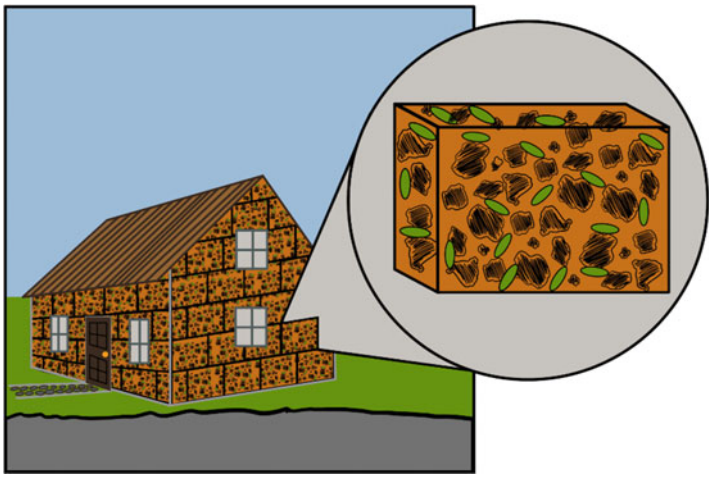

Fig. 2 Eco-manufactured modular building materials (MBMs) are a new paradigm for sustainable construction. Bricks (orange), mortar (black lines), and grouts (not shown) can be produced through biomineralization processes. Biologically produced building materials can potentially overcome several limitations inherent to conventional cement manufacturing and usage, such as high-energy manufacturing processes and lack of recyclability

are reported to require only 3.5% of the manufacturing energy of traditional engineered stone (bioMASON 2020). bioMASON reports that this energy reduction is achieved by avoiding the heat treatment necessary for traditional clay brick manufacturing (bioMASON 2020). bioMASON also reports that their products are lighter than natural stone, exceed performance in terms of CO_2 emissions, and possess higher compressive strength.

In a recent study, Heveran et al. (2020) engineered a living building material (LBM) using cyanobacteria to make biologically produced bricks. Cyanobacteria were placed in a sand-gelatin scaffold, and the bacteria increased the stiffness through photosynthesis-driven biomineralization (cf. Table 1). The resulting products did not only provide strength but also demonstrated the ability to self-heal when deformed. Self-healing requires long-term viability of microorganisms. This study suggests that lower temperatures and increased relative humidity (RH) increase cell survival with approximately 9% and 14% of cells being recoverable after 30 days at 4 °C at 50% and 100% RH; lower recoveries were observed at ambient conditions (22 °C and 24% RH) where cells were viable until day 7. The long-term viability of microbes must be improved further so that LBMs can sustain their structural and biological functions for the lifetime of structures (cf. "Concrete Remediation and Self-Healing Cement" section).

2.1.1.2 Biological Grout and Mortar

Grout and mortar are other materials commonly used in the construction industry. Grout and mortar are used for filling gaps between tiles and bricks among other uses. The difference between grout and mortar is that grout generally is being applied to fill and seal gaps between, e.g., tiles, but provides minimal structural support. Mortar is generally applied between bricks or under tiles and provides certain structural support during and after curing while also acting as a glue. Hence, grout must be able to penetrate and ultimately seal small gaps, while mortar must be viscous enough to support not only its own weight but also that of masonry placed above it. Most grouts and mortar are Portland cement-based, but synthetic grouts, such as acrylamide-, lignosulfonate-, and polyurethane-based grouts, are also in use; each of these compounds has its own environmental footprint (Achal and Kawasaki 2016). Biomineral-based grouts and mortar, which are under development, have potential to reduce the environmental footprint relative to the traditional grouts and mortars.

Literature regarding the use of biomineralization to produce a biogrout for building materials, e.g., tiling, is limited at this point. However, biogrouts have been demonstrated by multiple groups to have potential for concrete repair and self-healing applications. As mentioned above, grouts must readily fill gaps, voids, and cracks, often with the goal of preventing the entry of water after curing. Hence, tile grouts generally require lower viscosities than mortar. *[Note: The terms "grout," "grouting,"* etc. *are also used in the context of soil stabilization; the application of biomineralization-based grouting for soil stabilization is discussed in the next section ("b. Stabilization Applications")].* The biomineralization technology is

water-based; thus, low viscosity is one of its inherent characteristics. Minerals are generally precipitated through a biologically catalyzed, chemical reaction, allowing for the grout to develop in place. Biomineralization-based grouts might have advantages over traditional grouts since the microbes and enzymes are smaller than traditional cementitious grout particles and less viscous than, e.g., synthetic grouts, and thus might more efficiently penetrate small gaps before precipitating and forming bonds. Indeed, it is suggested that biogrout can be less expensive than chemical grouting while achieving unconfined compressive strengths comparable to traditionally used products (Achal and Kawasaki 2016; Li et al. 2015).

As mentioned above, mortar, in contrast to grout, needs to perform a structural function. Even during application, limited structural support needs to be provided to building components. For instance, mortar must maintain the spacing between masonry, such as bricks even during curing. Currently, there are no published works that specifically address the challenge of providing higher viscosity, mortar-like products using biomineralization methods. Furthermore, upon curing, significant structural strength (compressive strength) needs to be ensured along with other properties, such as fire resistance. Fire resistance of biobricks and biomortar is predicted to be comparable to traditional cement-based bricks and mortar since $CaCO_3$ is generally stable up to approximately 600 °C after which decomposition of $CaCO_3$ to CO_2 and CaO occurs at increasing rates (Abdel-Gawwad 2017). This decomposition also occurs in traditional cements and can result in decreases in compressive strength and other properties (Abdel-Gawwad 2017). The incorporation of organics into biobricks, biogrout, and biomortar must also be considered. While organics can increase viscosity and potentially elasticity, biomass generally begins decomposing around 250 °C and decomposes completely at temperatures around 500 °C (Abdel-Gawwad 2017). The effect of the loss of organics from the created biocement, grout, mortar, or bricks has not been investigated in detail.

2.1.2 Limestone Remediation

Many historic structures around the world, from the Great Sphinx to old churches to the Lincoln memorial, were constructed using limestone. Unfortunately, these structures are subject to weathering, exacerbated by the generally decreasing pH of rainwater, due to increasing atmospheric CO_2 concentrations and other acidic gases in the atmosphere (Nazel 2016; Villa et al. 2020). These carbonate-based stones and structures are vulnerable to gradual dissolution, leading to increased porosity, the accelerated entry of water, more rapid dissolution, increased freeze-thaw damage, and associated decreasing mechanical integrity (Marvasi et al. 2020; Nazel 2016; Tiano et al. 1999).

Limestone remediation is often focused on preventing the entry of rain- and meltwater, the restoration of mechanical integrity, and the protection of the weakened inner structure by establishing protective surface layers, filling existing pores, and reducing the porosity of deteriorated limestone (Fig. 3) (Nazel 2016). Existing remediation methods often include the use of chemicals, such as fluorinated polymer

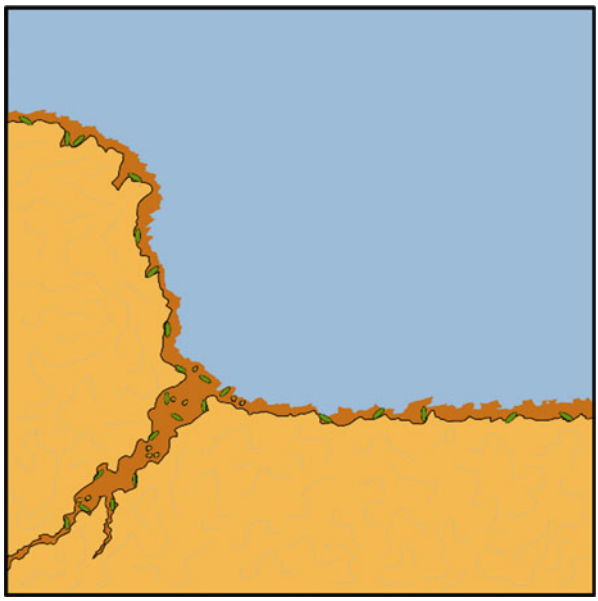

Fig. 3 Schematic indicating the potential for biomineralization-based approaches to protect limestone structures (light orange) by filling existing cracks and cover the limestone surface with biocement (dark orange with green organisms) to minimize the entry of acidic rainwater that would lead to limestone deterioration

coatings (Marvasi et al. 2020; Sadat-Shojai and Ershad-Langroudi 2009). Biomineralization could be an ecological alternative since biomineralization mimics the natural stone formation process (Marvasi et al. 2020) and is generally based on the use of low viscosity, aqueous fluids, which can readily penetrate pores and can be applied directly onto the surfaces using low-cost approaches, such as spraying (Castanier et al. 2000; Marvasi et al. 2020; Perito et al. 2014). As outlined in Table 1, several biomineralization approaches result in the production of carbonate minerals and have potential for the restoration of limestone structures. The use of alkalizing, calcium carbonate-precipitating microbial cultures could also combat the development of autochthonous acidifying microbial cultures, which can locally contribute to increases in porosity and decreasing mechanical strength due to localized acidification and associated dissolution of calcium carbonates (Castanier et al. 2000).

There are still several limitations to employing biomineralization-based approaches to building restoration. The use of microorganisms can result in a certain level of skepticism in the general population. The development of stains or off-color in the precipitates due to metabolic by-products associated with the biological production of calcium carbonates is also of concern. Furthermore, the possibility of subsequent growth of other microbes (e.g., airborne fungi) is a concern; fungi or other microorganisms, commonly referred to as "black molds," can cause damage or defacement to building materials. Mold growth could be stimulated by decaying bacteria, added enzymes or nutrients, or metabolic by-products generated during the biomineralization treatment (Nazel 2016). While Tiano et al. (1999) were unable to detect a color change on limestone, due to deposited biominerals, with the naked eye,

it could be detected quantitatively using a chromameter (Tiano et al. 1999). The addition of pigments has been suggested, which could alleviate the potential aesthetic issue of color differences (Castanier et al. 2000; Nazel 2016); in addition, a reduction of the amount of organics included in the treatment solutions or the use of enzymes instead of microbes could decrease potential worries regarding the use of living microbes and reduce the concern regarding subsequent growth of fungi or other microbes on the remediated surfaces. A remaining limitation is that mineral precipitation occurs predominantly on the surface of microporous structures, on which microbes or enzymes would be deposited (De Muynck et al. 2011; Marvasi et al. 2020). The use of smaller microbes (e.g., starved bacteria or spores), which transport more readily into and through porous media (Bouwer et al. 2000; Cunningham et al. 2007; Gerlach 2001), or the use of (much smaller sized) enzymes has potential to alleviate these limitations (De Muynck et al. 2011; Krajewska 2009a).

2.1.3 Concrete Remediation and Self-Healing Cement

As noted above, defects, such as tiny cracks or gaps, are one of the biggest problems in cement and concrete longevity because these defects can drastically reduce the life of the structure by causing corrosion of the cement, concrete, or their reinforcements. These defects can occur through quality issues during implementation, temperature fluctuations (freeze-thaw cycles), vibrations (earthquakes, traffic, construction), chemical corrosion, or other processes causing cosmetic or structural damage. Biologically induced mineral precipitation has been proposed for the remediation of cement and concrete as well as for the development of self-healing materials (Achal et al. 2015; Phillips et al. 2013a). In principle, biomineral-precipitating solutions and enzymes (or organisms) can either be applied once a defect has been discovered (remediation) or can be designed to be activated once a defect occurs (self-healing) (Fig. 4).

Establishing conditions appropriate for biomineralization to occur in cementitious materials remains a challenge. Cement, in contrast to limestone, is a very high pH environment with pH values as high as 13 combined with often low oxygen availability (Lee and Park 2018). Both these parameters can pose challenges for some microbes and enzymes because extreme pH values and low oxygen availability can negatively influence the survival and activity of microbes and enzymes. While the pH of water in cement generally decreases over time due to carbonation of the cement (Papadakis et al. 1989), it can remain a challenge to reliably provide pH values around 10 or lower, which are more amenable to supporting microbial growth and the activity of enzymes such as urease (Fidaleo and Lavecchia 2003; Lauchnor et al. 2015). Some organisms have been demonstrated to have high salt and pH tolerance while being ureolytically active, but there remains a need to identify more high pH-tolerant organisms and enzymes (Skorupa et al. 2019).

Treating cracked or cracking cement materials using surface-applied treatments is fairly straightforward unless cosmetics are of concern (as discussed above for many

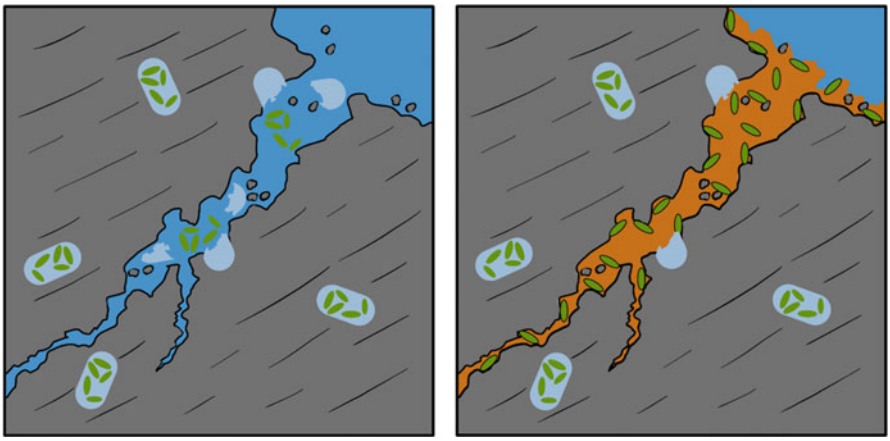

Fig. 4 Biomineralization-driven concrete remediation and self-healing. Existing cracks can be filled with biocement (orange) or self-healing cement can be designed, which contains microbes in the form of cells or endospores as well as chemicals that promote precipitation once damage occurs. Biomineral-precipitating bacteria or enzymes are envisioned to become active once cracks occur in the cement and reseal the developing fractures

limestone remediation projects). In one laboratory study, cement specimens were immersed in suspensions containing *Bacillus sphaericus*, and the resulting biomineral formation on the surface reduced subsequent water absorption by 65–90% and improved the resistance to freeze-thaw cycle damages (De Muynck et al. 2008). Biomineralization-based concrete repair approaches are suggested to be suitable for sealing cracks up to 2 mm in width (Achal et al. 2015; Wiktor and Jonkers 2016; Wiktor and Jonkers 2011). When crack healing was compared with control samples, significant differences were observed after 100 days of immersion in water (Wiktor and Jonkers 2011). In field trials, it was demonstrated that bacterial biomineralization systems can be used to create concrete with self-healing properties in applications such as irrigation canals and parking garages (Wiktor and Jonkers 2016). It has also been reported that this approach could be used to potentially recycle concrete and other building materials (Wiktor and Jonkers 2016). If post-cement damage treatment is pursued, active bacterial cultures or enzymes can be used, and oxygen, or other electron acceptor limitations, discussed below, is often not a concern.

The principal feasibility of using ureolysis-induced calcium carbonate precipitation by *Sporosarcina pasteurii* and other *Bacillus* sp. has been demonstrated by many researchers (see, e.g., reviews by Arias et al. 2017; Joshi et al. 2017; Krajewska 2009b; Phillips et al. 2013a). The feasibility of creating self-healing cements has also been demonstrated in principle (Erşan et al. 2016b; Wang et al. 2014a; Zhang et al. 2020). In cement structures cracks occur due to changes in temperature, pressure, and mechanical stresses (Jonkers et al. 2010), and most cracks start small. Thus, even slow precipitation, e.g., promoted by metabolic biomineralization, might be sufficient to seal the initially small apertures and prevent them from becoming larger (Alazhari et al. 2018). Studies have demonstrated *B. pseudofirmus*,

B. subtilis, and *B. alkalinitrilicus* are capable of self-healing cracks of <0.8 mm in concrete (Basilisk 2020; Jonkers et al. 2010). In these and other studies, the cracks were effectively sealed in the presence of water (Sharma et al. 2017). However, it is less clear whether bacteria or their spores can survive long enough and resuscitate quickly enough to reliably seal cracks inside cement or concrete under the wide range of conditions expected depending on season and climate (Bang et al. 2010; Mitchell et al. 2019; Sharma et al. 2017).

If self-healing of cement through biomineralization is desired for extended periods of time, the self-healing agents have to be incorporated into the cement or concrete (Wang et al. 2014b) and have to remain active, or need to be activated, inside the cement or concrete over the service life of the structure once damage occurs. It has been suggested that encapsulation of bacteria, their spores, and their incorporation into cement mixtures can increase spore survival (Alazhari et al. 2018; Wang et al. 2014b). Indeed, it has been proposed that enzymes or bacteria could retain sufficient self-healing potential for years to seal cracks that might develop (Sharma et al. 2017; Van Tittelboom et al. 2010). In addition, for self-healing to occur, sufficient calcium, electron donor, and acceptor are necessary; however, high concentrations of material other than cement and aggregate (sand, gravel, etc.) may have detrimental effects on the mechanical properties of the concrete (Alazhari et al. 2018). Thus, trade-offs between the amount of additional materials to be incorporated into concrete to ensure self-healing and the required mechanical properties of concrete need to be considered.

Once resuscitation of bacteria needs to occur, electron acceptors (e.g., oxygen), electron donors, and a carbon source need to be available. Limitations in the availability of any one of these can affect the rate of activation of bacteria, enzymatic activity, and thus the speed of self-healing. It has been proposed to incorporate capsules into cements, containing oxygen-releasing compounds, such as calcium peroxide (CaO_2), combined with electron donors, a carbon source, and an additional source of calcium, such as calcium lactate. The capsules would release these compounds upon crack formation and would promote microbial resuscitation, growth, activity, and ultimately $CaCO_3$ precipitation (Lee and Park 2018).

The existence of bacterial strains capable of growth in the absence of oxygen and calcium carbonate precipitation has also been demonstrated. In laboratory studies anaerobic growth of and calcium carbonate precipitation by, both, ureolytic and non-ureolytic organisms have been observed, such as fermenters, denitrifiers, sulfate reducers, and iron reducers (Hamdan et al. 2017; Skorupa et al. 2019; van Paassen et al. 2010b). Until now, only nitrate reduction seems to have emerged as a possibly viable alternative to urea hydrolysis (Erşan et al. 2016a, b), but other methods for concrete self-repair are being developed (Zhang et al. 2020).

Basilisk, a biotechnology startup company in the Netherlands (https://www.basiliskconcrete.com), focuses on next-generation cement additives. Basilisk produces admixtures for concrete self-repair and concrete remediation. Basilisk uses a metabolically driven biomineralization reaction, using bacterial cultures consisting of several *Bacillus* species. Basilisk indeed uses calcium lactate as the source of calcium and encapsulates spores and calcium lactate into concrete materials for

long-lasting performance. The technology is protected by several patents (Jonkers 2011; Jonkers 2009; Jonkers and Mors 2016; Wiktor and Jonkers 2014) and is designed to reduce maintenance requirements, extend service life, and protect concrete reinforcements. The *Bacillus* sp. spores used are estimated to survive up to 200 years as long as appropriate pH, temperature, oxygen, moisture, and nutrients are provided (Jonkers et al. 2010). Basilisk's concrete repair admixtures can be mixed and applied using conventional sprayers resulting in the formation of limestone. While promising, it is unclear at this point how long the potential for self-healing will remain active.

A similar approach for self-healing was used as part of the UK's first site trial of self-healing concrete (Davies et al. 2018). In a collaboration between academic (Cardiff University) and industrial (Costain) engineers, five concrete panels for a highway upgrading project were tested as part of the "Materials for Life" project. Researchers created five different concrete panels, one of them had bacteria in the cement mixture. When load-displacement curves were analyzed, the panel with bacteria exhibited a displacement of about 5.4 mm, while the other panels exhibited 9.2 mm displacement on average. Results after 6 months were sufficiently positive for the bacterially mediated self-healing process, but longer-term assessments have to be performed to verify applicability of reducing or removing the requirement for inspection, maintenance, and repair of concrete structures (Davies et al. 2018).

2.2 Stabilization Applications

2.2.1 Soil Stabilization

Soil is a complex mixture containing minerals, liquids, gases, organic matter, and organisms that help create a dynamic environment in which many biological, chemical, or physical processes are taking place. Soils can be highly heterogeneous, and inconsistent soil properties can cause structural damage or, worse, put human lives at risk. Soil stabilization is designed to provide consistent properties, and it is common practice for many construction and engineering processes including highway, building, and airfield construction, supporting earthen dams or embankments, irrigation networks, or preventing wind and water erosion. Regardless of the application, soil stabilization involves improving the mechanical properties of the soil by either mechanical or chemical means to achieve the properties needed, e.g., high strength and durability. Many different methods for soil stabilization (aka soil grouting) are available including biomineralization-based methods (Kalkan 2020; Mujah et al. 2017; van Paassen 2011).

Biomineralization can be applied to soils or other porous media to increase stability or enhance mechanical properties; if used for those applications, it is often referred to as biogrouting or biocementation of soils (*Note that the use of biomineralization as a potential tile grout was discussed above in the in the "Biological Bricks, Grout and Mortar" section and was also referred to as*

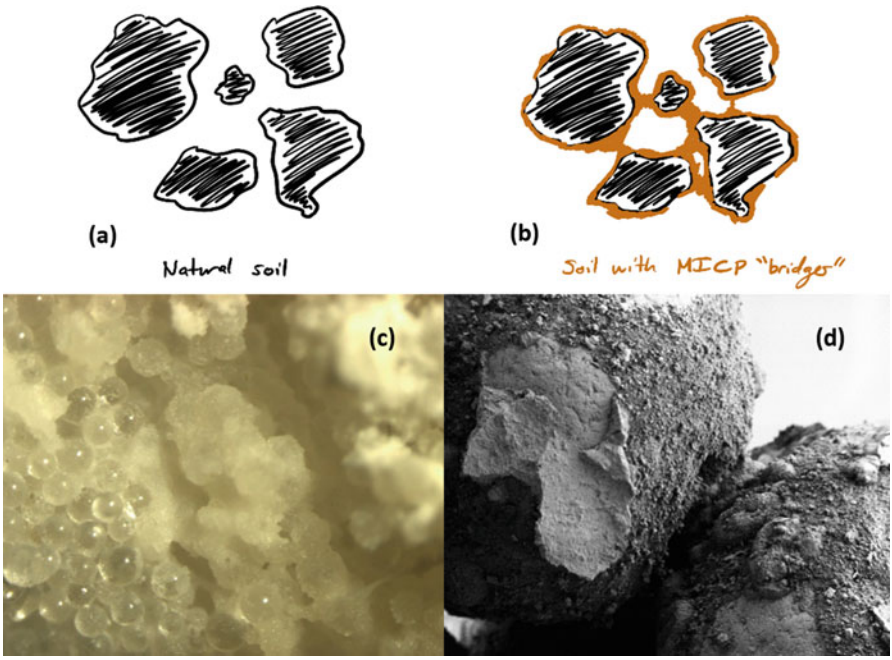

Fig. 5 Schematic representation of biomineralization-based soil stabilization or "biogrouting." (**a**) Soil particles not biomineralized represent unstable soils prone to soil liquefaction; (**b**) soil particles with mineral "bridges" (orange) between them. These bridging connections stabilize soils and make them less prone to liquefaction. (**c**) Stereoscope image showing glass beads cemented together by ureolysis-induced calcium carbonate precipitates; (**d**) SEM image showing sand grains connected by microbial ureolysis-produced calcium carbonate precipitates (**c**, **d**: Montana State University, unpublished data)

biogrout). As summarized in this section, biocementation has been applied at large scales and continues to be investigated as an alternative to the more traditional mechanical or chemical means of soil stabilization. Many of the current stabilization methods are reliant on mechanical means or materials with a significant energy and environmental footprint (Behnood 2018; Mujah et al. 2017). One of the most common methods of biomineralizing soil is microbially induced calcium carbonate precipitation (MICP) treatment, which allows soil particles to be bound together by microbially precipitated calcium carbonate, providing a stable connection (or "bridge") between the particles while maintaining sufficient permeability for water to infiltrate (Kalkan 2020; Mujah et al. 2017) (Fig. 5).

MICP-based soil stabilization can principally be accomplished in two ways: biostimulation and bioaugmentation. Biostimulation is achieved by providing nutrients to indigenous bacteria in order to stimulate growth and precipitation, which can be beneficial in order to adapt to certain local environmental conditions such as temperature or regulatory restrictions. Bioaugmentation is the method of supplementing the soil with exogenous bacteria and has been researched more

extensively for soil stabilization than biostimulation. Bioaugmentation is useful when hoping to achieve desired stabilization parameters quickly, and usually pre-cultivated organisms are used with well-known characteristics, such as *Sporosarcina pasteurii*. The ability to improve soil onsite using biocementation could significantly reduce the costs of soil improvement due to a decrease in costs associated with manufacturing and transporting materials, such as cement, bentonite, or other materials, used in more traditional soil stabilization methods (Gowthaman et al. 2019; Kalkan 2020; Mujah et al. 2017). Additional benefits might be achieved when biostimulation is utilized instead of bioaugmentation, because the materials and energy needed for pre-cultivating and transporting the bacteria are eliminated. In addition, more uniform precipitation may be achieved in the presence of native bacteria instead of injecting bacteria or enzymes into the soil and creating gradients of bacterial or enzyme concentrations, which in turn often result in nonhomogeneous mineral precipitation, though this risk can be alleviated through the use of well-designed injection strategies (Barkouki et al. 2011; Ebigbo et al. 2012; Hommel et al. 2016; Hommel et al. 2015). In addition, there is a risk of ecological impacts from introducing large amounts of non-native bacteria (Gomez et al. 2019), and introducing non-native organisms might also face regulatory restrictions. Overall, biostimulation may have the advantage of relying on organisms that have adapted to the local environment, including—but not limited to—adaptation to the prevailing dominant electron acceptor(s), but biostimulation-based implementations might be slower, at least initially, than bioaugmentation-based approaches (Gat et al. 2016; Phillips et al. 2013a).

Research by Gat et al. (2016) on the potential for biostimulation in arid and low nutrient environments, such as in coastal liquefiable sand, showed promise. This study investigated simple carbon sources (molasses and yeast extract), which are rich in organic carbon, and found that mineralization can be achieved even when only using molasses. This could be beneficial for future research and applications aimed at achieving soil stabilization using relatively common and inexpensive carbon sources, and reducing additional costs associated with bioaugmentation. One important note from this research is the recommendation of promoting slow increases in pH when attempting biostimulation because rapid pH increases can cause significant alterations to the native soil community (Gat et al. 2016).

Dhami et al. (2017) performed a comparison between bioaugmentation and biostimulation using soil samples from the Margaret River region in Australia. In the bioaugmented treatments, both *S. pasteurii* and *Bacillus cereus* were used for urease production and carbonic anhydrase production, respectively. Biostimulation and bioaugmentation promoting ureolysis were found to be more effective than bioaugmentation with carbonic anhydrase producers. It was also demonstrated that when high amounts of nutrients are present in the soil—either naturally occurring or through injection—both ureolytic and carbonic anhydrase augmentations were found to be effective, and the carbonate crystals from MICP grew to larger sizes than under low nutrient conditions. In addition, *S. pasteurii* and *B. cereus* were able to survive alongside indigenous organisms in high nutrient conditions, but the native bacterial populations experienced significant changes regardless of the treatment

method. A key takeaway from these results was that the choice of biomineralization method may largely depend on the organic carbon content of the soil and the time available for the treatment. Biostimulation seems to be very useful in carbon-rich environments, while bioaugmentation paired with supplemental nutrients may be favored in low nutrient soils (Dhami et al. 2017).

Gomez et al. (2019) compared the differences in biocementation between bioaugmentation with *S. pasteurii* and biostimulation of sandy soils using column experiments. Gradients of cementation developed throughout the columns and final calcite content between 0.5% and 5.3% by mass were observed. Near the inlet the soil was highly cemented, resulting in cone penetration resistances increasing by over 500% (up to 32.1 MPa) in the treated soils, and the shear wave velocities increased by 600% (up to 967 m/s). In addition, the biostimulated columns contained larger calcite crystals than the columns bioaugmented with *S. pasteurii*, while *S. pasteurii*-bioaugmented columns produced more overall crystals of smaller size (Gomez et al. 2019). Differences in amount, distribution, and crystal size of calcium carbonate could have an influence on the mechanical properties of porous media. This along with other work demonstrates strategies for achieving appropriate soil improvements depending on how soil stabilization is performed, therefore allowing customization based on the needs of the project and the regulatory framework.

Cost uncertainty is still one of the limitations of biomineralization for soil stabilization because so much of the research has been done on the laboratory scale using analytical-grade reagents. Using high purity reagents could be cost prohibitive for full-scale applications due to the amounts of urea and calcium chloride needed. Omoregie et al. (2019) compared the feasibility of using technical-grade reagents with laboratory-grade reagents along with using tap water or deionized water when preparing cementation solutions. Surface strength generally increased with increasing cementation solution concentrations, regardless of whether analytical- or technical-grade chemicals and water were used. Samples treated with the highest concentrations (1.0 M) achieved surface strength values of at least 4826 kPa when measured from the top surface (the handheld pocket penetrometer used to measure this had a maximum range of 4826 kPa). The surface strengths varied for the samples treated with 0.25 M, 0.5 M, and 0.75 M without a clear relationship between surface strength and type or concentration of cementation solution. Post-treatment XRD analyses revealed nearly identical calcium carbonate content and polymorph composition with ~93% calcite and ~ 7% vaterite for both the analytical-grade and technical-grade chemicals (Omoregie et al. 2019). These results along with the cost analysis indicate that technical-grade media may serve as a cost-effective alternative for biomineralization-based soil stabilization (Omoregie et al. 2019).

As described in Behnood (2018), one of the most common soil stabilization practices is chemical grouting. However, chemical grouting can be expensive, and it can be difficult to treat large volumes of soil due to the fairly high viscosity requiring high injection pressures and the viscosity increase over time (Mujah et al. 2017). Similar issues have been encountered with soil biocementation; rapid precipitation and premature clogging of the injection site can occur if the bacterial

suspension and the cementation solutions are injected simultaneously. Ebigbo et al. (2012) demonstrated that injection site clogging can be avoided and a much more uniform distribution of calcium carbonate can be achieved through an injection strategy, which includes rapid injection of bacteria, followed by a bacteria- and urea-free rinse, a rapid injection of a calcium and urea mixture, another calcium-free rinse, and a rest period to allow for precipitation. Mujah et al. (2017) reported a similar strategy, during which the bacterial suspension was injected first, followed by the calcium-urea solution to achieve a more homogenous soil treatment.

Another difference between chemical methods and biomineralization is the speed of the cementation process. Depending on numerous environmental factors such as temperature, concentrations of nutrients, pH, etc. the microbes and enzymes involved in the biocementation process can exhibit varying levels of activity which can make biocementation a more complex and slower process than chemical grouting. However, biomineralization-based grouting of soils might provide a sustainable alternative to chemical grouting due to lower toxicity, lower energy requirements, and tunable rates of solidification depending on bacterial (or enzyme) activity and supply of biocementation agents (Mujah et al. 2017; Reddy et al. 2013).

However, there are potential drawbacks with a biomineralization approach to soil stabilization. When the process involves ureolysis, the production of ammonia is a concern, especially when it has the potential to leach into groundwater. There are strategies to alleviate this potential threat through treatment of the process water and potentially utilizing the produced ammonium as fertilizer for local agriculture (Mujah et al. 2017). The effects of adding nutrients to soil and groundwater are also not always readily predictable but may contribute to the growth of unwanted microbes (Reddy et al. 2013).

Fly ash, a waste product from coal combustion, has not only been repurposed for building materials, it is also used in many applications including stabilization of soil and embankments. While the load bearing capacity of fly ash is generally lower than soil, ureolytic biomineralization using *S. pasteurii* stabilized fly ash and increased compressive strength by 25–390% (Yadav et al. 2020). In specific, fly ash samples were treated with the same number of bacteria and varying concentrations of urea and $CaCl_2$ between 0.1 M and 0.25 M. Relationships between fly ash particle size and bacteria size were determined to be important for the movement of the bacteria, with a particle size 50–400μm being the most favorable for bacterial transport (Yadav et al. 2020). The strength of untreated fly ash was 37.19 kPa compared to 183.31 kPa for the 0.1 M urea and 0.25 M $CaCl_2$ mixture. The other concentrations resulted in strength values ranging from 46.47 kPa to 171.61 kPa. The strength increase was attributed to higher amounts of calcium carbonate and a more uniform distribution of calcite throughout the fly ash. Significant reductions in permeability (by about one order of magnitude) were observed after some of the treatments compared to the untreated fly ash (Yadav et al. 2020).

Maintaining permeability during biomineralization treatments is important, since it allows for continued injections at relatively low injection pressures and increases the treatable volume of soil, fly ash, or similar (Yadav et al. 2020). van Paassen (2011) and Ebigbo et al. (2012) specifically discussed the importance of maintaining

permeability to achieve homogeneous distributions of $CaCO_3$ precipitates and how biomineralization can provide significant advantages over traditional chemical grouting techniques using resins, gels, or cement, which often drastically affect soil permeability. Ebigbo et al. (2012) developed an injection method (described in some detail above) and demonstrated experimentally and through mathematical modeling that this easily implemented method allows for a fairly homogeneous distribution of precipitated calcium carbonate. van Paassen's work (2010a and 2011) involved significant laboratory testing on sand columns and eventually a 100 m^3-scale demonstration in a testbed. It was found that approximately 43 m^3 of the sand were successfully cemented and had compressive strengths of up to 12 MPa. The cementation patterns on the 100 m^3 scale followed the patterns of the fluid flow through the soil but were unfortunately not homogenous (van Paassen et al. 2010a; van Paassen 2011). Subsequent laboratory and field tests were performed by van Paassen et al. to demonstrate the feasibility of stabilizing gravel beds with biogrout. Borehole collapse during horizontal directional drilling is a common problem, so several laboratory experiments, a mesoscale experiment in a 3 m^3 container of gravel and a field demonstration, were performed in the Netherlands. Gravel bed stabilization was successful, and up to 6% of the total dry weight of field samples were described to be calcium carbonate (van Paassen 2011).

Although biomineralization for the purpose of soil stabilization has primarily been performed using urea hydrolysis-induced calcium carbonate precipitation, there is emerging research into other microbially induced methods as well. Specifically, nitrate reduction-induced calcium carbonate precipitation may be a promising alternative and is often referred to as MIDP (microbially induced desaturation and precipitation). Initial successes on the laboratory and field scale have been demonstrated (van Paassen et al. 2010b; Wang et al. 2020a, b; Zeng et al. 2021). Nitrate reduction promotes calcium carbonate precipitation according to the reaction outlined in Table 1 with nitrogen gas being the major by-product. In contrast to the ammonium produced during urea hydrolysis, the nitrogen gas would not require removal and can result in desaturation of the soil, which can be desirable when trying to reduce the liquefaction potential of soils (Fig. 6). Both urea-hydrolyzing and nitrate-reducing microorganisms are ubiquitous in soils, and the addition of substrates such as calcium acetate and calcium nitrate will readily stimulate growth of denitrifying microbes. As outlined in Table 1, the activity of denitrifiers will increase carbonate alkalinity and promote the precipitation of calcium carbonate. A potential drawback of this method can include slower than urea hydrolysis-induced calcium carbonate precipitation because denitrification is a growth-dependent process while urea hydrolysis may be growth-independent. Furthermore, the produced nitrogen gas can impact the permeability and thus the calcium carbonate distribution through MIDP treatment. In addition, nitrite, nitrous oxide, and nitric oxide are all potential unwanted by-products, which can accumulate if nitrate reduction is incomplete, and thus would also require treatment of the process water and potentially soil gases (van Paassen 2011).

Wang et al. (2020b) recently summarized the potential for nitrate reduction-induced MIDP to stabilize soils that are prone to liquefaction in an effort to reduce

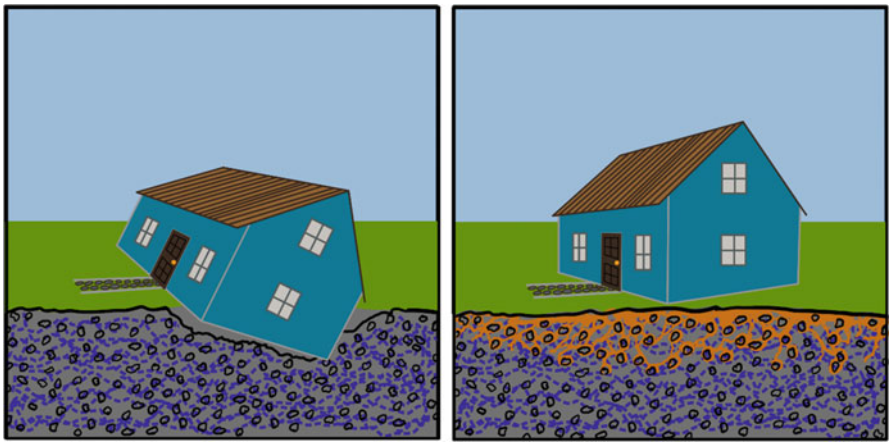

Fig. 6 Left, untreated loose soil can cause foundations to fail and structures to be damaged. Right, soil stabilized using engineered biomineralization

the risk to structures built on these types of soils. There are a number of research and development projects that have focused on the potential of using the combined desaturation of and calcium carbonate precipitation in porous media to improve soil properties (O'Donnell et al. 2017a, b; Pham et al. 2018). Media optimization demonstrated that denitrification and $CaCO_3$ precipitation rates were maximal with only small amounts of toxic by-products accumulating when the molar carbon to nitrogen ratio was 1:1.6 (Pham et al. 2018). Based on measurements of pore water pressure, volumetric strain and cyclic shear resistance behavior soils treated with MIDP were found to be at a significantly lower risk for liquefaction (He et al. 2014). Even when the saturation only decreased by 5%, shear strength was significantly increased (He et al. 2014). Wang et al. (2020b) reported details of work demonstrating that even a single MIDP treatment can reduce the saturation of soils to 80%; however, the saturation and mechanical properties achieved through MIDP appeared to vary depending on the type of soil and number of applications (Wang et al. 2020b). In summary, biomineralization-based soil stabilization technologies are beginning to mature to full-scale applications, and their potential is beginning to be recognized by contractors and customers. It is expected that full-scale applications of biomineralization-based biogrouting technologies will become common over the next decade.

2.2.2 Mine Tailings and Bioremediation

Remediation of mine tailings is another promising application of biomineralization. Mine tailings are often problematic because of the danger of collapse and the potential of releasing metals such as Cu, Pb, Zn, Cd, Cr, Se, and As, thus posing a risk to human and environmental health. Heavy metals can leach through rain- or

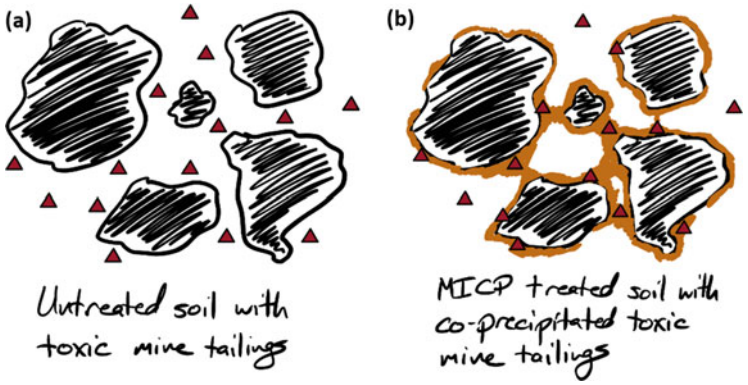

Fig. 7 (**a**) Untreated soil in the presence of toxic metals (red triangles) from mine tailings, (**b**) the biomineralization process can coprecipitate toxic metals initially present in the solution while also providing additional surface area for sorption

snowmelt waters. Immobilizing or otherwise shielding heavy metals from exposure to water can reduce the metal leaching rate (Reddy et al. 2013; Yang et al. 2016). There are a number of more traditional treatment methods that can be applied, including phytoremediation, thermal treatments, excavation, electro reclamation, and capping (Reddy et al. 2013; Yang et al. 2016). Biomineralization of soils or mine tailings loaded with heavy metals, as demonstrated by Yang et al. (2016), has been proposed as a treatment considering how stable MICP precipitates can be in multiple geological settings (Fig. 7).

Yang et al. (2016) isolated the urease-producing bacterium, *Bacillus firmus*, from acidic copper mine tailings at the Xinjiang Copper Industry Co. Ltd. in China. *B. firmus* XP8 exhibited high urease activity and resistance to high metal concentrations. XP8 cells were grown overnight and exposed to the contaminated soil for 7 days; uninoculated control samples maintained a pH of 5.6, while the pH of inoculated mine tailings rose from 5.6 to 7.7 within 7 days. The original soil had a pH of 2.7 because it had not yet been amended with the nutrient media. Soil pH is an important factor when considering this method of metal immobilization because higher pH encourages precipitation by affecting the solubility of metal hydroxides, carbonates, and phosphates (Yang et al. 2016). Because the bioavailability of a metal can influence its resulting toxicity, sample analysis was performed for five different fractions of metals (soluble-exchangeable, carbonate-bound, Fe/Mn oxide-bound, organic/sulfide-bound, and "residual fraction") to estimate bioavailability. The metal content of each fraction was divided by the total amount of that specific metal found in the mine tailing soil; this ratio was termed the distribution coefficient. Carbonate-bound metals increased after MICP treatment, while the soluble-exchangeable fractions decreased (Yang et al. 2016) demonstrating the ability of biomineralization-based technologies to reduce the bioavailability and mobility of toxic metals.

Zhao et al. (2017) found significant potential for MICP to be a sustainable and efficient method for treating water contaminated with heavy metals. Zhao et al. (2017) observed a cadmium removal efficiency of ~53% (10–4.7 mg/L) after 3 hours, and 61% after 48 hours using MICP promoted by a *Bacillus* sp. isolated from mine soil. Mugwar and Harbottle (2016) investigated the MICP-based remediation potential for cadmium, zinc, lead, and copper using *S. pasteurii*. They observed that, when the medium was amended with urea, microbial activity continued even in the presence of metal concentrations that were higher than previously determined minimum inhibitory concentrations (MICs). Their research suggests that even though microbial activity might be inhibited in the presence of heavy metals, with urea present there is sufficient ureolytic activity to promote the coprecipitation of heavy metals using MICP. As the metals coprecipitate, the toxicity of the solution is reduced and enables increased hydrolysis and precipitation. These results indicate that MICP remediation is possible even at metal concentrations significantly higher than estimated based on toxicity data as long as a large enough proportion of the initial microbial population survives, commences urea hydrolysis, and induces calcium carbonate precipitation. Li et al. (2013) performed a similar study and found that a strain of *S. pasteurii* was able to achieve greater than 90% removal of cadmium, zinc, copper, and lead within 2 h. Results of control treatments were not reported by Li et al. (2013); thus, differences in the rates and extent of metal removal compared to other studies could be due to abiotic processes (Li et al. 2013; Mugwar and Harbottle 2016).

Kumari et al. (2014) compared the ability of the ureolytic bacterium *Exiguobacterium undae* to remove cadmium from soils at 10 °C and 25 °C. After the original sample of soil was air-dried and autoclaved, 100 mg of $CdSO_4$ was added per 1 kg of soil followed by addition of an overnight culture of *E. undae*. Forty-five percent of Cd^{2+} were immobilized within 1 h at both temperatures, and after 5 h the immobilized Cd^{2+} reached 79% and 84% for 10 °C and 25 °C, respectively. After 2 weeks, the more bioavailable, soluble-exchangeable fractions of cadmium had been reduced by about 97% relative to untreated controls at both temperatures. Over the same 2-week period, the more stable, carbonate-bound form of cadmium in the soil increased approximately threefold to 71.4 mg kg^{-1} and 67.8 mg kg^{-1} for the 25 °C and 10 °C MICP treatments relative to untreated controls (Kumari et al. 2014).

As mentioned at the beginning of this section, the stabilization of mine tailings is also important. Gowthaman et al. (2019) evaluated the effectiveness of stabilizing soil slopes in cold subarctic regions by isolating *Lysinibacillus xylanilyticus*, an indigenous, ureolytic bacterium from soil samples taken from Onuma, Hokkaido, Japan. The bacterium was tested for growth and urease activity at temperatures ranging from −10 °C to 50 °C to address the potential of MICP for the treatment of mine waste tailings in colder regions. Most work, so far, has only been performed within the temperature range of 25 °C–60 °C (Gowthaman et al. 2019; Kumari et al. 2014). Little growth of *L. xylanilyticus* was observed above 40 °C, and urease activity appeared to be insignificant below 5 °C and above 25 °C, but relatively stable between these temperatures (Gowthaman et al. 2019). Soil stabilization

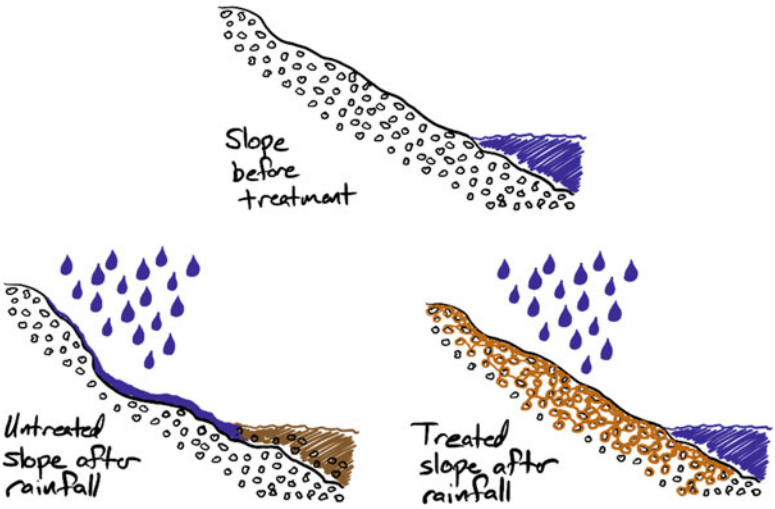

Fig. 8 Biomineralization treatments can stabilize slopes reducing erosion during runoff, snowmelt, etc.

experiments were performed with three types of sand with average particle sizes (D_{50}) of 1.6 mm, 0.87 mm, and 0.2 mm as well as with soil samples; the sand fraction of the soil had an average particle size (D_{50}) of 0.23 mm. In column experiments the MICP-treated sand was found to have a UCS (uniaxial compressive strength, estimated using a needle penetrometer) about 3.75 times higher than untreated sands. The authors concluded that the fine particles present in the slope soil—about 12% of this soil consisted of particles with a grain size of less than 125μm—were beneficial in providing support for the calcium carbonate bridging between larger sand grains. It was also noted by Gowthaman et al. (2019) that very fine particulate soils may have limited permeability that could limit infiltration of bacteria and cementation solutions into the soil, a challenge discussed above in the context of fly ash stabilization in the "Soil Stabilization" section. Recognizing that fine particles can aid in stabilization but can become problematic at higher percentages within the soil should be an important consideration in future biomineralization technology scale-up.

Gowthaman et al. (2019) also tested samples modeled as a physical slope instead of a column (Fig. 8). More than 80% of the soil was successfully stabilized with a 3–4 cm layer of cemented soil at the surface, while the soil below that layer was not successfully stabilized. The UCS of the slope surface was determined to be between 2 and 8 MPa with the higher strength values being obtained from the lower areas of the slope. This difference was attributed to the injection method, which likely caused the bacteria being transported preferentially toward the bottom of the slope sample.

2.2.3 Dust Suppression

Another problem being addressed by utilizing biomineralization is dust suppression and erosion control. Among other contributors to erosion, wildfires are becoming more frequent, and the altered chemical and biological makeup of burned soil can lead to problems with erosion, water quality, flood control, and general ecosystem health (Hodges and Lingwall 2020). Current technologies have not been able to provide a cost-effective method for treating large areas affected by forest fires in order to prevent erosion (Hodges and Lingwall 2020). Hodges and Lingwall (2020) explored the effects of wind and water on burned soils that were treated using MICP; both biostimulation and bioaugmentation were evaluated. *S. pasteurii* and different concentrations of biomineralization solutions, which consisted of urea, nutrient broth, ammonium chloride, and $CaCl_2$, were applied to soil samples (Fig. 9). In addition, some soil samples were treated with only the urea-broth solution with bacteria and no added calcium or with only the urea and Ca^{2+} solutions but no added bacteria to compare potential benefits of bioaugmentation vs. biostimulation. Erosion tests were performed at 10, 20, and 30 mph simulated wind speed on burned and unburned soils subjected to the above treatments (Hodges and Lingwall 2020). Successful treatments created a water-permeable crust that stabilized the soils through an increase in soil strength by 25–50 kPa. These MICP treatment methods were generally not effective against mass loss at higher wind speeds, but even a single application resulted in some stabilization and a thin crust layer which could play an important role in protecting the soil for long enough to allow new plant growth to develop and further stabilize the soil. At lower wind speeds, these biomineralization methods were more successful and proved effective for dust control for both burned and unburned soil. Similar to the smaller particles discussed above in the "Mine Tailings and Bioremediation" section, ash particles could be improving the stabilization of the soils by promoting calcium carbonate bridging between larger sand grains. In addition, it was found that there were beneficial effects through treatment with only urea solutions, only calcium solutions, or without the addition of bacteria. The reasons for these improvements have not

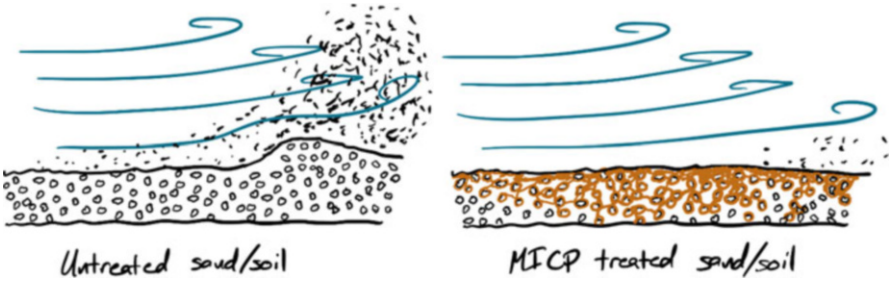

Fig. 9 Schematic representation of dust suppression using engineered biomineralization treatments. Microbially produced mineral precipitates cement together fine particles that would otherwise be eroded as dust during wind and weather events

been explored in depth, and further tests are being performed (Hodges and Lingwall 2020).

Similar to burned soils, sandy soils can also contribute to dust pollution, and many regions could benefit from dust suppression. Almajed et al. (2020) explored the use of enzymatically induced calcium carbonate precipitation (EICP) treatment to manage wind-caused erosion of desert sand. Multiple concentrations and combinations of urea, calcium chloride, sodium alginate (SA, a biopolymer), and powdered milk were applied to sand samples; EICP was promoted using jack bean urease. Multiple treatments were evaluated, including different molar urea to calcium chloride ratios (1:0.67 and 1:1.25); SA solutions of 0.5%, 1.0%, and 2.0%; and treatments with only $CaCl_2$, along with samples treated with only water or untreated samples (Almajed et al. 2020). All treatments, except the untreated controls and water-only treatments, formed a crust, and the resistance to wind erosion increased after curing the samples for 7 days. The erosion resistance remained effective after 28 days with erosion rates (percent of mass loss), staying below 0.01% for all treated samples. This represented a significant improvement over the erosion rate of the control and water-treated samples which were around 97% and 94%, respectively (Almajed et al. 2020). Similar to previous studies, the points of contact between soil particles were stabilized by the presence of calcium carbonate, which contributed to erosion resistance. An additional factor contributing to the wind resistance in the SA treated soils was the formation of alginate hydrogels created as divalent calcium ions replaced sodium ions within the sodium alginate. While the developed hydrogel increased the soils' ability to resist erosion and retain water, it also reduced the permeability of the soil making it more difficult for EICP treatment solutions to penetrate deeper into the soil; as a result, thinner crusts were observed in the SA-treated soils (Almajed et al. 2020).

Research and development are continuing with the goal of increasing the effectiveness and usefulness of biomineralization for multiple stabilization applications, including soil stabilization, stabilization, and immobilization of metals in mine tailings and other bioremediation applications, as well as in dust suppression. The use of microorganisms and enzymes to promote mineral precipitation offers potential benefits, including being more environmentally friendly, reducing costs, and energy usage. However, there is still limited use of this technology on the larger scale, and further research and development is needed.

2.3 Subsurface Applications

The earth's subsurface contains many important resources, such as water, minerals, oil, and gas. The subsurface is also used for the storage of natural gas and other compounds, such as wastes, wastewater, and CO_2 (Baines and Worden 2004; Bauer et al. 2013; Ferguson 2015). In addition, the subsurface is used for the purification of useful products, such as drinking water. A concern exists that contaminants from natural or anthropogenic sources can enter the subsurface where they can pose a risk

to human and environmental health. Technologies exist to inject or extract compounds into or out of the subsurface, and engineering applications, such as oil production, deep subsurface mining, groundwater management, and subsurface remediation, are common (Montana Emergent Technologies 2020; National Research Council 2005; Yudhowijoyo et al. 2018).

Leakage pathways around wells or in their vicinity can be problematic for any subsurface application since they can lead to loss of injected or stored fluids as well as result in inefficient recovery. However, safe injection into, storage in, and recovery from the subsurface are essential, and ensuring wellbore integrity is in turn essential for environmental and economic reasons. Wellbore integrity can be defined as the "application of technical, operational and organizational solutions to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well," and wellbore integrity concerns are often related to the development of leakage pathways (NORSOK Standard 2013). Leakage pathways can often be sealed using cement injections ("cement squeezes") with Portland cement remaining the most commonly used wellbore integrity remediation agent (Kirkland et al. 2020; Yudhowijoyo et al. 2018). Unfortunately, in some cases leakage pathways consist of very small aperture fractures or delaminations that can be difficult to seal because the low injectivity of these small aperture leakage pathways might require injection pressures higher than permissible during wellbore remediation, due to concerns regarding damage to the well or the formation. Thus, cement squeezing might be ineffective or even impossible because the fairly large cement particles simply might be too big to effectively enter and seal small apertures (Phillips et al. 2018). An advantage of biomineralization-based methods is that the minerals are formed in situ by microbes from aqueous solutions. Microbes are only a few micrometers in size and can therefore access areas inaccessible to regular cement (Cunningham et al. 2011; Kirkland et al. 2019; Phillips et al. 2013a; Phillips et al. 2018).

Enhanced oil recovery, wellbore sealing, and secure subsurface CO_2 storage are some of the applications, which have been demonstrated on the field scale using engineered biomineralization technology (Cunningham et al. 2011; Hommel et al. 2020; Mitchell et al. 2010; Montana Emergent Technologies 2020; Phillips et al. 2013b).

2.3.1 Finite Resource Recovery

Enhanced oil recovery (EOR) operations are designed to increase the recovery of finite oil and gas resources from existing reservoirs (Alvarado and Manrique 2010). Enhanced oil recovery is generally achieved through a process called "sweeping," during which fluids are injected into oil-bearing formations to push remaining oil out of the formation. Often water is injected into one well to "push" oil toward another well, which is pumping ("pulling") the oil out of the ground (Thomas 2008). The process becomes challenging if high permeability zones exist, through which the injected water escapes. These zones are often referred to as "thief zones" and transport injected fluids at rates faster than the oil-bearing formation, therefore

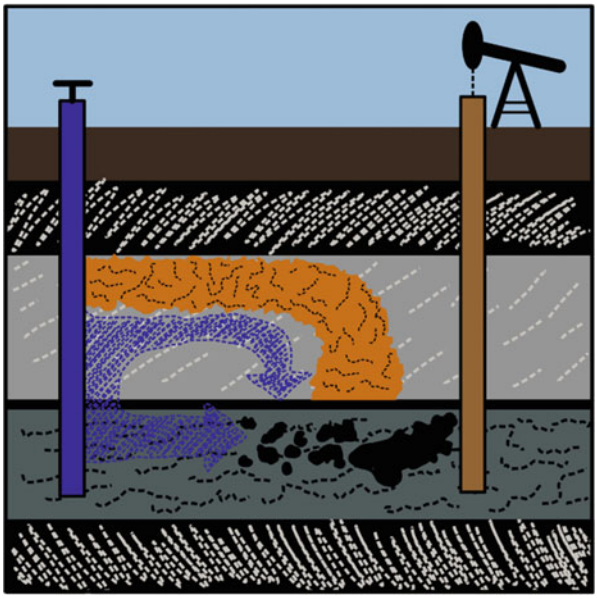

Fig. 10 Enhanced oil recovery enabled through microbial mineral formation. Biominerals (orange) block fractures or high permeability thief zones, thus directing the flow of sweeping fluids such as water or CO_2 (blue) through resource-rich zones, enhancing the recovery of oil (black)

reducing the net recovery of resources (Kirkland et al. 2020; Sen 2008). Even though having higher permeability, these thief zones still consist of formations with fairly small pores or fractures (Fig. 10). It can be challenging to reduce the permeability of these zones reliably using cement injection since cement cures over a finite amount of time and it is necessary to control where cementing occurs.

Biocementation fluids have viscosities similar to water and can be transported with the injection water into thief zones where the enzymes or bacteria adhere to the pore or fracture surfaces. Subsequent injection of biocementation fluids (e.g., urea- and calcium-containing solutions) promotes precipitation of minerals (e.g., calcium carbonate) in the areas where bacteria or enzymes are present, which reduces permeability (Ebigbo et al. 2012; Kirkland et al. 2020; Sen 2008). When permeability is reduced sufficiently in the thief zone, injected sweeping fluids will travel through oil-bearing zones for additional resource recovery as demonstrated by Kirkland et al. (2020).

Hydraulically fractured horizontal oil and gas wells in unconventional formations accounted for $<5\%$ of wells drilled in 2006 but $>75\%$ by 2016; these wells are now responsible for approximately 50% of US oil and gas production (EIA 2016; EIA 2020). However, these unconventional wells can exhibit rapid decline in production (as much as 60–80% after the first year) (Thomas 2008). Currently, wells drilled and hydraulically fractured to extract oil and gas may recover only 10% of the fossil fuels present in the formation because only the oil and gas close to a fracture can be extracted reliably due to the very limited fluid mobility in shale rocks (Thomas 2008). Thus, significant amounts of producible (but not accessed) reserves remain in the reservoir. One way to recover more oil and gas from these wells is by blocking

old fractures with diverting agents and refracturing the formation to open new fractures in the reservoir. Existing diverting agents are difficult to control in wells that may be several miles deep, but biomineralization may represent a new diverting agent technology that could be used to improve the success of refracturing to enhance the recovery of oil and gas from declining wells. However, additional research including an expansion of the temperature range, in which biomineralization could be used, and demonstrations at the reservoir scale are needed to assess the actual feasibility in the subsurface.

2.3.2 Wellbore Integrity

Oil and gas wells have been drilled for more than a century, and there are about 2.3 million abandoned and more than 900,000 active wells in the USA alone (EIA 2020; Townsend-Small et al. 2016). Many wells develop leaks, especially as they age (Boothroyd et al. 2016; Dusseault et al. 2000). Wells develop leaks because subsurface pressures and temperatures vary, resulting in contractions and expansions, shrinkage or cracking in the cement over time, and through ground movement from earthquakes or the drilling of nearby wells. Leaking wells are a problem for the oil and gas industry in several ways. First, the lost hydrocarbons represent lost revenue. Second, lost hydrocarbons are a source of air and water pollution in the vicinity of leaking wells and may even pose acute risks to human life in the case of dangerous gas buildup (Boothroyd et al. 2016; McKenzie et al. 2012). Third, even perceived pollution in the vicinity of an oil or gas well can cause negative public perception that is difficult to overcome and can cause financial harm. Repairing leaky wells potentially thousands of feet below surface can be expensive and is often unsuccessful (Bagal et al. 2016; Montana Emergent Technologies 2020).

Phillips et al. (2018) described the use of biomineralization to remediate a leakage pathway (channel) 310 m belowground located in the well cement at a well in Alabama. It was observed that MICP treatment using conventional oil field subsurface fluid delivery technologies (packer, tubing string, and a slickline deployed bailer) was successful in sealing the compromised wellbore cement. The authors injected urea-calcium solutions and microbial suspensions (*Sporosarcina pasteurii*). Injectivity decreased with the number of MICP treatments. A decrease in the pressure decay after shut-in, a measure of improved wellbore integrity, was also observed. The authors also observed a substantial deposition of precipitated solids in the original flow channel when comparing the pre- and post-MICP treatment cement bond logs suggesting the biomineralization treatment sealed the channel and could be used to remediate leakage pathways in oil and gas wells (Fig. 11).

Montana Emergent Technologies (MET) has trademarked a process called BioSqueeze, which uses ureolysis-induced calcium carbonate precipitation to seal difficult to seal wells (Montana Emergent Technologies 2020). Much of the required R&D was conducted in collaboration with Montana State University and has been published in various peer-reviewed journals (Kirkland et al. 2021a, b; Kirkland et al. 2019; Kirkland et al. 2020; Phillips et al. 2018). So far, MET has successfully

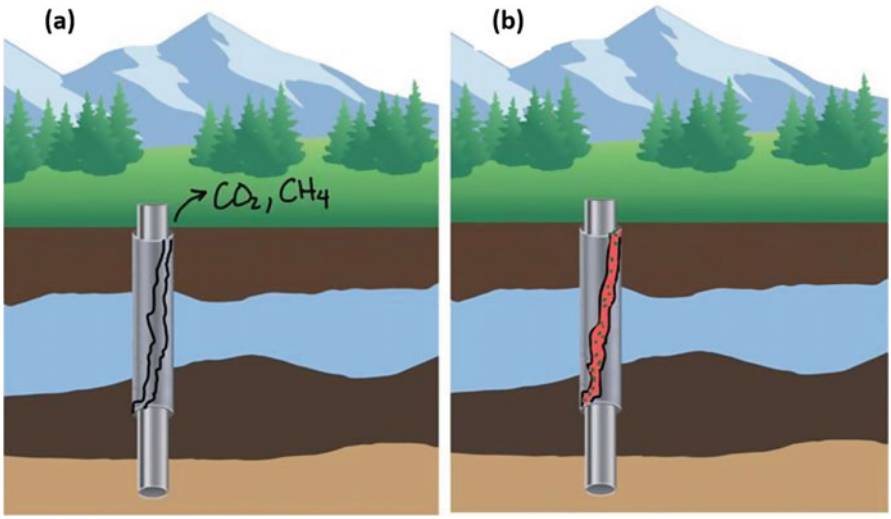

Fig. 11 (**a**) When wellbore integrity is disturbed, gas can leak through small apertures such as delaminations or fractures. (**b**) Microbial biomineralization has been demonstrated to be capable of sealing these small apertures and preventing the leakage of gases

completed more than 30 commercial scale BioSqueeze treatments often resulting in residual annular pressures of less than 1 psi.

Other envisioned applications are related to geologic carbon sequestration (GCS) and geothermal well drilling and operation. Concerns over global warming have stimulated a concerted effort to limit CO_2 emissions (IPCC 2014; IPCC 2018). Geologic carbon sequestration (GCS) has been proposed as one part ("wedge") in the battle of tackling the reduction of CO_2 emissions (Pacala and Socolow 2004). Carbon capture is suitable for large point sources, such as large fossil power plants and cement plants. CO_2 can be captured at the source and injected into the deep subsurface. One challenge with GCS is storage security, meaning the injected CO_2 must remain safely underground for at least decades, if not centuries (IPCC 2014; Kudryavtsev et al. 2012). Wellbore and caprock integrity are crucial to the success of GCS, and methods to seal potential leakage pathways around wells in aquifers containing CO_2 using ureolysis-induced calcium carbonate precipitation are under development (Kirkland et al. 2021a, b; Phillips et al. 2013b). Recently, Kirkland et al. (2021a, b) performed a biomineralization treatment of a compromised wellbore cement 300 m belowground under conditions that simulated the low pH that might be found in carbon sequestration storage environments. It was observed that biomineralization treatment reduced injectivity by 94% and that mineralization could be promoted in CO_2-affected brines. However, the authors concluded that additional research is required to assess the long-term seal integrity and ensure storage of CO_2 in GCS (Kirkland et al. 2021a, b).

Geothermal energy is gaining popularity since it represents a low carbon emission source for heat and electricity generation. The drilling of geothermal wells is

expensive, and a major cause of nonproductive drilling time is the loss of drilling fluids, aka lost circulation (Alsaba et al. 2014; Denninger et al. 2015; Mansour et al. 2019; Marbun 2013). The loss of drilling fluids occurs when fractures or other high permeability zones are encountered during drilling. If circulation is lost, lost circulation materials (LCMs), such as sawdust, mica, graphite, calcium carbonate, nylon fibers, mylar, or walnut shells, are often injected at high rates to stop losses of drilling fluids (Boukadi et al. 2004; Nayberg 1987). Existing LCMs are not readily immobilized in the formation or can degrade or erode over time, potentially requiring continuous addition throughout the drilling process. Biomineralization of LCMs could result in immobilization and create a more durable seal against the loss of drilling fluids. The use of biomineralization to enhance LCM performance is in the early stages of technology development, and to the authors' knowledge, no field demonstrations have been performed yet.

2.4 Other Potential Applications of Biomineralization

Biomineralization has also been demonstrated to be useful in areas such as art. Limestone and rock have long been used in the creation of sculptures. Recently, a group of interdisciplinary engineering and art undergraduate students at Montana State University used ureolysis-induced calcium carbonate biomineralization to design and sculpt an approximately 0.9 m × 0.3 m × 0.3 m large replica of the Bridger Mountain range as well as an approximately 1 cm × 5 cm × 7 cm replica of the MSU mascot, the Bobcat, using biomineralization approaches (Fig. 12) (Troyer et al. 2017). The Bridger Mountain range is located just outside of Bozeman (MT, USA) and served as the inspiration for the biomineralized replica. As described in Troyer et al. (2017), the project was supported through a design contest, "Engineers Make a World of Difference," sponsored by the Norm Asbjornson College of Engineering at Montana State University to promote the spirit of discovery and imagination for the engineering students. Loose sand was treated with microbes and urea-calcium solutions until a solid cohesive block was formed roughly representing the outline of part of the Bridger Mountain range. Subsequent carving and sculpting of the relief resulted in a replica of the Bridger mountains. In the development of the

Fig. 12 (Left) 0.9 m × 0.3 m × 0.3 m biomineralized replica of the Bridger Mountain range. (Right) Biomineralized replica of the Montana State University mascot, the Bobcat

Bobcat mascot replica, ureolytic biomineralization techniques were used to biocement loose sand inside a Bobcat-shaped cookie cutter, which was subsequently painted in Montana State University colors.

2.5 Conclusions and Outlook

Biomineralization is a natural process with significant potential for engineering applications. While this book focused on various minerals and various processes related to the precipitation and dissolution of minerals through microbial activity, this chapter focused on developed and currently developing applications. A review is presented of parameters that influence biomineralization for engineering applications associated with development of novel construction materials, soil stabilization to mitigate hazards to public health, and subsurface applications such as improving wellbore integrity. By far, the most frequently utilized mineral is calcium carbonate, and urea hydrolysis is the most frequently researched microbial metabolism to initiate mineral precipitation. Applications in construction, soil stabilization, and the sealing of leaky wells have advanced the furthest, and some of them have been commercialized. Other technologies are on the verge to full-scale application and thus commercialization. Much research and development work remains to be performed in this field, and additional applications for biomineralization will be developed in the construction, environmental, biotechnology, and medical fields.

These research and development activities will contribute to the development of environmentally friendly methods and products as well as economic competitiveness. Biological manufacturing methods, such as engineered mineral precipitation, can significantly reduce energy-intensive cement manufacturing activities and contribute to resource and climate conservation. The world is expected to add more than two trillion square feet of new building space by 2060, which is equivalent to adding another New York City every month for the next 40 years (UN Environment 2017). Microbially induced calcium carbonate precipitation has the potential to reduce the net carbon footprint of building and construction materials, but work remains to develop this technology for the wide range of applications that cement currently dominates (Davies et al. 2018). In addition, biomineralization has been demonstrated to be useful in areas such as art. There are also applications where biomineralization does not directly compete with traditional cement, including the coprecipitation of certain groundwater contaminants such as strontium (Lauchnor et al. 2013; Mitchell and Ferris 2006a) and restoring the integrity of wells with ultrafine leaks. Engineered microbial mineral formation has grown from a theory and proof-of-principle vision to a technology being applied in the marketplace.

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