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Biomineralization in cement and concrete research

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Abstract

Biomineralization refers to the biological processes through which living organisms produce minerals. In recent years, biomineralizing microorganisms have been used to stabilize soil or to impart a self-healing or self-sealing mechanism to damaged cement and concrete materials. However, applications of biominerals in cement and concrete research can extend far beyond these applications. This article focuses on the biomineralization of calcium carbonate ($CaCO_3$) and silicon dioxide (SiO_2) and their past, present, and future potential applications in cement and concrete research. First, we review the mechanisms of $CaCO_3$ and SiO_2 biomineralization and the micro- and macroorganisms involved in their production. Second, we showcase the wide array of biomineral architectures, with an explicit focus on $CaCO_3$ polymorphs and SiO_2 morphologies found in nature. Third, we briefly summarize previous applications of $CaCO_3$ and SiO_2 biomineralization in cement and concrete research. Finally, we discuss emerging applications of biominerals in cement and concrete research, including mineral admixtures or raw meal for portland cement production, as well as other applications that extend beyond self-healing.

Keywords: Biomineralization; Cement; Concrete; Calcium carbonate ($CaCO_3$); Silicon dioxide (SiO_2)

1 Introduction

Biomineralization is the biological process by which living organisms produce minerals. By mass, calcium carbonate ($CaCO_3$) is the most abundant biomineral found in nature [1]. Microorganisms, such as bacteria [2], fungi [3], and coccolithophores [4], and macroorganisms, such as mollusks [5] and coral [6], are well known to biomineralize $CaCO_3$. The biomineralization of silicon dioxide (*i.e.*, silica) (SiO_2) [7–10], calcium phosphate (*i.e.*, apatite) [11,12], magnesium hydroxide (*i.e.*, brucite) ($Mg(OH)_2$) [13–15], iron oxides (*e.g.*, hematite, magnetite) (Fe_2O_3) [16,17], and aluminum oxide (*i.e.*, alumina) (Al_2O_3) [7,18,19] also occurs in a multitude of micro- and macroorganisms, such as diatoms [9], bacteria [17], mollusks [5] and other higher-level organisms [20–23].

$CaCO_3$ and SiO_2 biomineralization has been applied in select applications relevant to the field of cement and concrete research. These areas include soil stabilization [24], beneficiation of recycled concrete aggregates [25] and recycled plastic aggregates [26], living building materials [27], and self-healing [2,28] or self-sealing [29,30] concrete. While most applications concern $CaCO_3$ biomineralization, one study [31] recently showed that biomineralized SiO_2 from diatoms exhibit moderate to high pozzolanic reactivity, indicating their suitability as a supplementary cementitious material (SCM). Despite the prevalence of $CaCO_3$ and SiO_2 biomineralization in nature, the applications of biomineralization in cement and concrete research are predominantly limited to these few examples.

In this work, we elucidate how biomineralization can be leveraged to further the development of sustainable and resilient cementitious materials. First, we outline the main mechanisms of biomineralization, with a focus on the two most common biominerals produced by living organisms, $CaCO_3$ and SiO_2. Second, we showcase the wide variety of $CaCO_3$ polymorphs and SiO_2 morphologies and discuss the potential for their physical and chemical tunability. Finally, we highlight past examples and future opportunities for direct applications of these materials in cement and concrete research. Lastly, we highlight the challenges that will need to be addressed to translate biomineralization technologies from the benchtop to a commercially viable scale.

2 Mechanisms of $CaCO_3$ and SiO_2 Biomineralization

2.1 $CaCO_3$ Biomineralization

$CaCO_3$ biomineralization is mediated by the metabolic activity of micro- and macroorganisms. In this section, we review four of the most common mechanisms of $CaCO_3$ mineralization: urea hydrolysis, photosynthesis, sulfate reduction, and protein-mediated biomineralization. Most involve the production of carbonic acid, which is further decomposed into the bicarbonate anion (HCO_3^{2-}) that can subsequently

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react with free calcium (Ca^{2+}) if it is present in the surrounding media. The result is the formation of biologically architected $CaCO_3$ with properties that can be tuned by tailoring the mineralization kinetics *via* controlling the metabolic activities of the organism [32,33].

2.1.1 Urea hydrolysis

The urea hydrolysis mechanism of $CaCO_3$ biomineralization is well understood [3,34–37]. $CaCO_3$ biomineralization *via* urea hydrolysis is a vital process for bacteria, such as *Sporosarcina pasteurii* [38], and fungi, such as *Fusarium cerealis* [3]. These organisms employ urea hydrolysis to break down urea so that it may be consumed as a carbon source in exchange for energy. These organisms can biomineralize and produce $CaCO_3$ if Ca^{2+} ions are present in the media. Without Ca^{2+}, however, these organisms will not biomineralize.

The urea hydrolysis mechanism of $CaCO_3$ biomineralization is as follows:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{urease\ enzyme} H_2CO_3 + 2NH_3 \quad (1)$$

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

$$2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^- \quad (3)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (4)$$

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

The biomineralization reaction is catalyzed by the metabolic production of the urease enzyme. In the presence of urea, urease will catalyze the decomposition of urea into carbonic acid and ammonia. The carbonic acid will subsequently dissociate into bicarbonate and hydrogen ions, which lowers the pH. However, the ammonia will react with water to form ammonium and hydroxide ions, which increases the pH. The hydroxide and bicarbonate anions then react to form carbonate anions and water. The former can react with free Ca^{2+} to yield precipitated $CaCO_3$. Images of biomineralized $CaCO_3$ through urea hydrolysis are shown in Figure 1(a)-(c).

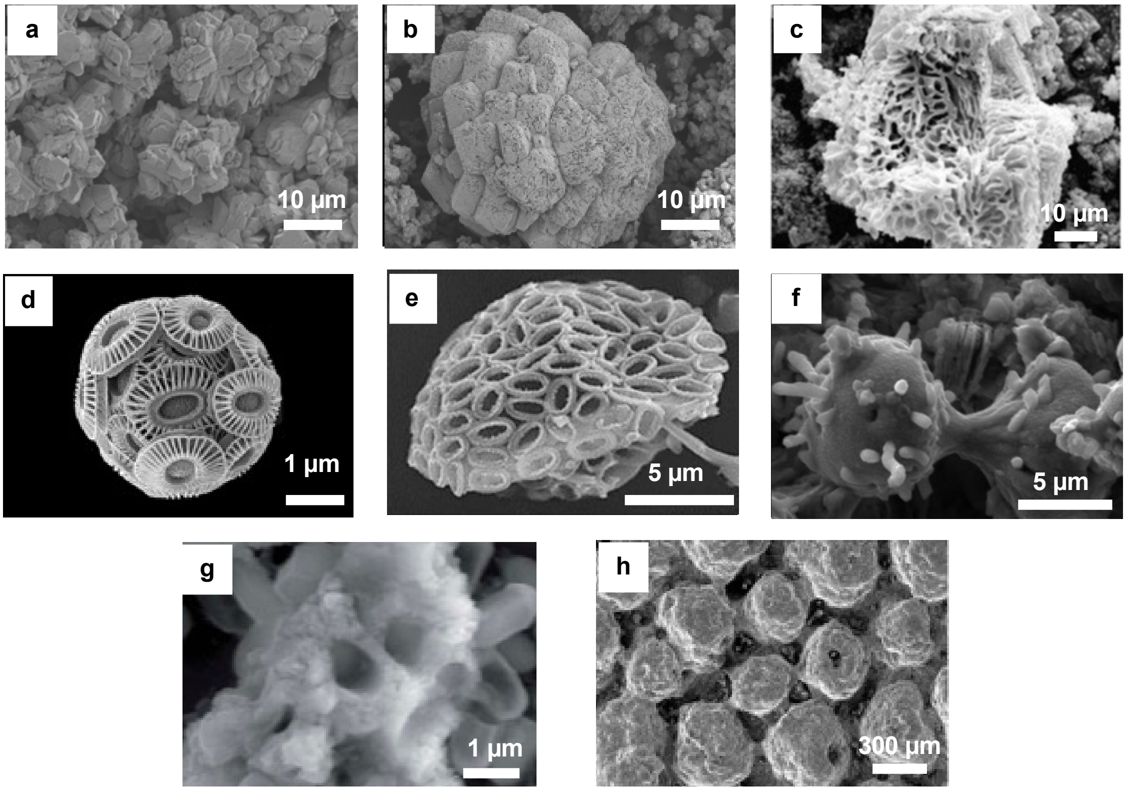

Figure 1. Biomineralized $CaCO_3$ produced via (a-c) urea hydrolysis [(a) S. pasteurii (Heveran et al. [32], CC BY 4.0) (b) Escherichia coli (Heveran et al. [32], CC BY 4.0), (c) Bacillus lentus (Wei et al. [39], CC-BY-NC), (d-e) photosynthesis [(d) Emiliana huxleyi (Neukermans et al. [40], CC-BY), (e) Pleurochrysis dentata (Chen et al. [41], CC-BY-4.0), (f) sulfate reduction [Desulfovibrio bizertensis (Lin et al. [42], copyright 2018 Elsevier), and (g-h) protein-mediated biomineralization [(g) bacterial precipitation Bacillus subtilis (Liu et al.[43], CC-BY-NC 3.0), (h) Sphaerovum erbeni eggshells (Grellet-Tinner et al. [44] copyright 2012 SEPM).

From a cement and concrete research perspective, advantages of $CaCO_3$ biomineralization *via* urea hydrolysis include the autonomous production of higher quantities of biomineralized $CaCO_3$ compared to other $CaCO_3$ biomineralization mechanisms on a per-volume basis (*e.g.*,1.6-9.8 mg/L from ureolysis [45] compared to 0.8-2.2 mg/mL from photosynthesis [46]). In addition, the high-pH tolerance of spore-forming, biomineralizing microorganism species (*e.g.*, *Bacillus sphaericus*, *Phoma herbarum, Bacillus subtilis, Sporosarcina pasteurii*) [2,3] are a notable advantage, given the high pH of the pore solution within hydrated cement paste. However, disadvantages of urea hydrolysis include the production of ammonia and ammonium as byproducts of $CaCO_3$ biomineralization and the need to add an exogenous source of Ca^{2+} (*e.g.*, $CaCl_2$) to the media, which can then lead to the addition of undesirable byproducts (*e.g.*, chloride anions) to the cementitious matrix [38]. In addition, the cost and availability of urea-rich media has been noted as another significant challenge impeding widespread adoption. Nevertheless, $CaCO_3$ biomineralization *via* urea hydrolysis has been widely employed in cement and concrete research because of the potential benefits that $CaCO_3$ biomineralization can impart to cementitious materials (see Section 4).

2.1.2 Photosynthesis

By definition, photosynthesis is the metabolic process by which organisms produce energy and mass *via* biochemical reactions involving light and carbon dioxide (CO_2) [47]. Photosynthetic microorganisms, including certain strains of cyanobacteria [48] and phytoplankton (*e.g.*, coccolithophores) [4], and macroorganisms, such as calcareous macroalgae [49], produce $CaCO_3$ through photosynthesis-driven biomineralization. Coccolithophores alone are responsible for sequestering and storing ~ 1.5-5.9 $GtCO_2$/year (~ 0.4-1.6 GtC/year) as biomineralized $CaCO_3$ [50], which equates to ~ 3.4-13.4 Gt $CaCO_3$. Photosynthesis-driven $CaCO_3$ biomineralization is mediated by the production of carbonic anhydrase (CA), an enzyme that catalyzes the rapid conversion of CO_2 into carbonic acid [51].

The photosynthesis mechanism of $CaCO_3$ biomineralization is as follows:

$$CO_2 + H_2O \xrightarrow{CA\ Enzyme} H_2CO_3 \quad (6)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad (7)$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (8)$$

While these reactions represent the most prominent pathway for photosynthesis-driven $CaCO_3$ biomineralization [47], carbonic anhydrase (CA) is known to facilitate other $CaCO_3$ biomineralization pathways in which it forms metal complexes with zinc (Zn^{2+}) and Ca^{2+} to yield bicarbonate and, ultimately, biomineralized $CaCO_3$ [52]:

$$CA - Zn - H_2O \leftrightarrow CA - Zn - OH^- + H^+ \quad (9)$$

$$CA - Zn - OH^- + CO_2 + H_2O \leftrightarrow CA - Zn - H_2O + HCO_3^- \quad (10)$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (11)$$

Photosynthesis-driven $CaCO_3$ biomineralization has two distinct advantages. First, the economics of $CaCO_3$ biomineralization *via* photosynthesis are advantageous. Most photosynthetic species that biomineralize $CaCO_3$ are marine micro- and macroorganisms, which require only sunlight, seawater, and CO_2. Second, photosynthesis-driven $CaCO_3$ biomineralization is a form of direct CO_2 capture and storage. CO_2 dissolves into the media with assistance from carbonic anhydrase. This CO_2 is converted to inorganic biominerals (*i.e.*, $CaCO_3$) and organic molecules (*e.g.*, lipids, proteins, carbohydrates) that comprise the micro- and macroorganism cell bodies. Disadvantages of $CaCO_3$ biomineralization *via* photosynthesis include lower quantities of biominerals per volume basis and the pH sensitivity of biomineralizing strains of photosynthetic microorganisms, which makes them less suitable for direct incorporation into concrete mixtures. Instead, researchers have found other means to leverage photosynthesis-driven biomineralization. For example, Murphy *et al.*, explored the use of $CaCO_3$ derived from coccolithophores, which are biomineralizing photosynthetic microalgae, as a nucleating agent in portland limestone cement (PLC) paste [53]. Researchers have also used photosynthesis-driven biomineralization to produce enzymatic [54] or living building materials [31] (see Section 4). Images of biomineralized $CaCO_3$ through photosynthesis are also shown in Figure 1(d)-(e).

2.1.3 Sulfate Reduction

Sulfate reduction is an intermediate step for energy production in some species of anaerobic bacteria, including *Desulfovibrio bizertensis* [55] and *Desulfomicrobium baculatum* [56]. While biomineralization *via* sulfate reduction is less studied than urea hydrolysis or photosynthesis, the mechanism of biomineralization is similar in that the formation of carbonic acid is key from a biochemical standpoint.

There are two sulfate reduction mechanisms of $CaCO_3$ biomineralization. The first involves the dissociation of calcium sulfate, where the cell produces formaldehyde (*i.e.*, CH_2O) and converts it to sulfuric acid (H_2S), bicarbonate, CO_2 and water as part of the intermediate step [47,57,58]:

$$CaSO_4 + 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \quad (12)$$

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- + CO_2 + H_2O \quad (13)$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (14)$$

Sulfate reducing organisms require an exogenous source of calcium sulfate in the medium to nucleate an external layer of

$CaCO_3$ directly on its cell membrane, which then leads to subsequent precipitation and growth of $CaCO_3$ from the medium onto the cell-templated $CaCO_3$ [22].

The second mechanism is similar to the first, except that it involves the metabolic production of calcium sulfate rather than relying on an external source:

$$CaSO_4 + 2CH_2O \rightarrow CaS + 2CO_2 + 2H_2O \quad (15)$$

$$CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S \quad (16)$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (17)$$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \quad (18)$$

In terms of its utility, sulfate reduction is less advantageous than urea hydrolysis or photosynthesis because it necessitates the production of formaldehyde and H_2S. Additionally, sulfate reduction has limited potential in self-healing concrete applications because the reaction itself decreases the pH [59]. Interestingly, some sulfate-reducing organisms can be found in highly alkaline environments [59,60], which is why the mechanism could still be investigated for different cement and concrete applications in which the H_2S can be captured or toxicity is not an issue. An example of $CaCO_3$ biomineralized *via* sulfate reduction is shown in Figure 1(f).

2.1.4 Protein-mediated

Protein-mediated $CaCO_3$ biomineralization is observed in mollusks, crustaceans, and avian eggs [61]. In protein-mediated biomineralization, surface proteins, such as those rich in arginine [62] act as positively charged nucleation sites that facilitate the interactions between CO_3^{2-} and Ca^{2+} present in the surrounding media. The proteins seed amorphous $CaCO_3$ (ACC) minerals that precipitate and grow into larger $CaCO_3$ minerals comprised of ACC or one of the other polymorphs of $CaCO_3$ (*i.e.*, calcite, aragonite, vaterite) (see Section 3). This mechanism has a few distinct advantages in that (1) biomineralizing microorganisms that leverage protein-mediated $CaCO_3$ biomineralization can produce larger quantities of $CaCO_3$ and (2) the kinetics of mineralization and the resultant biomineral architectures could theoretically be tailored by modulating the expression of surface proteins. However, the macroorganisms that leverage this mechanism in nature have a long growth cycle, resulting in limited quantities unless large farms or naturally occurring deposits can overcome such a limitation. In addition, protein-mediated $CaCO_3$ formation *ex vivo* is less characterized when compared to the three prior mechanisms (ureolysis, photosynthesis, and sulfate reduction), where the specific sequence and compounds are less well defined due to the sheer number and variability of protein properties in nature. There is significant work ongoing to define precise mechanistic steps [63-65], which is promising for applying these principles on a larger scale in the future. Figure 1(g)-(h) show images of protein-mediated $CaCO_3$ biomineralization.

2.2 SiO_2 Biomineralization

SiO_2 biomineralization is an integral structure-forming process in sea sponges and diatoms [9,66] (see Figure 2). While the biochemical mechanisms of silica biomineralization are not fully understood at the time of writing [9,67], studies of sea sponges and diatoms have elucidated that the presence of silicic acid in the media is critical for SiO_2 mineralization. Sponges use silicateins (*i.e.*, silica-rich proteins) to template and mineralize silicic acid into spicule structures in a process akin to protein-mediated $CaCO_3$ biomineralization [5,66]. However, the exact SiO_2 biomineralization mechanism in sea sponges is still under investigation [66,68]. On the other hand, SiO_2 biomineralization in diatoms is better understood. Diatoms concentrate silicic acid into silica pools internal to the diatom. The accumulation of silicic acid results in the polycondensation and eventual precipitation of amorphous SiO_2. This precipitation of SiO_2 is aided by polyamines and polysilaffins within the cell. It is hypothesized that the occurrence of positively charged functional groups in both polymers attracts negatively charged silica anions to create the pools, thereby facilitating polycondensation [9,67]. The precipitated SiO_2 forms the basis of the intricate microporous exoskeletons that are characteristic of most diatom species (see Figure 2c).

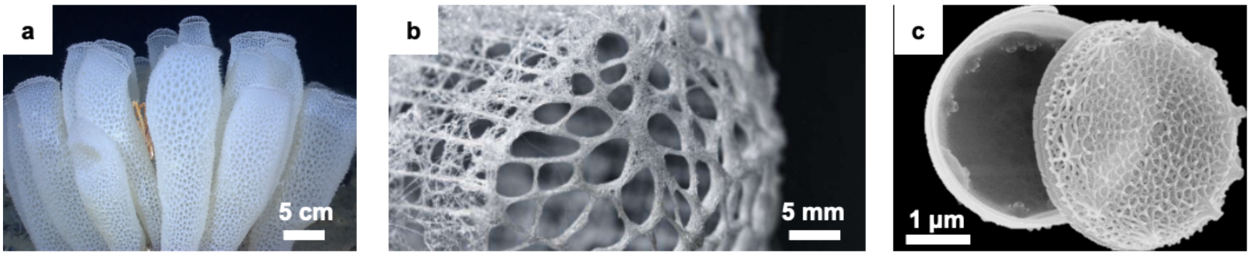

Figure 2. SiO_2 biomineralization in sea sponge *Euplectella aspergillum* at (a) centimeter scale (Imbler [69], within permissions by NOAA) and (b) millimeter scale (Monn [70], CC-BY-ND), and (c) the diatom species *Thalassiosira pseudonana* (Piccinetti et al. [71] CC-BY-4.0).

In terms of advantages, most microorganisms that biomineralize SiO_2 are photosynthetic and found in marine environments, which minimizes their media and growth requirements to sunlight, seawater, and CO_2, along with trace nutrients. In fact, diatoms alone are responsible for ~ 20% of photosynthetically fixed CO_2 on Earth [72]. Diatoms are relatively resilient, and some species exhibit fast growth rates compared to others. Additionally, diatoms have been shown to incorporate a variety of other metal ions, including aluminum [73], magnesium [14], and zinc [74], into their biomineral architectures, which suggests an ability to tune their chemical composition. Their structures are also highly amorphous, which makes them more reactive than other silicates (*e.g.*, clays) that may require calcination to increase reactivity. Some disadvantages include the slow growth of some species capable of SiO_2 mineralization (*e.g.*, sponges), along with the relatively low cell densities of diatoms, particularly when compared to other microorganisms [75].

3 $CaCO_3$ and SiO_2 Biomineral Architectures

3.1 $CaCO_3$ Biomineral Architectures

Biomineralized $CaCO_3$ can form as one of four polymorphs: calcite, aragonite, vaterite, or ACC (see Figure 3). Natural limestone deposits, ancient pelagic (*i.e.*, marine) sediments, are mainly composed of calcite and aragonite [76]. Calcite and aragonite are more thermodynamically stable than vaterite and ACC at ambient temperatures and pressures. Biologically precipitated vaterite has been shown to transition to a more stable phase (*i.e.*, calcite, aragonite) over time [77]. This transformation is known to take place in a matter of 10-20 hours in DI water [78], and the biological systems have been shown to facilitate the increase Mg ions in solution [77], which is known to stabilize aragonite and vaterite in solution [78]. ACC is most commonly found *in vivo* and tends to be thermodynamically unstable *ex vivo* [79]. Understanding the differences in these polymorphs is of particular interest due to their differences in physical and chemical stability and how that stability can affect cement hydration and strength when different $CaCO_3$ particles are added to a cementitious system [80].

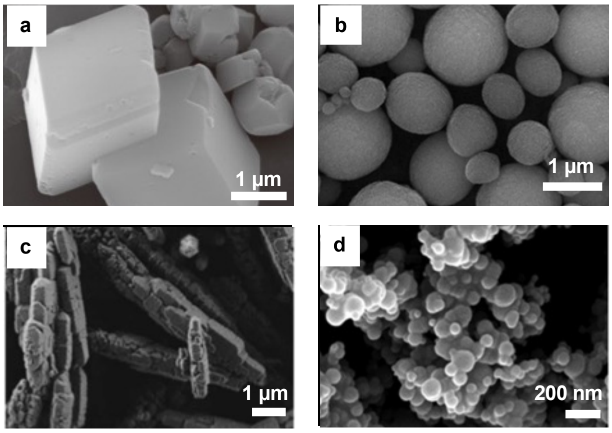

Figure 3. Morphologies of (a) calcite (Yang et al. [81], CC BY 4.0), (b) vaterite (Gilad et al. [82], CC BY NC 3.0), (c) aragonite (Myszka et al. [83], CC BY NC 3.0), and (d) amorphous calcium carbonate (ACC) (Xto et al. [84], CC BY 4.0).

Calcite, the most stable $CaCO_3$ polymorph, is characterized by its rhombohedral microstructure [85]. Calcite is known to be biomineralized by bacteria [2], algae [86], fungi [3], and sponges [87]. Nanoscale biomineralized calcite crystals can form aggregates up to 200 μm, but the size depends on the conditions within the cells and the size of the cell itself [32,42,53,88]. Coccolithophores form individual coccoliths comprised mostly of calcite that can be much smaller in size (*i.e.*, 1-4 μm) [53,86,89]. Researchers have shown that individual coccolithophore species and growth conditions, including temperature, pH, and CO_2 exposure [89], have a significant effect on coccolith formation.

Aragonite, the second most stable polymorph of $CaCO_3$, is characterized by its orthorhombic crystal structure [90]. Aragonite can be found in nature alongside calcite. Aragonite is known to be biomineralized by coral [6] and mollusks. [5,91]. Nacre is an example of biomineralized aragonite layered in a lamellar structure with a protein matrix. The proteins provide a scaffold for aragonite nucleation, while the aragonite provides strength to the nacre [5]. When precipitated in solution at ambient temperatures, aragonite has a tendency to redissolve into solution and precipitate as calcite [90,92], but aragonite is stable enough to exist on its own at ambient temperatures and pressures.

In comparison to calcite and aragonite, vaterite is the least stable crystalline polymorph. Vaterite is biomineralized by fish [93], ascidians [94], snails, and bacteria [93,95–97]. Pure vaterite will dissolve in water and reprecipitate as calcite at ambient temperatures or vaterite at elevated temperatures through a dissolution-precipitation reaction. The instability (*i.e.*, water solubility) of vaterite has been leveraged for applications that require readily soluble $CaCO_3$ [98]. From a cement and concrete research perspective, vaterite has been shown to precipitate, along with calcite and aragonite, in self-healing concrete applications [99].

ACC is the least stable $CaCO_3$ polymorph. ACC is generally a precursor to other forms of biomineralized $CaCO_3$ [77,79,84] in which it is precipitated and temporarily stabilized before it transforms into a more stable polymorph. ACC has been shown to be stabilized by organic molecules *ex situ* [88] and can exist as stable intracellular structures (or inclusions) *in situ* in some prokaryotes [100]. However, the exact mechanisms of its initial formation and stability remain under investigation [84,100]. Evidence of ACC biomineralization was first found in eukaryotic organisms [79]. ACC has also been identified in prokaryotic organisms [100]. In biological systems, ACC provides a number of functions, such as scaffolding for tissues and even influence the short-range crystalline order of crystalline polymorphs of $CaCO_3$ [101], most particularly of calcite and aragonite [102].

3.2 SiO_2 Biomineral Architectures

In terms of morphological features, SiO_2 forms spicules, as with sea sponges, or frustules, as with diatoms. Sea sponges use SiO_2 to build these spicules to make up their skeletons, which exhibit different structural features throughout their cross-section [103]. These spicules are visible on the macroscale as tree-like growths that branch upwards and away from the base of the seafloor [66]. At the microscale, these spicules are composed of long, cylindrical spines, which are generally made of micrometer-scale sheets stacked on top of each other [104]. The spicules are typically composed of semi-crystalline filaments, which contain crystalline and amorphous SiO_2 and crystallized protein [23]. Thus, the exact degree of crystallinity of the SiO_2 can be difficult to quantify due to the crystallized proteins within the spicules [66].

Diatoms use SiO_2 to build their exoskeletons, or frustules. Figure 4 illustrates the morphological diversity of diatom frustules. These frustules are porous to enable the function of organic valves used for transport. Diatom frustules, which are generally on the order of micrometers [15,103,105], are typically composed of amorphous or semi-crystalline SiO_2 [73]. Similar to sponges, this characterization is often complicated by interfering chemical components, where in diatoms, this is generally in the form of incorporated and surface elements, such as aluminum [7,106], iron [15], and magnesium [8,14]. The incorporation of such metals helps limit the dissolution of amorphous silica in the frustule, thereby enhancing its chemical and structural stability.

4 Applications of $CaCO_3$ and SiO_2 Biomineralization to Cement and Concrete Research

4.1 $CaCO_3$ Biomineralization Applications

$CaCO_3$ biomineralization *via* urea hydrolysis has been widely employed in cement and concrete research. Ureolytic microorganisms have been applied in most self-healing [55,113,114] and self-sealing [55,113] concrete applications. Ureolytic biomineralization has also been shown to increase the durability of concrete through porosity reduction and through the propensity of some microorganisms to bind potentially harmful compounds, such as free chloride ions [2]. Recycled aggregate beneficiation has also been explored using microorganisms capable of ureolytic biomineralization. In a seminal study conducted by Grabiec *et al*. [115], the authors found that $CaCO_3$ biodeposition can reduce the porosity and water demand of recycled aggregates. Bakr and Singh [116] demonstrated enhanced strength of cementitious systems with recycled aggregates that were pre-treated with a ureolytic biomineralization process. Another study examined how well strains isolated from concrete aggregates performed in a similar application [117]. In addition to increasing the strength of stabilized soils [24,34,113], heavy metal immobilization within soils has also been enhanced through urea hydrolysis-driven biomineralization [34,38,113].

More recently, researchers in the field of synthetic biology have shown that calcium carbonate polymorphs and mechanical properties can be tailored by modulating the metabolic activity of microorganisms capable of ureolytic biomineralization. Heveran *et al*. demonstrated how ureolytic organisms could tailor the polymorphism of $CaCO_3$ when using engineered strains of *E. coli* [32]. These same strains were used in a subsequent study to produce biomineralized living building materials [118]. Other researchers have isolated the urease enzyme and used it directly to enhance biomineralization in soil stabilization applications in which ensuring the long-term viability of the microorganisms is less feasible [38].

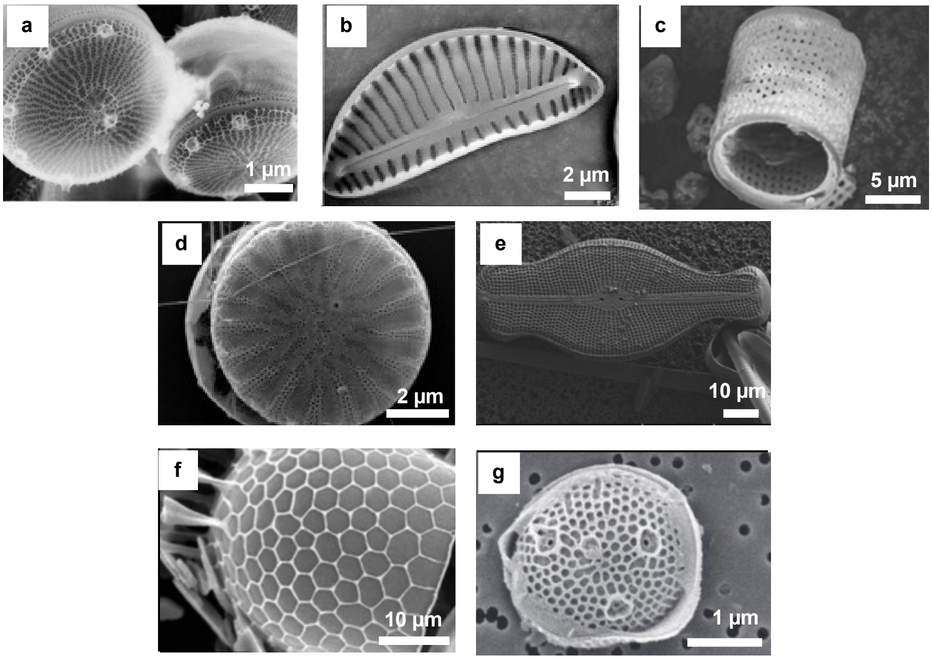

Figure 4. Morphological diversity of diatom frustules. (a) Thalossiosira pseudonana (Sumper et al. [9], copyright 2008 Wiley-VCH), (b) Navicula sp. (Wang et al. [107], copyright 2012 Springer Science+Business Media, LLC), (c) Melosira sp. (Zhang et al. [108], copyright 2011 Springer Science+Business Media, LLC), (d) Cyclotella sp. (Rorrer et al. [109], CC BY 4.0), (e) Didymosphenia geminate (Zgłobicka et al. [110], CC BY 4.0), (f) Chaetoceros gacilis (Hildebrand [111], copyright 2008 American Chemical Society), (g) Minidiscus comicus (Leblanc et al. [112], CC BY 4.0).

Applications of $CaCO_3$ biomineralization *via* photosynthesis have been less explored in cement and concrete research. One study conducted by Rizwan *et al*. [119] showed how the introduction of photosynthetic microorganisms into cement paste systems can decrease porosity, although whether these effects persist at later ages and whether the microorganisms can survive long-term is largely unknown. Noting the aggressive pH environment in traditional cementitious materials, some researchers are rethinking the matrix into which biomineralizing microorganisms are embedded. For example, in the seminal study on living building materials [120], researchers used photosynthetic microorganisms capable of biomineralization to strengthen and toughen a sand-hydrogel scaffold. The data showed that microbial survivability within the sand-hydrogel scaffold was 9% to 14% after 30 days, which exceeded previous reports on microbial survivability in self-healing concrete applications (0.1% to 0.4%) for similar timeframes [32]. Murphy *et al*. produced $CaCO_3$ using coccolithophores, biomineralizing microalgae, and showed that it could serve as a functional CO_2-negative $CaCO_3$ filler in PLC pastes [53]. Wang *et al*. [54] isolated the carbonic anhydrase enzyme and used it to make an enzymatic construction material. The authors used gelatin, carbonic anhydrase, calcium chloride dihydrate solution, and ambient CO_2 to generate a mortar with comparable compressive strength to conventional mortars.

Applications of biomineralization *via* sulfate reduction are limited in comparison to ureolytic biomineralization. Byrd *et al*. [121] demonstrated that biomineralization *via* sulfur reduction in a citrate production process yielded a calcite-rich sediment, which could provide additional benefit of improving the durability of concrete vessels in which the reactions were taking place. Sulfate reduction has also been used to reduce uranium stored in concrete, which can reduce the risk of corrosion induced by uranium and its associated compounds [122]. While sulfate reduction has only been achieved chemically in this application, the results suggest that similar results could be achieved using a biological approach. In wastewater concrete pipe applications, biomineralizing sulfur reducing microorganisms could potentially enhance concrete strength and increase durability by reducing the rates of microbially induced concrete corrosion [123].

Protein-mediated biomineralization in cement and concrete research has focused on studying the effects of adding biomineralized shells and protein additives into cementitious systems. For example, cement replacement with eggshells have been shown to reduce the embodied carbon emissions of concrete [124,125]. Ground oyster shells have been shown to reduce porosity in geopolymer systems [126] and decrease chloride diffusion in portland cement systems [127]. Compressive strength has been shown to increase at an optimized level of cement substitution, but the optimal percent substitution and corresponding increase in strength is source-dependent [128] and likely affected by other $CaCO_3$ characteristics, such as particle size, surface area, chemical composition, and residual organic polymer content. Oyster concrete, in which ground oyster shells are used in lieu of fine and coarse aggregates, has also been explored [129]. Oyster concretes are promising due to being abundant and having a long history of use as part of the more broad category of tabby concrete [130]. Tabby concrete is not unlike Roman concrete. It is a type of lime-pozzolan concrete in which oyster shells are calcined to form quicklime and combined with a reactive, siliceous SCM. Studies have also used oyster shells as fine aggregate substitutes, but their use as a coarse aggregate replacement warrants further investigation [131]. Martin et al. used powdered milk to enhance ureolytic biomineralization, where the powdered milk acted to increase precipitation quantity and bond strength at the $CaCO_3$-SiO_2 interface of the sand samples utilized in the study [132]. Another study by Baffoe and Ghahremaninezhad demonstrated how different proteins are more or less effective in supporting biomineralization. They showed that while Albumin was able to stabilize vaterite, calcite, and aragonite on a sliding concentration, whey protein showed negligible difference compared to control, which the authors attributed to differences in protein surface charge and hydrophobicity of the proteins involved [133].

4.2 SiO_2 Biomineralization Applications

Applications of SiO_2 biomineralization in cement and concrete research was limited at the time of writing. Sand, clays, slag, and fly ash, are the most dominant SiO_2 sources for applications such as cement clinkering, fine aggregate, and cement replacement. Biological SiO_2 applications have been limited to the use of agricultural waste (*e.g.*, rice husk ash [134,135]) or diatomaceous earth [136] as SCMs. One study evaluated the pozzolanic reactivity of biosilica harvested from freshly cultured diatoms (*i.e.*, *Thalassiosira pseudonana* and *Phaeodactylum tricornutum*) in accordance with ASTM C1897 [31]. Aside from metakaolin, diatom biosilica extracted from *T. pseudonana* exhibited the highest bound water content (9.9 ± 0.6 g/100 g dried paste), indicating high pozzolanic reactivity. Contrastingly, diatom biosilica extracted from *P. tricornutum* was less reactive (4.3 ± 0.1 g/100 g dried paste) but exhibited similar pozzolanic reactivity to a Class F fly ash. Overall, the data highlighted the potential to grow reactive biominerals for use as alternative SCMs using CO_2-sequestering microorganisms.

4.3 Emerging Applications, Opportunities, and Challenges

In addition to the previous examples, biomineralized $CaCO_3$ and SiO_2 have other potential uses within cement and concrete field. For example, biomineralized $CaCO_3$ and SiO_2 could be used to replace raw meal in portland cement production. The use of photosynthetic production of CO_2-storing, biomineralized $CaCO_3$ as a limestone replacement could theoretically reduce the embodied carbon emissions of portland cement manufacturing. Biomineralized SiO_2 from diatoms could also be used to replace the silica provided by clays and sand during cement production. To produce the $CaCO_3$ or SiO_2 in a photosynthetic manner, cement producers would need access to seawater and CO_2. The potential use of CO_2 waste streams (*e.g.*, flue gas) from cement manufacturing for microorganism growth is an advantage of this approach.

Microorganisms can produce nanoscale $CaCO_3$ and SiO_2, rendering these particles excellent candidates as reactive additives to cementitious systems [80]. The reactivity of these particles could be tailored by physically or genetically modulating the biomineralization process. For example, $CaCO_3$ could be rendered more reactive by targeting the formation and stabilization of more reactive $CaCO_3$ polymorphs (*i.e.*, vaterite, aragonite, ACC) or more intricate morphologies (*i.e.*, higher surface area). The chemical composition of biomineralized SiO_2 extracted from diatoms could be modified to include other beneficial metal cations (*e.g.*, Al, Fe) through doping of the culture media. To that end, biomineralized SiO_2 could also be used in the production of sodium silicate (*i.e.*, waterglass) that is necessary for alkali activation or, if doped with Al, reactive precursors for alkali-activated cements.

The use of enzymes to produce biomineralized cementitious materials is an emerging area of high-impact scientific research. Enzyme-based mineralization has several advantages over conventional biomineralization mechanisms, including fewer resources that are otherwise required for full-scale growth. As evidenced by the work with urea [34,38] and some emerging work with carbonic anhydrase [34,137], the enzymes need only be present in small quantities to achieve similar degrees of mineralization to systems containing the living microorganisms. Conversely, the exact inhibition effects of cement pore solution and other additives on the catalytic behavior of enzymes are not fully understood and require further investigation [52].

As with any novel material technology, there are several challenges to consider in regard to widespread implementation of $CaCO_3$ and SiO_2 biomineralization. First, at-scale cost and scale of production is a key consideration. One promising aspect is that the global capacity of oceanic $CaCO_3$ is estimated to be 5.48 billion metric tons [138,139], and biogenic SiO_2 from surface ocean would be estimated to be 14 billion metric tons [140]. The cost of scaling the production of biomineralized $CaCO_3$ and SiO_2 will differ by biomineralization mechanism and organism species. To that end, photosynthesis-driven $CaCO_3$ and SiO_2 biomineralization have a cost advantage over other biomineralization mechanisms, given that the energy and material inputs (*e.g.*, sunlight, seawater) are abundantly available. At-scale production cost of biomineralized $CaCO_3$ and SiO_2 could be further ameliorated through the valorization of organic byproducts (*i.e.*, lipids, proteins, carbohydrates), which may have applications in biofuels [75], catalysis [7], and medicine [141]. In addition to cost, elucidating the effects of new biominerals on fresh- and hardened-state properties of cementitious materials is a key technical challenge. This challenge is particularly relevant to new material systems (*e.g.*, enzyme-based building materials) whose long-term durability needs to be understood prior to widespread implementation. Finally, shifting paradigms within the cement and concrete industry from one historically rooted in mining and extraction of minerals to one centered on cultivation (*i.e.*, farming) of minerals remains a barrier but one that perhaps soon will be overcome in light of the current climate crisis and a steady global shift toward fully regenerative practices.

5 Conclusions

Biomineralization is an emerging area of interest within the field of cement and concrete research. In this work, the mechanisms of $CaCO_3$ and SiO_2 biomineralization were reviewed, and the morphological diversity of $CaCO_3$ and SiO_2 architectures were highlighted and discussed. In addition, this work reviewed traditional applications of $CaCO_3$ and SiO_2 biomineralization in cement and concrete research, including self-healing, self-sealing, soil stabilization, and recycled aggregate beneficiation, along with emerging applications, such as biomineralized $CaCO_3$ fillers in cementitious materials and the production of living and enzymatically mineralized construction materials. Potentially new application areas of $CaCO_3$ and SiO_2 biomineralization were highlighted, including the use of $CaCO_3$ and SiO_2 as the raw materials for portland cement, SCM, and alkali-activated cement production. Finally, this work addressed the challenges and barriers to implementing new material technologies in the field, such as cost and scale of production, as well as the technical, regulatory, and perception barriers that must be addressed prior to widespread implementation.

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WVS is listed as a co-inventor on a patent application PCT/US2020/020863 and PCT/US2020/058344 filed by the University of Colorado. WVS is a co-founder and shareholder of Prometheus Materials, Inc. and Minus Materials, Inc. and a member of their advisory boards.

Authorship Statement (CRediT)

Nicolas D. Dowdy: Conceptualization, Investigation, Writing-original draft, Writing-reviewing and editing, Visualization. Wil V. Srubar III: Conceptualization, Writing-original draft, Writing-reviewing and editing, Supervision, Visualization, Project administration, Funding acquisition.

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