Formation of magnesium calcite mesocrystals in the inorganic environment only by using Ca^{2+} and Mg^{2+} and its biological implications

Li-Mei Shang, Jun Jiang* and Shu-Hong Yu*

ABSTRACT Magnesium calcite (Mg-calcite) mesocrystal is widespread in the biominerals with specific functions. Until now, it remains challenging to obtain Mg-calcite mesocrystals without organic additives and the formation mechanism of Mg-calcite mesocrystals in the ocean is not clear yet. We report here the synthesis of corn-like Mg-calcite mesocrystals from pure amorphous calcium carbonate (ACC) via a facile method only by using Ca^{2+} and Mg^{2+} . The obtained Mg-calcite is composed of many nanocubes with common crystallographic orientation, which shows very good single crystal feature. In the crystallizing procedure, the ACC nanospheres rapidly agglomerate into Mg-calcite corn-like mesocrystal by oriented attachment (OA) in a certain direction, which belongs to the non-classical nucleation. By this method, the molar ratio of Ca^{2+} and Mg^{2+} plays a vital role in the whole crystallization procedure, which may shed a new light on disclosing the mechanism behind for the effect of seawater in the formation of biological Mg-calcite in nature.

Keywords: calcium ion, magnesium calcite, mesocrystal, amorphous calcium carbonate, seawater

INTRODUCTION

Calcium carbonate is widely present in nature, such as Earth's crust, marine organism, and natural minerals [1–3]. In recent years, its excellent optical and mechanical properties have attracted more and more interest [4–7]. Many additives have been chosen to control the morphology and polymorph of calcium carbonate to study the nucleation and crystallization mechanism in solution [8–14]. It is worth pointing out that the magnesium ion is prominent among these additives because of its various functions in biomineralization study, such as inducing the aragonite [15], incorporating into the amorphous calcium

carbonate (ACC) to obtain amorphous calcium magnesium carbonate (Mg-ACC) [16–19], substituting Ca in the calcite lattice to form Mg-calcite [20–23].

Interestingly, Mg-calcite is widely found in many marine organisms, such as sea urchin teeth, coralline red algae, red coral and calcareous sponges [24]. Many studies so far have focused on the formation of the Mg-calcite because of its excellent mechanical properties compared with common calcite [25]. For example, Raz *et al.* [21] obtained Mg-calcite along with aragonite in the presence of macromolecules extracted from skeletons of coralline algae. Qi and co-workers [26] reported that high-Mg calcite in pure phase can be synthesized from the polymer-stabilized Mg-enriched ACC under ambient conditions. Nevertheless, the formation mechanism of Mg-calcite in the ocean is not very clear yet. The seawater is the living environment of marine organisms; therefore, the composition of seawater is significant for the biomineralization of Mg-calcite [27,28]. As well known, Mg^{2+} and Ca^{2+} are abundant in seawater [29]. The molar ratio of Ca^{2+} and Mg^{2+} has been proved to influence the formation of Mg-calcite [26,30], in which the effect of Ca^{2+} is still undefined. In the study of simulated biomineralization, Ca^{2+} is usually used as a reactive ion to form CaCO_3 [31,32]. However, to date, the significance of the Ca^{2+} to induce Mg-calcite from pure ACC has not been realized yet.

The notion of mesocrystal has been coined to describe the superstructure consisting of individual nanocrystals with common crystallographic orientation [33]. Many biominerals such as sea urchin spicule, egg shell, and foraminifer have been found to possess the mesocrystal structure with specific functions, where calcium carbonate nanocrystal acts as an assembling unit [34–36].

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Previous researchers discovered that Mg-calcite mesocrystal could be obtained with the participation of organic additives [37,38].

Herein, we report a simple route for the formation of corn-like Mg-calcite mesocrystals through the crystallization of pure ACC powder only by using Ca^{2+} and Mg^{2+} . The obtained mesocrystals are composed of many nanocubes with common crystallographic orientation, which show very good single crystal feature. The whole experiment is based on the pure ACC as precursor in the simple inorganic environment, in which the interesting effect of Ca^{2+} and Mg^{2+} on the phase transition and nucleation of CaCO_3 has been discovered. By this method, we point out that the molar ratio of Ca^{2+} and Mg^{2+} plays a key role during the growth process of corn-like Mg-calcite mesocrystals, which implies that the seawater is an important factor in the formation process of biological Mg-calcite.

EXPERIMENTAL SECTION

Materials

Anhydrous calcium chloride ($M_W = 111$), anhydrous sodium carbonate ($M_W = 105.9$) and hexahydrate magnesium chloride ($M_W = 203.3$) were commercially available in analytical grade and used without further purification.

Instruments

X-ray diffraction (XRD) data were carried out on a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite monochromatized Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained on a Zeiss Supra 40 scanning electron microscope at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was performed on a Hitachi H7700 transmission electron microscope with a CCD imaging system and an accelerating voltage of 100 kV. High-resolution TEM (HRTEM), selected area electron diffraction (SAED), scanning transmission electron microscope energy disperse spectra (STEM-EDS) and elemental mapping were recorded on a JEOL-2100F with an acceleration voltage of 200 kV. The Mg:Ca molar ratio was analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Atomscan Advantage (Thermo Jarrell Ash Corporation, USA) instrument. Thermal gravimetric analysis (TGA) was measured by a TGA Q5000IR analyzer under N_2 flow with a temperature ramp of $10^\circ\text{C min}^{-1}$. Focused ion beam (FIB) was processed on FEI, Helios NanoLab650. Nano computed tomography (Nano-CT) was conducted at the National Synchrotron Radiation Labora-

tory's soft X-ray imaging station.

Synthesis of Mg-calcite mesocrystal

Typically, the ACC powder was prepared according to a previous report [39]. A little difference is that the ACC gel was dried in vacuum oven at 35°C in our experiment. Then, 50 mg ACC powder was fully dispersed into 20 mL inducing crystallization solution by ultrasonication. The still crystallization process was conducted under ambient condition for 48 h. Finally, the product was collected by centrifugation (5000 rpm, 2 min), cleaned with absolute ethanol for several times and then dried in vacuum oven. The dried samples were kept in a desiccator. $[\text{Ca}^{2+}]/[\text{Mg}^{2+}] = 0:0$ means the inducing crystallization solution is pure deionized water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C , pH 6.92). The pH of the solution was tested by Mettler Toledo pH meter at 25°C for three times to obtain the average result. $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$ and pH of the inducing crystallization solution are shown in Table S1.

Calculation

The equilibrium of precipitation and dissolution of ACC powder is

the solubility product constant (K_{sp}) of ACC at room temperature is $4.0 \times 10^{-7} (\text{mol L}^{-1})^2$ [40]. When the ACC powder achieves the equilibrium of precipitation and dissolution in the inducing crystallization solution ($[\text{Ca}^{2+}]/[\text{Mg}^{2+}] = 2:5$), the calculated equilibrium concentration of CO_3^{2-} ($[\text{CO}_3^{2-}]$) is $1.9030 \times 10^{-5} (\text{mol L}^{-1})^2$.

The supersaturation of the inducing crystallization solution at the beginning is

$$S = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}}, \quad (2)$$

the solubility products K_{sp} of different polymorph at room temperature in Equation (2) are as following: calcite = $3.3 \times 10^{-9} (\text{mol L}^{-1})^2$, aragonite = $4.4 \times 10^{-9} (\text{mol L}^{-1})^2$, vaterite = $1.2 \times 10^{-8} (\text{mol L}^{-1})^2$ [41].

$$S_{\text{Mg-calcite}} = \frac{[\text{Ca}^{2+}]^{(1-x)} [\text{Mg}^{2+}]^x [\text{CO}_3^{2-}]}{K_{\text{sp}}}, \quad (3)$$

where x ($0 < x \leq 0.085$) in Equation (3) represents the molar fraction of magnesium ion incorporated into the calcite lattice in our experiment and the solubility of Mg-calcite (the magnesium content about 8.5%) is similar with aragonite [42].

After calculation, $86.5 < S_{\text{Mg-calcite}} \leq 93.5$, $S_{\text{Aragonite}} = 86.5$,

$S_{\text{Vaterite}} = 31.7$; therefore, Mg-calcite should preferentially deposit in the inducing crystallization solution at the beginning.

RESULTS AND DISCUSSION

The pure ACC without any additive was exploited as precursor in our experiment. Therefore, we can eliminate impurity interference and study the crystallization mechanism of Mg-calcite mesocrystal more clearly. This precursor was prepared by rapidly mixing CaCl_2 and Na_2CO_3 solutions at low temperature (almost 0°C). The size of pure ACC particles is about 40–50 nm (Fig. S1a and b). At the meantime, the XRD pattern has no obvious peaks but only two swells (Fig. S2), and the SAED pattern (Fig. S1c) is a halo rather bright ring, which could prove the precursor is amorphous [26].

It is commonly known that calcite is the most stable and easy-to-obtain phase in thermodynamics for CaCO_3 [41], so when the quantitative pure ACC powder is dispersed in deionized water at room temperature for two days, the pure rhombohedral calcite is obtained (Figs 1a and 2a). When the deionized water is replaced by MgCl_2 solution without changing other parameters, the pure straw-like aragonite is formed (Figs 1b and 2b). This is because Mg^{2+} can significantly increase the surface energy of calcite and raises its nucleation barrier, while aragonite is much less affected [28]. Interestingly, when moderate Ca^{2+} was leaded into this MgCl_2 solution, the whole crystallization process took place in mixed solution of

CaCl_2 and MgCl_2 , other parameters do not change. The product is the corn-like Mg-calcite, which consists of many nanocubes (Figs 1e and 2e). The obtained crystals with the length of $2\ \mu\text{m}$ and the width of $1\ \mu\text{m}$ are shown in Fig. 1e. Therefore, the effects of Ca^{2+} and Mg^{2+} on the nucleation and phase transition of pure ACC are obvious.

We found that the molar ratio of Ca^{2+} and Mg^{2+} in the crystallization environment plays an important role in the formation process of Mg-calcite. When $[\text{Ca}^{2+}]/[\text{Mg}^{2+}] = 0.5:5$, the mixture of aragonite and low Mg-calcite is obtained (Figs 1c and 2c). When $[\text{Ca}^{2+}]/[\text{Mg}^{2+}]$ increases to 1:5, the pure Mg-calcite is obtained in which the magnesium content is 6.19 mol% according to the shift of (104) peak in the XRD pattern [43] (Figs 1d and 2d). With further increased $[\text{Ca}^{2+}]/[\text{Mg}^{2+}]$ to 2:5, the obtained product has the maximum magnesium content (8.67 mol%) (Fig. 2e), which is consistent with the result of the TGA in Fig. S3 [16]. When the molar ratio of Ca^{2+} and Mg^{2+} increases to 3.5:5 and 5:5, the morphology of Mg-calcite is changed and less Mg (<5 mol%) is found to be incorporated into the crystal lattice (Fig. S4, Figs 1f and 2f). The main results are summarized in Scheme 1.

As we all know, Ca^{2+} is particularly attractive as an important reaction ion in biomineralization. However, here, according to the results in Scheme 1, it is important to note that Ca^{2+} also has an effect on the phase and morphology control of calcium carbonate by influencing the supersaturation (calculation in the EXPERIMENTAL SECTION).

Figure 1 SEM images of the crystallizing products when changing the molar ratio of Ca^{2+} and Mg^{2+} at room temperature in the inducing crystallization solution. (a) 0:0; (b) 0:5; (c) 0.5:5; (d) 1:5; (e) 2:5; (f) 5:5. $[\text{Ca}^{2+}] = 20\ \text{mmol L}^{-1}$, $[\text{Mg}^{2+}] = 50\ \text{mmol L}^{-1}$ as the molar ratio of Ca^{2+} and Mg^{2+} is 2:5; the total volume of the inducing crystallization solution is 20 mL.

Figure 2 XRD patterns of different crystallizing products when changing the molar ratio of Ca^{2+} and Mg^{2+} in the inducing crystallization solution. (a) 0:0; (b) 0:5; (c) 0.5:5; (d) 1:5; (e) 2:5; (f) 5:5; (calcite is indicated as C, aragonite is indicated as A, the XRD standard cards are PDF#47-1743 and PDF#41-1475, respectively; (104) peak in calcite is indicated as blue dashed line).

The higher-magnification SEM image of the Mg-calcite ($[\text{Ca}^{2+}]/[\text{Mg}^{2+}] = 2:5$) is shown in Fig. 3b, indicating that many nanocubes (about 100 nm) insert alternately in a certain direction to assemble the corn-like Mg-calcite with a length of 2 μm and a width of 1 μm . Furthermore, the edge is angular due to the stacking as displayed in the TEM image (Fig. 3a). We selected different regions on the whole corn-like Mg-calcite to do the electron diffraction (Fig. 3a). When selecting the single nanocube (red circle in Fig. 3a), the result is the single crystal diffraction in

Scheme 1 Scheme of the relationship between the molar ratio of Ca^{2+} and Mg^{2+} in the inducing crystallization solution and the polymorph of CaCO_3 (low Mg-calcite means the magnesium content less than 5 mol% [42]).

which the spots are corresponding to the (-102) , (202) , (104) and (006) facets, respectively (red frame in Fig. 3a); when enlarging the scope to 200 nm (yellow circle in Fig. 3a), the (104) facet diffraction spot has angular misorientation of about 10° (yellow frame in Fig. 3a); when further expanding the range of option to 500 nm (green circle in Fig. 3a), more points have the same angular deflection (green frame in Fig. 3a). Besides, to verify the overall crystal orientation, we selected the region in middle of the corn-like Mg-calcite (purple circle in Fig. 3a), the diffraction spots also have the angular de-

Figure 3 (a) The TEM image (the diameters of red, yellow, green and purple circles are 100, 200, 500, 500 nm, respectively) and the corresponding SAED patterns encircled with same color (the small angle of every two dashed-line is 10°). (b) The large magnification SEM image. (c) STEM image of Mg-calcite mesocrystal; EDS elemental mapping images: (fuchsia) Ca; (green) Mg.

flection of about 10° (purple frame in Fig. 3a). These results adequately prove that the obtained product is mesocrystal with single crystal feature [44,45]. The STEM-EDS elemental mapping images (Fig. 3c) show that Ca and Mg are homogeneously distributed throughout the whole mesocrystal, implying that Mg successfully inserts into the lattice of calcite.

To explore the formation mechanism of Mg-calcite mesocrystal, the time-dependent crystallization process of the obtained Mg-calcite mesocrystal was studied (Fig. 4). At the beginning, after 30 s, some ACC particles aggregate into corn-like crystal with some dispersed ACC particles adsorbed on the surface for further growth (Fig. 4b, Fig. S5a and b). When prolonging the reaction time to 1 min, all of the products are corn-like crystals (Fig. S5c) without any ACC particles. From 0.5 to 32 h, the nanospheres gradually grow to irregular nanocubes (Fig. 4c–f). Until 32 h, the corn-like Mg-calcite basically consists of sequential cubes (Fig. 4f) and the nanocubes turn more and more angular from 32 to 48 h (Fig. 4f–h). The crystallized product in Fig. 4h was processed by the FIB with the ion gun voltage of 30 kV (Fig. S6a and b) and then the cross section was processed with lower ion gun voltage of 2 kV, and some nanoparticles showed up (red circle in Fig. S6c). Meanwhile, the Nano-CT image (Fig. S6d) also shows that the nanoparticles distribute on the whole Mg-calcite. Therefore, we can draw a conclusion that the interior as well as the surface of each Mg-calcite is composed of nanoparticles. Besides, we obtained the intermediate product at different reaction times when changing the molar ratio of Ca^{2+} and Mg^{2+} . The results in Figs S7 and S8 clearly show that Mg^{2+} could induce the

aragonite whose intermediate is monohydrocalcite when $[\text{Ca}^{2+}]/[\text{Mg}^{2+}] = 0.5$ or $0.5:5$ [11], which further proves that Ca^{2+} could be beneficial for the formation of calcite when adding Ca^{2+} into Mg^{2+} solution. Furthermore, we characterized the magnesium content in the product with different crystallization times by XRD (Fig. S9) and ICP. The ICP results (Table S2) are similar to that of the product after crystallization for 48 h, which means the magnesium contents in the whole product at different reaction times resemble the final product. However, the magnesium content calculated by the XRD pattern gradually increases with time, which implies Mg^{2+} gradually incorporates into the lattice of calcite during the crystallization procedure. The difference between the results of ICP and XRD is that the magnesium content calculated by the XRD pattern means the magnesium has inserted into the crystal lattice of calcite, while the ICP result means the magnesium contents are in the lattice spacing and the surface of the crystal in the whole crystallizing product [21,46]. The results in Table S2 reveal that Mg^{2+} was adsorbed on the surface of crystallized product at the beginning and incorporated into the lattice of calcite gradually as the morphology optimizing during the ripening process.

The possible crystallization mechanism of Mg-calcite mesocrystal is illustrated in Scheme 2. Firstly, when the pure ACC powder disperses in the CaCl_2 and MgCl_2 mixed solution, Mg^{2+} and Ca^{2+} are both around the ACC particles in the crystallization environment. Subsequently, Mg^{2+} is adsorbed and restricted in the corn-like crystal which consists of many spherical particles by oriented attachment. Meanwhile, some dispersed ACC particles

Figure 4 SEM images of Mg-calcite obtained at different reaction times when the molar ratio of Ca^{2+} and Mg^{2+} at room temperature in the inducing crystallization solution is 2:5. (a) 0 h; (b) 30 s; (c) 0.5 h; (d) 8 h; (e) 16 h; (f) 32 h; (g) 40 h; (h) 48 h. $[\text{Ca}^{2+}] = 20 \text{ mmol L}^{-1}$, $[\text{Mg}^{2+}] = 50 \text{ mmol L}^{-1}$ as the molar ratio of Ca^{2+} and Mg^{2+} is 2:5, the total volume of the inducing crystallization solution is 20 mL.

Scheme 2 Possible crystallization mechanism of Mg-calcite mesocrystal. (a) Mg^{2+} and Ca^{2+} around the pure ACC particles. (b) Dispersed ACC particles adsorbed on the surface of corn-like crystal. (c) The ACC particles adsorb directly at certain direction forming corn-like crystal with restricted Mg^{2+} . (d) Irregular nanocubes consist of corn-like Mg-calcite. (e) Corn-like Mg-calcite mesocrystal with angular edge.

are still adsorbed on the surface for further growth. With prolonging time, Mg^{2+} gradually incorporates into the lattice of calcite as the morphology optimizing during the ripening process.

The different conditions are applied in the crystallization process, such as the reaction temperature and the relative concentration of ACC. The main results are shown in Figs S10 and S11, respectively. With the increasing temperature from -4 to 60°C , the size of assembled units becomes larger (Fig. S10). This can be interpreted as that reaction temperature influences the crystallizing kinetics. When the temperature rises, the growth rate of assembled units becomes faster. Furthermore, the relative concentration of ACC powder also has a tiny effect on the morphology of the crystallization product (Fig. S11): when gradually increasing the relative concentration of ACC powder, the diameter of the corn-like Mg-calcite mesocrystal becomes larger because more ACC particles agglomerate at the beginning.

CONCLUSIONS

In summary, we report a facile method to prepare the unique corn-like Mg-calcite mesocrystals by using Ca^{2+} and Mg^{2+} in the inorganic environment. Each Mg-calcite is constructed by many nanocubes with common crystallographic orientation, which shows excellent single crystal feature. A new crystallization mechanism of Mg-calcite has been proposed based on the effects of Ca^{2+} and Mg^{2+} on the nucleation and phase transition of pure ACC. This work highlights the role of the molar ratio of Ca^{2+} and Mg^{2+} in the crystallization process of Mg-calcite mesocrystals, which may shed a new light on the mechanism interpretation for the important role of seawater

in the formation process of biological Mg-calcite.

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- Author contributions** Yu SH supervised the project and wrote the paper. Jiang J and Shang LM conceived the idea and wrote the paper. Jiang J and Shang LM carried out the experiments, analyzed the results, and wrote the paper. All authors discussed the results and assisted during the manuscript preparation.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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钙离子镁离子共存的纯无机环境中镁方解石介观晶体的形成及其生物学意义

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摘要 镁方解石介观晶体广泛分布于具有特殊功能的生物矿物中. 至今, 在排除有机添加剂的参与后合成镁方解石介观晶体仍是一个很大的挑战, 同时海洋中镁方解石的形成机理尚不明确. 本工作以纯的无定形碳酸钙(ACC)为前驱体, 在钙离子镁离子共存的无机环境中控制结晶条件得到了由许多共同结晶取向的纳米晶组成的玉米状镁方解石. 在结晶过程中, ACC纳米球通过定向附着迅速聚集得到镁方解石介观晶体, 属于非经典成核机理. 我们发现钙离子和镁离子的摩尔比在整个结晶过程中起着至关重要的作用, 这能为揭示自然界海水中生物镁方解石的形成机制提供新的思路.