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Review

Cyanobacteria as Biocatalysts for Carbonate Mineralization

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Abstract: Microbial carbonate mineralization is widespread in nature and among microorganisms, and of vast ecological and geological importance. However, our understanding of the mechanisms that trigger and control processes such as calcification, *i.e.*, mineralization of CO_2 to calcium carbonate ($CaCO_3$), is limited and literature on cyanobacterial calcification is oftentimes bewildering and occasionally controversial. In cyanobacteria, calcification may be intimately associated with the carbon dioxide-(CO_2) concentrating mechanism (CCM), a biochemical system that allows the cells to raise the concentration of CO_2 at the site of the carboxylating enzyme ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco) up to 1000-fold over that in the surrounding medium. A comprehensive understanding of biologically induced carbonate mineralization is important for our ability to assess its role in past, present, and future carbon cycling, interpret paleontological data, and for evaluating the process as a means for biological carbon capture and storage (CCS). In this review we summarize and discuss the metabolic, physiological and structural features of cyanobacteria that may be involved in the reactions leading to mineral formation and precipitation, present a conceptual model of cyanobacterial calcification, and, finally, suggest practical applications for cyanobacterial carbonate mineralization.

Keywords: calcification; calcium carbonate; carbon sequestration; cyanobacteria

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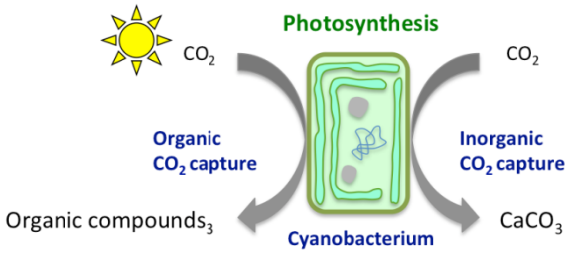
1. Introduction

In addition to reducing CO_2 to organic compounds via photosynthesis, many cyanobacteria mineralize CO_2 to recalcitrant carbonates, such as $CaCO_3$. Thus cyanobacteria present two different modes of CO_2 capture, one via photosynthesis and the Calvin-Benson-Bassham (CBB) cycle where CO_2 is captured and converted to organic compounds, and another via carbonate mineralization, e.g., calcification, where CO_2 is converted to carbonate minerals (Figure 1). The ratio of organic to inorganic carbon production (R_{OI}), differs between species of cyanobacteria and environmental conditions. Although the phenomenon of microbial calcification has long been recognized, its physiological function is unknown. Calcification is a prominent feature of many cyanobacterial species [1–6] and cyanobacterial calcification is of vast biogeochemical and ecological significance [2,4,5,7–13]; magnificent illustrations of cyanobacterial calcification are stromatolites [14–16] and whiting events, very fast, large-scale precipitations of fine-grained $CaCO_3$ together with organic compounds that can turn entire water bodies such as Lake Michigan into a milky state [17–20]. A comprehensive understanding of carbonate mineralization is necessary for us to fully appreciate and employ this process in efforts to model and predict carbon cycling and budgets, to elucidate paleoenvironments, and apply it in biological CCS. In this review, we discuss carbonate mineralization in cyanobacteria, with focus on calcification and, in so doing, provide some details about methodology currently applied in the field, and consider the significance of the process in a wider perspective.

Figure 1. Two modes of CO_2 fixation in cyanobacteria.



2. Chemical Reactions Governing CO_2 Conversion into Carbonate Minerals

The solubility of carbon dioxide (CO_2) in water is higher than that of the other three most abundant gases in the Earth atmosphere (N_2, O_2, and Ar). However, its equilibria are somewhat complicated. The dissolved CO_2 reacts with water to form carbonic acid:

$$CO_{2\,(aq)} + H_2O \leftrightarrows H_2CO_3 \quad (1)$$

Subsequently, the carbonic acid dissociates to form bicarbonate (HCO_3^-), releasing H^+ into the solution. A fraction of HCO_3^- further dissociates to form carbonate (CO_3^{2-}):

$$H_2CO_3 \leftrightarrows HCO_3^- + H^+ \quad (2)$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \quad (3)$$

The concentration of H_2CO_3 at circumneutral pH is small, and the dissolved CO_2 from Reactions (2) and (3) occurs predominantly as HCO_3^-. If the solution is natural water, e.g., lake or seawater,

carbonate anions can interact with the cations present in the solution to form insoluble carbonates. For example, if Ca^{2+} is present, $CaCO_3$ can be formed. Precipitation of $CaCO_3$ can be described with the following Reactions:

$$Ca^{2+} + 2HCO_3^- \leftrightarrows CaCO_3 + CO_2 + H_2O \quad (4)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3 \quad (5)$$

with Reaction (5) dominating in seawater [21]. In both cases, two moles of alkalinity are consumed per formation of one mole of $CaCO_3$. Precipitation of $CaCO_3$ from the solution lowers its pH. Because of this, and since a greater fraction of dissolved inorganic carbon (DIC) is present as $CO_{2\,(aq)}$ at low pH, the formation of $CaCO_3$ in seawater stimulates an increase in the concentration of $CO_{2\,(aq)}$ and promotes its outgassing [22]. This is opposed to the photosynthetic conversion of CO_2 into organic matter [23], which serves as a transient carbon sink:

$$CO_{2\,(aq)} + H_2O \leftrightarrows CH_2O + O_2 \quad (6)$$

It is important to note that formation of both insoluble carbonates and organic matter pulls the equilibria of the carbonate species to the right to replace the removed (bi) carbonate ions in the solution.

Three crystalline polymorphs of anhydrous $CaCO_3$ are known to occur in nature, calcite, aragonite, and vaterite. The first two are by far the most abundant forms of biologically produced $CaCO_3$ [24]. The crystal structure of calcite is rhombohedral, whereas that of aragonite is orthorhombic. The different structures of the mineral polymorphs lead to a difference in their physical and chemical properties [25], of which the solubility is of major importance for the mineralization process. The solubility product for each carbonate mineral is defined as:

$$K_{sp\ mineral} = [Ca^{2+}] \times [CO_3^{2-}] \quad (7)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ refers to, respectively, the calcium and carbonate ion activities in a solution saturated with respect to the mineral, at a given temperature, salinity, and pressure. Calcite is the most stable polymorph while vaterite is the most soluble, *i.e.*, $K_{sp\ calcite} < K_{sp\ aragonite} < K_{sp\ vaterite}$. The $CaCO_3$ saturation state of the solution, Ω, is expressed as:

$$\Omega_{mineral} = \frac{[Ca^{2+}] \times [CO_3^{2-}]}{K_{sp\ mineral}} \quad (8)$$

At Ω >1 the solution is supersaturated and at Ω < 1 it is undersaturated with respect to the $CaCO_3$ mineral [25]. As mentioned above, the Ω is linked to temperature, pressure, and salinity through the dissociation constant. Contrary to the typical increase of solubility with increasing temperature observed for most minerals, the solubility of calcite decreases with increasing temperature, as does the solubility of CO_2 gas in water. Changes in pressure affect the partial pressure of CO_2 (pCO_2) and thus the amount of gas dissolving in the solution. Increase in ionic strength of the solution leads to decrease of ion activity, affecting solubility of carbonates. Presence of particular ions e.g., Mg^{2+} and PO_4^{2-} is known to specifically inhibit $CaCO_3$ precipitation [26,27]. Magnesium calcites ($Mg_xCa_{1-x}(CO_3)$) are an important subgroup of the $CaCO_3$ minerals, frequently produced in natural environments. With up to 30 mol % $MgCO_3$ in the case of some biogenic calcites, solubility of the magnesium calcites is strongly influenced by their magnesium content. Properties and a mode of formation of dolomite

($CaMg(CO_3)_2$), one of the most abundant sedimentary minerals, are known in less details than for most other carbonates. Though marine and many other natural waters generally are greatly supersaturated with respect to both magnesite ($MgCO_3$) and dolomite, these cannot form directly from aqueous solutions under near Earth surface conditions [28] due to a high energy of hydration of the Mg^{2+} ion and a kinetic barrier hindering formation of complex and well-ordered structure of the minerals. Instead, a variety of magnesium carbonate hydrates (e.g., nesquehonite, $MgCO_2 \cdot 3H_2O$) and hydroxyhydrates (e.g., hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) form from solution [29].

$CaCO_3$ precipitation in solutions without a nucleation surface (homogeneous nucleation) is often impeded by kinetic barriers, as seen in systems supersaturated with Ca^{2+} and CO_3^{2-} such as the oceans [29]. Such kinetic barriers include the high energy of hydration of the calcium ions, the low concentration and activity of the carbonate ions, and the presence of high concentrations of sulfate and magnesium ions [29,30]. The addition of a surface on which the crystal can nucleate (heterogeneous nucleation) can dramatically reduce kinetic barriers in the calcification. There is increasing evidence that many processes traditionally considered as purely physico-chemical, such as carbonate mud production during whiting events [31,32], particle formation such as ooids and peloids [33–35], and carbonate cycling in terrestrial environments [36–38], have an organic and/or biological origin. Relative abundance of stable isotopes in the precipitate can bear witness to the nature of its origin [39]. Thus enrichment of carbonate minerals with ^{12}C indicates that the carbon was derived from the degradation of the organic carbon e.g., by sulfate reducing bacteria, while enrichment with ^{13}C co-localizes carbonate precipitation with photosynthesis, actively depleting the ^{12}C pool [40,41].

Mineralization by microbial calcification (Reactions (4) or (5)) is generally considered to be biologically induced, as opposed to biologically controlled. While biologically controlled mineralization is an organized process where cells exert a high degree of control over nucleation and crystallization, and that usually results in specialized structures such as shells, biologically induced mineralization is a more diffuse phenomenon that depends on various metabolic activities that result in an alkaline (micro) environment and cell surface properties such as nucleation sites for mineralization [24,42,43].

3. Cyanobacteria

Cyanobacteria are Gram-negative bacteria that carry out oxygenic photosynthesis and are thought to be the origin of chloroplasts of plants and eukaryotic algae via endosymbiotic events in mid-Proterozoic [44]. Through their photosynthetic capacity cyanobacteria have been tremendously important in shaping the course of evolution and ecological change throughout Earth's history [45], and they continue to contribute to a large share of the total photosynthetic harnessing of solar energy and assimilation of CO_2 to organic compounds. It is estimated that half of global photosynthesis is carried out by phytoplankton [46], with cyanobacteria being, at times, the dominant contributors to CO_2 fixation [47]. Indeed, >25% of current global photosynthesis can be accounted for by the two genera of marine cyanobacteria, *Synechococcus* and *Prochlorococcus* [48].

Cyanobacteria thrive in the majority of ecosystem habitats on Earth; they successfully populate freshwater and marine environments, hot springs, and cold dry valleys, coping with extremes in salinity, light quality and availability, UV radiation, pH, dryness, desiccation, temperature, and

pressure. Similarly, they exhibit an unusually wide range of morphologies, from submicron-size unicellular free-living cells to complex well-structured mat communities comprising several cyanobacterial lineages and intra- and inter-lineage functional differentiation [47]. Many cyanobacteria are diazotrophs and can assimilate not only CO_2 but also fix atmospheric nitrogen (N_2) and convert it to organic matter [49]. There are three major ecological groups of cyanobacteria in the aquatic environment: (i) mat-forming species, composing biofilms over rocks, sediments, and submerged plants; (ii) bloom-formers, most common in nutrient-rich water bodies, e.g., coastal ocean zones, eutrophic streams and lakes; and (iii) picocyanobacteria (< 2 μm in diameter) that are often abundant in open oceans and clear water lakes. The mat-forming cyanobacteria have a particularly long history. Some of these organisms form laminated, lithified structures called stromatolites. Those formations exhibit a striking resemblance to the fossil stromatolites [15,50] found all the way back to the Precambrian. The stromatolite communities, thought to have been the main primary producers on Earth for more than 1 billion years throughout the Proterozoic, are much less abundant today [51]. Another group of aquatic cyanobacteria worth mentioning comprises colonial non-bloom-formers, which are common in a variety of aquatic habitats, including mesotrophic lakes, wetlands, and saline waters [52]. Many cyanobacteria, especially those forming colonies or biofilms, excrete organic polymeric substances to form extracellular formations e.g., sheaths or capsules [53,54]. The function of these exopolymeric substances (EPS) may be to allow association of cells, facilitate gliding, support uptake of micronutrients, and absorb heavy metals from the solution. The EPS can serve as a nucleation surface for mineralization and therefore is also a critical component of the carbonate mineralization process in many cyanobacteria and other bacteria (see further discussion in Section 3.2).

3.1. The CO_2-concentrating Mechanism

CCMs seem ubiquitous in cyanobacteria [55], although their presence has not been confirmed in all of the around 1500 described cyanobacterial species [56]. A CCM may provide a means for enhanced carbonate mineralization by elevating pH at the immediate cell exterior, and thus increasing the supersaturation level of the microenvironment in respect to a mineral. During oxygenic photosynthesis (Figure 2), CO_2 is converted to organic compounds via the CBB cycle, utilizing ATP and NAD(P)H as energy and reducing equivalents, respectively (Figure 2). Light energy is harvested by the two photosystems, Photosystem II (PSII) and Photosystem I (PSI), associated with the light-harvesting phycobilisome complex. Light energy in PSII and PSI excites electrons, supporting an electron transport from water to $NADP^+$ through an electron transport chain involving a large number of redox components, including the two photosystems, Plastoquinones (PQ), the Cytochrome b/f complex, plastocyanin (PC), and Ferredoxin-NADPH oxido-reductase (FNR). The electron transport in the thylakoid membrane generates a H^+ gradient, which is the driving force for ATP synthesis by the ATP synthase. ATP and NADPH produced by photosphosphorylation are used to fuel the Calvin cycle in the carboxysome/cytosol, whereby atmospheric CO_2 is reduced to organic compounds by Ribulose-1,5 bisphosphate carboxylase/oxygenase (Rubisco; EC 4.1.1.39) and other enzymes. Rubisco is encumbered with the ability to use not only CO_2 but also O_2 as substrate, a property that, together with its slow turnover number, severely impairs Rubisco's carboxylation efficiency. For aquatic cyanobacteria and algae, the situation is exacerbated by the poor availability of CO_2 in water, with a

diffusion rate 10^4 times slower than in air [57]. Consequently, many microorganisms including cyanobacteria have evolved inducible mechanisms that allow the cells to raise the concentration of CO_2 at the carboxylation site of Rubisco up to 1000-fold over that in the surrounding medium [58–60]. Details of the CCM differ between cyanobacteria but the salient features include a series of bicarbonate (HCO_3^-) and CO_2 transporters and the carboxysome, a protein-enclosed micro-compartment that houses (most of) the Rubisco population and also contains the enzyme carbonic anhydrase (CA; EC 4.2.1.1) [61] (Figure 3). CO_2 enters the cells mainly via HCO_3^-/Na^+ symports but also through diffusion of CO_2, which is converted to HCO_3^- during the uptake through membrane-associated CA activities. Cytosolic HCO_3^- is subsequently imported to the carboxysome and converted to CO_2 by carboxysomal CA. The ensuing H^+ consumption (Reaction (9)) is transmitted as a pH increase to the cell exterior, contributing to the cell surface alkalization that is established by H^+ consumption by the photosynthetic electron transport. Alkalization, combined with accumulation of Ca^{2+} ions transported to cell surface by Ca^{2+}/H^+ antiporter and/or attracted by negatively charged residues in the cell wall, increases the $CaCO_3$ saturation state in a solution layer surrounding the cell, presumably leading to $CaCO_3$ precipitation. Under conditions of low inorganic C (C_i), e.g., in alkaline environments, when CO_3^{2-} species dominate over CO_2 and HCO_3^-, the CCM is induced and activated, supporting active transport of HCO_3^- across the outer and plasma membranes into the cytosol. The transport is facilitated through HCO_3^-/Na^+ symports or ATP-driven uniports [60]. Capture of CO_2 via diffusion is facilitated by CA-harboring NADPH dehydrogenase (NDH) complexes on the thylakoid and plasma membranes that convert the incoming CO_2 to HCO_3^-:

$$CO_2 + H_2O \leftrightarrows H^+ + HCO_3^- \quad (9)$$

Figure 2. The photosynthetic machinery in cyanobacteria. Photosynthetic electron transport and ATP synthesis in thylakoid membranes. Modified from Jansson *et al.* [23].

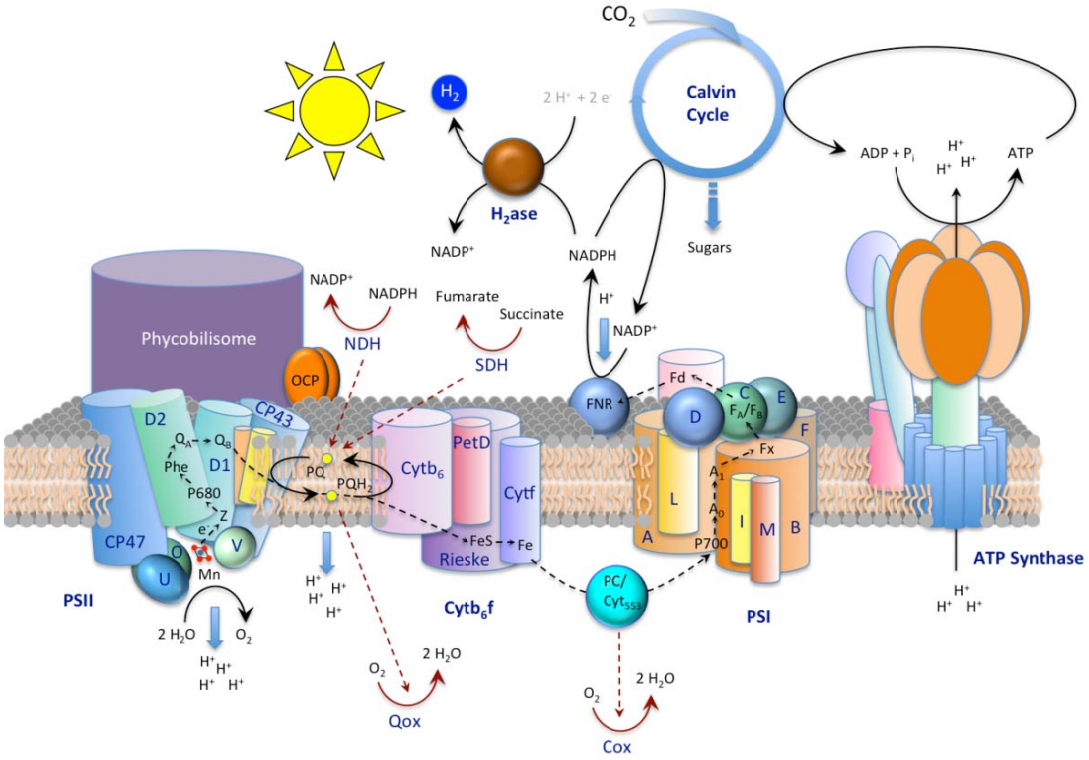
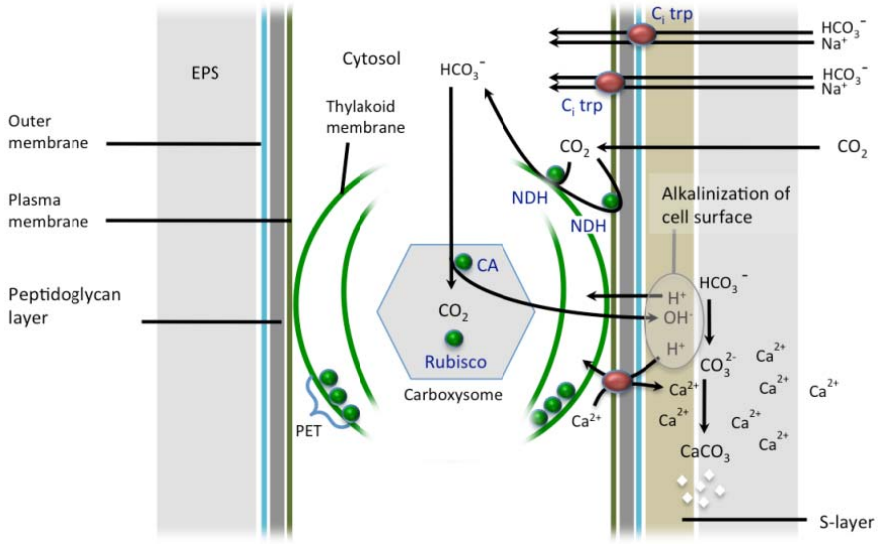


Figure 3. Model of the CO_2-concentrating mechanism (CCM) and calcification in a cyanobacterial cell. Modified from Riding, 2006 [5].



Under these conditions, HCO_3^- is the predominant C_i species taken up by the cells. The cytosolic HCO_3^- subsequently enters the carboxysome where it is converted by CA to CO_2 (Reaction (9)) for the Rubisco reaction, consuming H^+ that subsequently contributes to increasing pH of the solution. At non-limiting C_i concentrations, e.g., in a neutral environment or under high CO_2 partial pressure, the CCM recedes to a basic, constitutive level, characterized by mainly CO_2 uptake [60].

Since most, if not all, cyanobacteria are equipped with a CCM [55] but not all of those exhibit calcifying abilities, particularly in marine environments [62], it is clear that the CCM and calcification are not necessarily linked. This is also illustrated by reports demonstrating cyanobacterial calcification in the absence of photosynthesis (see further Section 4 below).

3.2. Exopolymeric Substances

Exopolymeric substances are important nucleation surfaces for mineralization in many cyanobacteria. Indeed, a large number of bacteria are able to synthesize and secrete extracellular EPS [53]. Such EPS are chiefly of polysaccharidic nature that can either remain covalently linked or loosely attached to the cell surface, or be released into the surrounding environment. The latter is referred to as released polysaccharide substances (RPS) or released EPS (r-EPS) [63,64]. The exopolysaccharides can be classified into two groups, homopolysaccharides (HOPOs) and heteropolysaccharides (HEPOs). The HOPOs are composed of one single type of monosaccharide, and are synthesized from sucrose in a reaction catalyzed by sucrases [65,66]. The HEPOs represent a variety of high-molecular-mass hydrated molecules containing different sugar residues. They are synthesized by the combined activity of various glycosyltransferases (GTs) [66]. HEPOs can also contain acylated amino sugars and noncarbohydrate components such as glycerol, acetate, and lactate. The composition of bacterial EPS varies with the type of microorganism, growth phase, and environmental conditions.

Production of EPS is widespread in cyanobacteria [54]: more than a hundred cyanobacterial strains, belonging to 22 different genera, are known to produce EPS [67]. Many cyanobacteria invest a

considerable amount of their energy in EPS biosynthesis, and the EPS can constitute a substantial proportion of their biomass production (>60% dry weigh) [68]. The cyanobacterial EPS (cyano-EPS) can be divided in two groups, the ones associated with the cell surface, and the RPS. The cell surface-linked EPS is referred to as sheaths (thin, dense film loosely surrounding cells or cell clusters), capsules (thick layer intimately associated with the cell surface), or slimes (mucilaginous material dispersed around the cell) [69–71]. The RPS are soluble portions of polysaccharide material released into the environment. The composition of cyano-EPS exhibits some unusual features compared to EPS from other bacteria [66]: (i) the presence of sulfate groups and uronic acids, which both contribute to the anionic nature of the cyano-EPS, confers a negative charge and a "sticky" behavior. The number and distribution of charged groups are responsible for the ability of the cyano-EPS to chelate cations, notably metal ions; (ii) many cyano-EPS also contain ester-linked acetyl groups, peptides, and deoxysugars like fucose and rhamnose. These groups render the EPS hydrophobic and provide emulsifying properties; (iii) in contrast to EPS synthesized by other bacteria, cyano-EPS are complex HEPO structures, most of them containing six or more different kinds of monosaccharides. This high number of different monosaccharides generates a wide range of linkage types, and is the reason for the high number of possible structures and architectures, and the presence of complex repeating units in the cyano-EPS. Cyano-EPS can also contain polypeptides enriched in different amino acid residues, e.g., Glu- and Asp-rich small proteins.

The physiological roles for cyano-EPS are likely to be numerous. Although little experimental evidence exists for particular functions, it is known that the EPS in a variety of bacteria provide protection against dehydration, phage-induced lysis, phagocytosis, and antibody recognition. The ecological roles of cyano-EPS may include protection against desiccation, salinity, UV-irradiation, oxidative stress, and predation; increase the availability of light, nutrient uptake, N_2 fixation (prevent entry of oxygen in heterocysts), and movement (gliding), and in establishing symbiotic association with other organisms [15,71,72]. While cyano-EPS play an important role in binding and sequestration of necessary trace elements, at the other end of the spectrum, by the same token EPS are crucial for protecting cells against toxic metals. Cyanobacteria are well-known for their capacity to chelate and sequester many metal cations, *i.e.*, Cr^{6+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} in their EPS [69,73–83]. The affinity of cyano-EPS for different metals is strain-dependent, and it differs between EPS and RPS [77].

EPS can play a key role in influencing carbonate precipitation through multiple mechanisms (e.g., [84–86]). For example, negatively charged groups in the EPS can recruit cations such as Ca^{2+} and Mg^{2+}, thereby facilitating carbonate formation. On the other hand, by tightly binding bivalent cations the EPS can inhibit carbonate formations. Also, EPS can favor carbonate precipitation by forming heterogeneous microdomains that support different types of microbial metabolism, and by serving as an energy and carbon source for heterotrophic bacteria [87]. The properties of the EPS also influence the mineralogy of the precipitated $CaCO_3$ crystals [88].

3.3. S-layers

Nucleation of $CaCO_3$ formation by cyanobacteria often occurs on the external surface layer (S-layer) of bacterial cell wall. First demonstrated in 1953 in *Spirillum* species [89], S-layer was subsequently found in hundreds of different species belonging to all major phylogenetic groups of

bacteria and archaea [90,91]. This "two-dimensional array of proteinaceous subunits" covering the entire surface of the cell with highly porous lattice is commonly composed of a single homogeneous protein or glycoprotein species. The protomers, ranging from 25 to 200 kDa [92], are translocated mainly as precursors containing an N-terminal signal peptide [91]. Mature proteins undergo self-assembly on the cell surface, forming 5–20 nm thick lattice with a rather smooth outer and a more corrugated inner surface. The subunits are held together and onto the supporting envelope layer mainly by non-covalent forces including hydrophobic interactions and hydrogen bonds, as well as ionic bonds involving divalent cations or direct interaction of polar groups [91]. *In vitro* self-assembly studies indicated that the information required for this assembly is entirely contained within the individual S-layer subunit [93,94]. However, there is little overall identity for either the primary or secondary structure of the protomers, at least in most bacteria [90]. The S-layer subunits are arranged in oblique (*p*1, *p*2), square (*p*4), or hexagonal (*p*3, *p*6) symmetry with center-to-center spacings of the morphological units varying between 2.5 and 35 nm [95,96]. Well-defined pores with a diameter of 2–8 nm occupy between 30% and 70% of the surface area [95]. With rare exceptions, the isoelectric points (pIs) of S-layer proteins, typically containing a high content of acidic and hydrophobic amino acids, are in the weakly acidic pH range [94,97]. Glycine- and aspartate-rich regions frequent in S-layer proteins are thought to function in calcium ion bridging to the outer membrane [98,99].

The regulatory mechanisms involved in biosynthesis of S-layers are not yet clear. Thus in most organisms studied, the rate of synthesis of S-layer subunits appears to be strictly controlled since only minor amounts of S-layer proteins can be detected in the growth medium. Along with this, a few organisms were reported to produce and shed a considerable excess of these proteins into the surrounding medium [100]. If present, S-layer proteins can comprise up to approximately 15% of the cellular protein [90]. Efficient production and maintenance of S-layers require a considerable amount of resources, attesting to the physiological and evolutionary importance of S-layers in microorganisms. Although no function has yet been defined for all the characterized S-layers, there is a list of functions proposed or determined for specific species examined. This includes determining and maintaining cell shape, cell envelope integrity, cell adhesion and surface recognition, and affecting an efficiency of phagocytosis in Gram-positive bacteria [101,102]. In *Bacillaceae*, S-layers could delineate the periplasmic space and, consequently, delay or control the release of exoenzymes [103,104].

No S-layer is present in the Gram-negative *E.coli*—the most extensively studied bacterial model organism. However, S-layer structures and S-layer-encoding genes were identified in many other Gram-negative bacteria, including species of *Aeromonas*, *Campylobacter*, *Caulobacter*, *Fusobacterium*, *Thermus etc.* [105,106]. Also, more than 60 cultivated strains of cyanobacteria are known to possess an S-layer [98], most of which are of *p*6 lattice symmetry [107]. In the marine *Synechococcus* sp. WH8102, inactivation of the *swmA* gene, encoding the S-layer protein, impacts cell motility [98,108]. However, absence of SwmA had no significant effect on the susceptibility of cells to grazing by the heterotrophic cosmopolitan dinoflagellate *Oxyrrhis marina* [109]. In *Synechococcus* sp. strain GL24, the hexagonal S-layer units were reported to function as discrete crystallization nuclei for fine grain mineral formation [110,111].

4. Cyanobacterial Carbonate Mineralization

As stated in the Introduction, carbonate mineralization by cyanobacteria is of major ecological and geological significance, and it has been the subject of a vast number of laboratory and field investigations. A representative list of published experimental studies is shown in Table 1. Cyanobacteria may catalyze the carbonate mineralization reaction(s) by increasing the saturation state of the environment intimately associated with the cell, with respect to the mineral. This can be done by one or both of two means [61]: metabolic activity altering a pH of the environment and passive and/or active ion concentration. The photosynthetic electron transport in the thylakoids and the CA activity in the carboxysome (Reaction (8)) both consume cytosolic H^+, resulting in a net increase of OH^- in the cytosol. Neutralization of this imbalance, e.g., by the activity of a Ca^{2+}/H^+ antiport, generates an alkaline microenvironment on the outer cell surface. The alkaline pH shifts the equilibria of the bicarbonate buffer system (Reactions (2) and (3)) to the right and generates localized regions of increased CO_3^{2-} concentrations at the cell exterior (Figure 3). Recruitment of Ca^{2+} to the cell surface occurs from the surrounding medium and also via the export of Ca^{2+} through the Ca^{2+}/H^+ translocator. A second mechanism by which cyanobacteria can catalyze carbonate precipitation is by the presence of ordered Ca^{2+}/Mg^{2+}-binding groups on the cell surface [6,12], e.g., glutamate and aspartate residues, or carboxylates and sulfonates. Those groups serve as nucleation sites for initiation of the $CaCO_3$ precipitation.

Table 1. Examples of experimental laboratory- and field-based studies analyzing carbonate precipitation mediated by cyanobacterial cultures and communities. Abbreviations: Ara, aragonite ($CaCO_3$); ACC, amorphous $CaCO_3$; Cc, calcite ($CaCO_3$), Dol, dolomite ($CaMg(CO_3)_2$); Dyp, Dypingite ($Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O$); hMag, Hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$); Mg-Cal ($Mg_xCa_{1-x}CO_3$), magnesium calcite; ND, not determined.

Species	Culture conditions	Mineral	Ref.
Synechococcus PCC 8806, *Synechococcus* PCC 8807	Artificial seawater (ASNIII)	ND	[112]
Synechococcus, *Planktothrix*	Freshwater medium (BG11)	Cc	[113]
Synechococcus PCC 7942	$NaHCO_3$ + $CaCl_2$ solutions	Cc	[114]
Synechococcus PCC 7942	Freshwater medium (Z/10)	ACC, Ara, Cc	[115–117]
Trichodesmium erythraeum IMS101	Artificial YBCII based seawater	Ara	[118]
Artificial cyanobacterial mat incl. *Calothrix*, *Phormidium*, and *Pseudanabaena* spp.	Seawater	Mg-Cc, Ara	[119,120]
Major species	**Environmental conditions**	**Mineral**	**Ref.**
Synechococcus GL24	Meromictic lake	Ara	[121]
Pleurocapsa group	Soda lake	Ara	[122]
Phormidium spp.	Seawater lakes	Mg-Cc	[123]
Phormidium cf. *crosbyanum*, *Phormidium* sp. TK1, *Schizothrix* sp.	Seawater	ND	[124]

Table 1. *Cont.*

Major species	Environmental conditions	Mineral	Ref.
Coccoid and filamentous cyanobacteria incl. *Rivularia* type	Fossil and active tufa formations associated with freshwater springs, waterfall, and wet areas	Cc, Ara	[125]
Dichothrix spp.	Seawater	Cc, Ara	[9]
Rivularia haematites	Calcareous streams and freshwater lake	ND	[126]
Homoeothrix crustacean	Calcareous stream	Cc	[127]
Lyngbya sp.	Alkaline wetland	Dyp, Ara	[13]
Coccoid and filamentous cyanobacteria incl. Nostocales, Chroococcales, Oscillatoriales, and Pleurocapsales spp.	Alkaline brackish caldera lake	hMag, Ara	[128]
Diatoms and filamentoud cyanobacteria incl. Lyngbya and Gloeocapsa spp.	Alkaline lake	hMag	[129,130]

Thus EPS, possessing both the highly hydrated nature facilitating ion accumulation and concentration [131] and the negatively charged residues [121], is frequently found to be linked to the mineralization processes [8,84,116,132]. Cyanobacterial S-layers, providing ordered ion-binding groups and frequently being the outermost defining layer of the cell, was also shown to undergo mineralization[110,111]. Furthermore, the encrusted patches of S-layer were reported to be shed by cyanobacteria, probably in attempt to prevent total encasement in mineral and subsequent death of the cell [18,121]. With calcium carbonates comprising the major array of minerals associated with cyanobacteria, relatively few studies reported precipitation of magnesium carbonates (Table 1). In most cases, biologically-induced formation of magnesium carbonates was confined to Mg-rich alkaline environments. Hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) was detected in stromatolite-like formations of the Lake Salda, Turkey, and the deposition mineral was mediated by a microflora of diatoms and cyanobacteria [129,130]. Dypingite ($Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O$) was reported to be produced in mats of cyanobacteria enriched from alkaline wetland near Atlin, British Colombia [13]. Precipitation of dolomite, one of the most abundant sedimentary carbonate minerals, was shown to be mainly facilitated by metabolic activities of methanogens and sulfur reducing bacteria actively increasing alkalinity and/or pH of the environment (e.g., [133–138]). The capability of cyanobacteria to induce dolomite formation remains to be clarified.

We don't yet know the physiological or biochemical function(s) (if any) of calcification in cyanobacteria, although some possibilities have been suggested [61]. Calcification may provide a means to buffer the pH rise generated by the CCM machinery [139]. Also, since calcification will remove Ca^{2+} from chemical equilibria and may offer a means to sustain an active efflux of Ca^{2+} via the Ca^{2+}/H^+ translocator, it generates a H^+ gradient that may enhance nutrient and HCO_3^- uptake [140,141]. Another benefit of carbonate precipitation may be to prevent inhibition of the HCO_3^- transporters by CO_3^{2-} ions [141,142], or to provide cyanobacteria with a calcerous shell as a protective layer against

excessive light exposure [143]. In a Ca^{2+}-rich environment, calcification may also serve as a process to remove toxic levels of Ca^{2+} ions [144]. Finally, it should be noted that microbial calcification in aquatic environments results in release of CO_2 (Reaction (4); however, see Section 5 below), so it also is possible that cyanobacteria benefit from calcification by an increase in availability of CO_2 for Rubisco. In this context it is pertinent to consider the suggestion by Martinez *et al.* [113] that cyanobacteria need a protective mechanism against carbonate precipitation on the cell exterior. They argued that precipitation of carbonate minerals on the cell surface would prevent photosynthesis by interfering with HCO_3^- uptake. Such a view can be taken to mean that cyanobacterial carbonate mineralization is simply a consequence of the environment. Although this may be true, the notion that a calcified cyanobacterial cell surface is detrimental to photosynthesis or cell survival is not substantiated. For example, a layer of calcified EPS may fully or partly detach from the cell, and for the freshwater cyanobacterium *Synechococcus* sp. GL24, which contains an S-layer, it was proposed that the calcified S-layer is shed, followed by synthesis of a nascent S-layer [18,121]. The protective mechanism invoked by Martinez *et al.* hinges on a positive cell surface charge at alkaline pH, as determined by Zeta-potential (ζ-potential) measurements, thereby impeding recruitment of Ca^{2+} ions to the cell surface [113]. These findings differ from ζ-potential measurements of cyanobacteria such as the marine *Synechococcus* sp. PCC 8806 (Kamennaya, N.A. *et al*. unpublished [145] and the freshwater strain *S. leopoliensis* [117], which showed negative surface charge at circumneutral or alkaline pH and a shift toward less negative charge upon binding of Ca^{2+}. Similar results were obtained by Dittrich and Sibler for freshwater *Synechococcus* sp. [146] .The strains used by Martinez and coworkers are only identified as *Synechococcus* sp. and *Planktothrix* sp., and we don't know details about their cell surface properties, or to what extent they are representative of other cyanobacteria.

It is clear from the above that the process of cyanobacterial calcification differs between different environmental conditions. Moreover, the onset and mechanistic details of calcification are also subject to taxonomic control. As an example, carbonate minerals produced by coccoid cyanobacteria are often found in the EPS between cells, whereas in filamentous strains mineralization results in the formation of a tube surrounding the trichome (filament) [1]. Another example is the recent finding of a cyanobacterial strain that produces intracellular carbonate minerals [147] (see also Section 5 below).

Since no enzymatic process is directly involved in carbonate mineralization, the conventional biochemistry tool kit remains inapplicable to studies of calcification in cyanobacteria. Dynamics of $CaCO_3$ precipitation in cultures of cyanobacteria can be deduced from temporal shifts in (i) Ca^{2+} concentrations, using inductively coupled plasma atomic/optical emission spectroscopy (ICP-A/OES) [13,83,110,112] atomic absorption spectroscopy [16,129,148,149], or Ca^{2+} ion-specific electrodes [16,132] and (ii) carbonate chemistry of the solution. Speciation and concentrations of carbonate species in equilibrium from any two of the species measured (pH, total DIC, and total alkalinity) can be calculated with computer programs, e.g., CO_2calc [150], CO_2Sys [151], PHREEQE [152] and others. The presence of micrometer-scale crystals can be directly detected with bright-field [87] and cross-polarized microscopy [84]. Autofluorescence from cyanobacteria coupled with biorefringence from crystals reveals space relations between cells and crystals. Furthermore, epifluorescent microscopy can be used to detect Ca^{2+}-chelating fluorophores, e.g., calcein and tetracycline [36]. Electron microscopy, e.g., scanning (SEM) [13,31,36,38,87,88,129] and transmission (TEM) [31,110,111,116] electron microscopies, provides details about the morphology, thickness and localization of the

precipitates. Electron microscopy-coupled Energy Dispersive Spectrometry (EDS) [36,87,88,110,111,144] gives information about elemental composition of the precipitate and links structural characteristics of the crystalline matter to its chemical composition. X-ray Diffraction (XRD) [13,87,116,129,139,144] and Raman microscopy reveal the type of non-amorphous crystalline polymorphs in the precipitate based on the crystal symmetry, e.g., distinguishing between rhombohedral calcite and orthorhombic aragonite. Relative abundance of stable isotopes (e.g., C, O) in carbonate precipitates is detected with mass spectrometry [9,13,62,129]. Two synchrotron based methods—Near Edge X-ray Absorption Fine Structure (NEXAFS) [116] and Fourier Transform Infrared (FTIR) [83,88] spectroscopy, can detect unique absorptions indicative of different forms of carbonates. Finally, Time-of-Flight Secondary Mass Spectrometry (ToF-SIMS), a sensitive surface method, can be applied to detect calcification in its early stages (Kamennaya, N.A. *et al*., unpublished [145]).

5. Practical Implications of Cyanobacterial Carbonate Mineralization

The dual capture of CO_2 in cyanobacteria, into one organic form as biomass, and one inorganic form, with formation and precipitation of carbonate minerals (Figure 1), leads to several aspects of potential practical importance for a wide range of research areas, including paleontology, geology, ecology, and climate change.

(1) As a general phenomenon, microbial calcification in a natural setting, such as the oceans, is considered a net source for atmospheric CO_2. However, whether oceanic cyanobacterial communities provide a net source or sink for CO_2 depends on the R_{OI} (see Introduction); at values >0.6, the system incorporates enough CO_2 into biomass for it to function as a net sink, whereas a value <0.6 indicates that the system is a net source [153]. Additionally, field and laboratory measurements of systems with cyanobacteria or other calcifying organisms showed released CO_2/precipitated carbonates ratios (Ψ) of 0.1–0.006, which starkly deviate from the theoretically calculated Ψ of 0.6 in seawater (no relation to the threshold value for R_{OI}) and close to 1.0 in freshwater [154]. Further, laboratory and field investigations of microalgal blooms indicated that microbial calcification can act as a CO_2 sink [139,155]. It was suggested that possible explanations for this apparent discrepancy between theoretical and experimental results were (i) recapture of the released CO_2 by photosynthesis and (ii) enhanced sedimentation of both organic and inorganic carbon. A thorough understanding of the organic and inorganic carbon fluxes in different cyanobacterial communities, the carbonate mineralization process, the interplay between calcification and photosynthesis, and how this interaction may be influenced by climate change is critical for correct calculations of the global carbon budget under present and predicted climatic regimes.

(2) Carbonate mineralization by cyanobacteria and other microorganisms can also be biogeochemically coupled to weathering of silicate minerals. Biologically accelerated weathering (BAW) of silicates occurs both chemically and mechanically via production by microorganisms of extracellular enzymes, chelates, simple and complex organic acids, alcohols, and EPS [156–161]. The combined cyanobacterial activities of accelerated silicate weathering and carbonate mineralization may therefore provide an important sink for atmospheric CO_2 in terrestrial systems [162] (see bullet 5 below).

(3) Detailed knowledge about the mechanisms and environmental requirements (e.g., optimal nutrient and light availability, maximal allowable concentration of mineralization inhibitors, saturation state of the solution with respect to the minerals precipitated) for cyanobacterial calcification is crucial for our ability to reconstruct paleoenvironements. For example, the question arises as to what extent CO_2 concentrations during Earth's history, with a range from present atmospheric level (PAL) to 30 times PAL in the Phanerozoic [6] and up to 80–600 times PAL in the Precambrian [163,164], have been permissible with cyanobacterial calcification. Similarly, as we learn more about cyanobacterial carbonate mineralization under high CO_2 conditions, we may be able to complement and/or modify interpretations that explain the presence of fossil records for calcareous cyanobacteria from the early Phanerozoic (Cambrian) [5,19], or for aragonite structures from the Precambrian [165].

The recent isolation of cyanobacteria that form intracellular carbonates [147], morphologically and chemically resembling those of a long-known but uncultured giant sulfur bacterium, *Achromatium oxaliferum* [166], opens the door to a new direction in studies on carbonate mineralization in cyanobacteria, and presents a fascinating, although challenging, task for those involved in patching up our paleontological landscape [147,167].

(4) The capacity of cyanobacteria to thrive in high CO_2 concentrations makes them an attractive system for beneficial recycling of CO_2 from point sources such as coal-fired power plants via biofuel synthesis [168]. In this regard, it becomes important to further our understanding of the interactions between the two modes of CO_2 utilization. For example, for cyanobacteria-based biofuel production, it is desirable to funnel as much of the captured CO_2 as possible to biofuel synthesis at the expense of carbonate formations. However, at the same time, we may want to consider the possibility that the carbonate mineralization process confers metabolic benefits, e.g., by providing extra CO_2 for photosynthesis, or by generating H^+ to facilitate nutrient uptake [61,141].

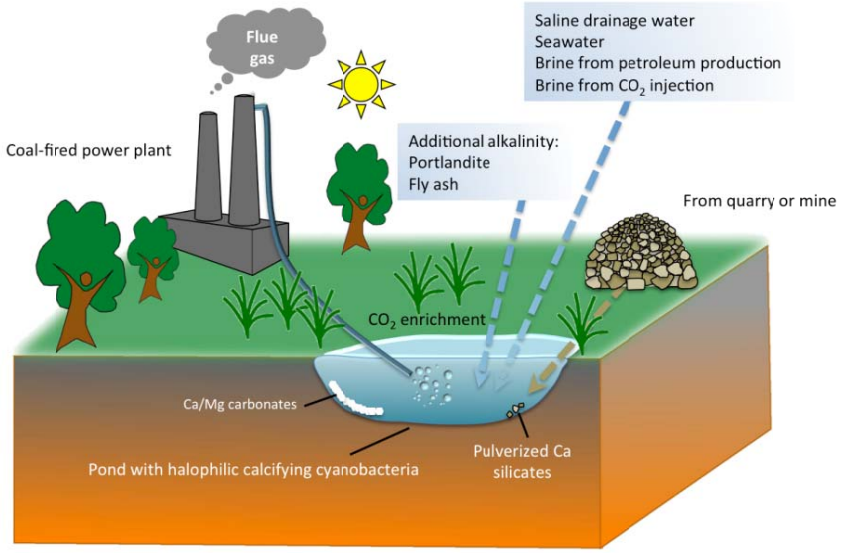
(5) Finally, exploitation of biologically induced carbonate mineralization may offer the potential to engineer systems whereby cyanobacteria could act as solar-powered catalysts in biological CCS, e.g., by capturing CO_2 in flue gas from coal-fired power plants and converting it to carbonate salts for storage, once a suitable source of alkalinity is present. This concept is not novel. Calculations by Lee and colleagues [112,169], based on whiting events and microcosm experiments, suggested that calcification by the marine cyanobacterium *Synechococcus* sp. PCC 8806 over an area of 70 km^2 could account for around 2.5 MT $CaCO_3$ per year, which translates to half of the CO_2 produced by a 500 MW power plant. From laboratory experiments, Yates and Robbins [139] concluded that a single bloom (3.2×10^9 L) of the eukaryotic microalga *Nannochloris attomus* could precipitate 1.6×10^3 T of $CaCO_3$ in 12 h. The same authors also studied marine whiting events on the Bahama Bank and concluded that blooms of cyanobacteria and green algae could sequester close to 5700 $T \cdot C \cdot yr^{-1}$ as $CaCO_3$ [170]. The potential role of cyanobacteria in carbon sequestration by carbonate mineralization linked to BAW has been discussed by Ferris *et al.* [162] and was also proposed at a 2003 National Academy of Sciences workshop [171]. A similar approach using coccolithophorid algae was evaluated in a DOE-funded project [172]. The possibility of using consortia of cyanobacteria, microalgae and heterotrophic bacteria for simultaneous biomass production and CCS via carbonate mineralization and BAW of tailings was demonstrated by Power and colleagues for CO_2 emissions from the Diavik Diamond Mine, Canada and the Mt Keith Nickel Mine, Western Australia. [173] and from an asbestos mine in Canada [174]. They concluded that ponds with the microbial community would be able to produce

carbonates in the range of 23 to 841 $T \cdot yr^{-1}$ for the Diavik site, and 6520 to 52,700 $T \cdot yr^{-1}$ for Mt Keith, requiring 2 and 11 GL of water, respectively, for the two mines.

Several issues need to be addressed to seriously evaluate the possibility for biological CCS via cyanobacterial carbonate mineralization: (i) First and foremost, it is not clear if the alkalinity generated by cyanobacterial metabolism suffices to drive the reaction toward a net CO_2 consumption, particularly at CO_2 levels such as those in flue gas (~5%–15%) when the CCM would be suppressed. If not, additional alkalinity can be provided, e.g., as the mineral portlandite ($Ca(OH)_2$) or as fly ash, *i.e.*, silicate-containing residues from chimneys of coal-fired power plants with a strong pH buffering capacity. Alternatively, and as all added to above, hydrolysis of silicate minerals by microbially accelerated weathering may be used to drive the pH up, simultaneously releasing cations for carbonate mineral precipitation. Silicate minerals offer an abundant supply of calcium; calcium and magnesium silicates are plentiful in the Earth's crust and, hence, as mentioned above, the potential capacity for sequestration of anthropogenic CO_2 as stable carbonates by accelerated weathering linked to carbonate mineralization is exceptionally large. Important calcium silicates include wollastonite ($CaSiO_3$) and plagioclase feldspars ($(Na,Ca)(Si,Al)_4O_8$ and $CaAl_2Si_2O_8$), which is abundant in mafic and ultramafic rocks. To what extent the cost and logistics of such arrangements would be economically viable is an open question; (ii) an obvious question is what will happen during the course of diurnal light-dark cycles; will formed $CaCO_3$ dissolve, or can the system be constructed such that the $CaCO_3$ is continuously withdrawn for storage; (iii) seawater, saline drainage water, waste brines from desalination or other industrial processes can all serve as ample Ca^{2+} sources. However, if needed, Ca^{2+} can also be supplied as porlandite, fly ash, which may contain up to 20% CaO, gypsum ($CaSO_4 \cdot 2\ H_2O$), or silicate minerals. Again, cost and logistics need to be considered; (iv) To be of industrial relevance, the scale of any CCS operation with ponds of calcifying cyanobacteria is likely to command a large area. Whether such a demand can be satisfied by marginal land or other non-arable areas remains to be found out. The results presented by Lee *et al*., Yates and Robbins, and Power *et al*. [112,139,169,173] discussed above give some indications on the ecological footprint required. As more data become available, it will be possible to make and refine models where different inputs, such as cyanobacterial species or consortia, sources of alkalinity, Ca^{2+} and water, and pond size, are entered.

Despite these many outstanding questions, we finish with a futuristic scenario describing carbonate mineralization by halophilic cyanobacteria as a means for biological CCS (Figure 4): Many cyanobacteria are halophilic and thrive in saline and hypersaline waters. Such waters include seawater, saline drainage water, waste brines from desalination or other industrial processes, and water produced from the oil and gas industry, or from geological CCS. Apart from delivering the water volumes for cyanobacterial cultivation, saline waters also provide calcium for the calcification process. The levels of Ca^{2+} in saline drainage water or waste brines are usually very high. Other Ca^{2+} sources include gypsum, portlandite and fly ash. The ability of using diverse water and calcium sources for cyanobacterial calcification improves the likelihood of co-locating power plants and calcification sites. Portlandite or fly ash can also be added to boost alkalinity. Alternatively, hydrolysis of silicate minerals may be used to drive the pH up, simultaneously releasing cations for carbonate mineral precipitation.

Figure 4. Pictorial rendition of utilizing halophilic calcifying cyanobacteria for biological CCS of point-source CO_2.



6. Conclusions

In this review we have described our current understanding of cyanobacterial carbonate mineralization. We have discussed the metabolic, physiological and structural features of cyanobacteria that may be involved in the reactions leading to mineral formation and precipitation, presented a model of cyanobacterial calcification, and, finally, considered some practical applications pointing to the importance of cyanobacterial carbonate mineralization. As should be obvious from the presentation, much further research is needed to provide us with the necessary insight in cyanobacterial carbonate mineralization to fully appreciate its role in the global carbon cycling, to predict how this role will be affected by climate change, to improve our interpretation of paleontological data, and to exploit cyanobacterial carbonate mineralization for biological CCS. For example, we need to find out if, how, and to what extent calcification benefits cyanobacterial cells or communities, and the biotic and abiotic processes that promote carbonate mineralization in cyanobacterial populations. Moreover, to exploit carbonate mineralization, e.g., for biological CCS, it becomes important to carry out laboratory experiments and scaled-up trials to select suitable strains and environmental conditions, e.g., to provide required alkalinity. The possibility to genetically engineer cyanobacteria for improved calcification and formation of magnesium-rich carbonates should also be considered. Finally, it is worth noting that the information we gain from understanding the processes involved in cyanobacterial carbonate mineralization could be used to develop and implement biomimetic systems for CCS.

Although this is a review about cyanobacterial carbonate mineralization, it is worth repeating that calcification is a widespread phenomenon among microorganisms. Thus much of what is discussed in Section 5 is applicable also to eukaryotic microalgae, *Bacillus*, *Pseudomonas*, and *Vibrio* spp., and sulfate-reducing bacteria. However, cyanobacteria occupy a distinctive position in the context of carbonate mineralization by virtue of their early and extensive fossil records, their photoautotrophic lifestyle, their importance in shaping the course of evolution and ecological change throughout Earth's history, their tolerance to high CO_2 levels, and their enormous (and unexplored) diversity.

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