Effect of Inorganic Additives on the Growth of Silica-Carbonate Biomorphs

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Silica-barium carbonate biomorphs are complex precipitate microstructures that form by purely inorganic processes. They display life-like morphologies with smoothly curved surfaces that are not restricted to crystallographic symmetries. We investigate the morphogenetic influence of inorganic dopants that compete with the barium carbonate precipitation. Trace deposition of alkaline earth or transition metal additives causes significant changes to the crystal morphologies. In the case of Pb^{2+} and Ag^+ ions, biomorph growth is disrupted by the formation of competing precipitates. Similarly, the addition of Ca^{2+} , Mg^{2+} , and Zn^{2+} induces the rapid crystallization of witherite or amorphous silica-carbonate aggregates at enhanced growth rates. By comparison, the addition of strontium ions results in the assembly of classic biomorphs such as cardioid sheets and helices. The procedures reported here exemplify the use of co-depositing agents to influence the compositional and crystallographic properties in a manner similar to magnesium-doped biogenic calcites.

Keywords: A1. Biocrystallization, A1. Crystal morphology, silica, carbonate, biomorph

1. Introduction

Living organisms have evolved creative crystallization pathways for building inorganic structures with remarkable precision and control [1]. The exploration of *in vitro* systems that mimic these biomineralization processes is gaining considerable interest due to their potential relevance to materials synthesis [2–4]. An important model is the crystallization of barium carbonate in alkaline silica solutions, which produces crystal aggregates with life-like morphologies [5–8]. These so-called biomorphs are characterized by smoothly curved surfaces such as sheets and helices that grow free of the constraints of crystallographic symmetries. At the nanoscale, the structures are composed of crystalline barium carbonate nanorods assembled within an amorphous silica matrix to a hierarchical architecture reminiscent of natural biominerals [9–11]. Despite their complex morphology, the synthesis of silica-carbonate biomorphs is remarkably simple. An alkaline solution of barium and silicate ions is exposed to the diffusion of atmospheric carbon dioxide [8,12,13]. The continuous influx of CO₂ into the reaction medium prompts the co-precipitation of BaCO₃ and silica, which assemble into a composite structure.

Several studies have reported the synthesis of non-BaCO₃ biomorphs composed of other alkaline earth carbonates. Replacing barium with strontium ions yields crystal aggregates with typical biomorph architectures such as helical filaments and twisted ribbons [12,14]. In contrast, magnesium carbonate-based aggregates do not assemble smoothly curved morphologies that could be classified as biomorphs. Also calcium carbonate presents an interesting case; biomorph formation is only possible at elevated temperatures or other conditions that promote the deposition of aragonite rather than calcite crystals [13,15,16]. These efforts have been aimed towards generalizing the synthesis of barium carbonate-silica biomorphs to other systems. In this context, the incorporation of dopants into biomorph structures remains significantly understudied, despite its immense relevance to biomineralization and geochemistry [17–20]. These natural systems exemplify the effects of inorganic dopants on the polymorph selection, the development of specific crystal faces, and the stability of amorphous species. In the current manuscript, we investigate the effect of inorganic additives that compete with the deposition of barium carbonate during biomorph growth.

2. Experimental methods

2.1 Sample Preparation

Silica-carbonate biomorphs are synthesized in alkaline solutions according to the method by García-Ruiz et al. with slight variations [8]. A 4 mL crystallization solution ($[\text{BaCl}_2] = 1\text{--}5\text{ mM}$, $[\text{Na}_2\text{SiO}_3] = 8.4\text{ mM}$) is placed in a Petri dish (Greiner Bio-One, 35/10 mm) that is open to the air. Different alkaline earth metal and transition metal ions (M^{n+}), namely Mg^{2+} , Sr^{2+} , Ca^{2+} , Pb^{2+} , Ag^+ , and Zn^{2+} are added in concentrations spanning a range of 0.1–4 mM. In our systematic study, the total metal ion concentration ($[\text{Ba}^{2+}] + [\text{M}^{n+}]$) is kept constant at 5 mM. We adjust the initial pH to 10.2–10.9 by adding a few drops of 0.1 M HCl. The biomorph structures mature to their final shapes within 8–24 hours.

2.2 Instrumental characterization

We collect optical microscopy images using a Leica DMRB transmission microscope equipped with a charge coupled device camera (COHU 2122-1000). For scanning electron microscopy (SEM), the biomorphs are deposited on a rectangular glass substrate (1 cm $\times$ 2 cm). Images are acquired using a JEOL 5900 and a JEOL 7401F Field Emission-SEM. The chemical composition of the biomorph structures is determined using an IXRF energy dispersive X-ray spectroscopy (EDS) analyzer. For powder X-ray diffraction (PXRD) measurements, the crystal aggregates are obtained from five to eight 20 mL solutions. A PANalytical X'pert PRO is operated at the Cu K α emission line with 0.0167° steps. The data are analyzed using the HighScore Plus software package. We also collect dynamic light scattering (DLS) profiles using an ALV/CGS-3 Compact Goniometer System equipped with a 633 nm Helium-Neon laser source and a variable angle ALV-7004 digital correlator (ALV-GmbH, Langen, Germany). The auto-correlation functions are fitted to a cumulant series using correlator software and the distribution profiles of the particle size are computed as the corresponding Laplace transforms. Variation of the scattering angle (80°, 90°, 100°, 110°) results in no appreciable deviation from the reported trends.

3. Results and discussion

3.1 Control Morphologies

Figure 1 shows optical microscopy images of silica-carbonate biomorphs obtained from a solution of barium and silicate ions with no inorganic additives. As reported in the literature [8,10], the principal morphologies obtained in this system are sheets, worms, and helicoids (Figure 1a). The leaf-like sheets emerge from spherical aggregates and grow in radial direction along the bottom of the container. Worm-like braids and twisted helicoids occur when the edge of a sheet curls out-of-plane and away from the growth substrate. However, these structures sometimes grow independently and inter-convert, often extending to a few hundred micrometers. Qualitatively different patterns are observed at the solution-air interface (Figure 1b). The shape of these biomorphs has a striking similarity to flowers sitting on leaf pads. Notice that the sheet surfaces are characterized by banded patterns that are particularly obvious around the globules (black arrows, Figure 1b). These oscillatory features represent topographic modulations that form during biomorph growth [21].

3.2 Morphology Characterization

In the following, we consider the morphologies in Figure 1 as the reference structures for our experiments and investigate the effect of inorganic additives that compete with the crystallization of barium carbonate. The most obvious candidates are alkaline earth metal ions (M^{2+}), specifically Ca^{2+} , Mg^{2+} , and Sr^{2+} . We also probe the influence of the transition metal ions Ag^+ , Pb^{2+} , and Zn^{2+} . All of these species readily form carbonate precipitates with solubilities comparable to $BaCO_3$.

The results of our systematic study are illustrated in a phase diagram that shows the wealth of pattern formation accessed by adding inorganic dopants at various concentrations (Figure 2). The percentage values represent the ratio of the inorganic additive $[M^{2+}]$ to the sum of $[M^{2+}]$ and $[Ba^{2+}]$. Note that the total metal ion concentration is kept constant at 5 mM. For the lowest probed calcium ion concentration, the biomorph architectures already show a marked deviation from the control morphologies: the flower structures that float close to the solution surface develop nodules at the edges and the formation of leaves is largely inhibited. When $[Ca^{2+}]$ is increased to 0.5 mM (or 10 %), the deposits assemble cauliflower-like globules. At higher calcium concentrations, the formation of complex crystal aggregates is almost completely inhibited resulting in precipitate networks with no distinct features. By comparison, sub-millimolar amounts of Mg^{2+} , Zn^{2+} , or Pb^{2+} cause less drastic changes to the biomorph structures. At dopant levels of 2 % and 10 %, the predominantly flower-and-leaf-shaped patterns are recovered, in addition to interesting acorn-like biomorphs. Increasing the dopant concentration to 1 mM (20 %) produces the pre-requisite globules, but these structures do not evolve into biomorph leaves. Interestingly, biomorph growth is more amenable to the presence of silver ions. We observe the familiar flowers and leaves at $[Ag^+]$ as high as 2.5 mM (50 %). When $[Ag^+]$ is increased to 4 mM (80 %), the biomorphs are replaced by a thick film of crystal aggregates. Finally, the addition of Sr^{2+} ions has a minimal effect on the obtained structures; biomorphs are formed at all strontium ion concentrations. As a visual aid, the dashed, red border highlights the reaction conditions that do not produce carbonate aggregates with any distinguishable morphology. The solid, blue border in Figure 2 groups the reaction conditions which produce biomorph architectures similar to the control patterns.

Figure 3 shows electron micrographs for three representative examples of the crystal aggregates. As noted earlier, the addition of calcium ions prompts the formation of the cauliflower-like shapes with an average diameter of 30 μm (Figure 3a). For the magnesium-doped solutions, the depositing crystallites form spherical assemblies from which smooth rods emerge (Figure 3b). The SEM micrographs also confirm that the addition of strontium ions does not significantly affect the deposited morphologies (Figure 3c). Furthermore, the inspection of the crystal aggregates at higher magnification reveals the main morphological difference between the biomorphic and non-biomorphic structures. Notice that the calcium-doped crystals show pseudo-hexagonal features of the order of few micrometers. Similarly, the magnesium containing structures assemble micro-prisms elongated along the c-axis and typically twinned at the $\{110\}$ planes. These distinctive crystal habits strongly suggest that witherite is the main crystalline component. Importantly, the expression of microscale euhedral geometries prevents the formation of smoothly curved biomorphs. By comparison, the strontium-doped biomorphs are composed of hierarchically aligned nanorods. Clearly, the assembly of these nano-sized building blocks is necessary for the morphogenesis of curved mesoscale structures such as helices, worms, and sheets.

3.3 Chemical Composition

The chemical composition analyses reveal a non-uniform distribution across different regions of the same structure. For example, the euhedral crystallites in Figure 3b (region 1) are composed predominantly of BaCO_3 (83 %) and a smaller amount of SiO_2 (12 %). The BaCO_3 content drops drastically in region 2 and region 3 which consist mostly of SiO_2 (72 % and 92 % respectively). As anticipated, the percentage of MgCO_3 mirrors the trend in BaCO_3 and is equivalent to 4.8 %, 2.2 %, and 0.9 % in the three respective regions. In some cases, the heterogeneous distribution of the inorganic additive can be even more pronounced. For example, the spherical aggregate in Figure 4e contains only 2.2 % SrCO_3 in region 1 as compared to 10.5 % SrCO_3 in the leaf-like sheet (region 2). These observations suggest that a local change in the chemical environment induces a sharp alteration in the morphology and the composition of the deposited biomorphs.

Surprisingly, the dopant carbonates constitute a relatively small percentage compared to the depositing barium carbonate. The crystal aggregates are mostly composed of BaCO_3 (45-65 %) in addition to a considerable percentage of silica (30-45 %). By comparison, the mole fraction of the depositing MgCO_3 or CaCO_3 does not exceed 5 %, even when the dopant ions are as high as 20 % in the corresponding solutions. We emphasize that these relatively small amounts are sufficient to completely alter the mesoscale architecture of the deposited biomorphs. In contrast, SrCO_3 crystallization accounts for up to 30 % in equimolar $[\text{Sr}^{2+}]$ and $[\text{Ba}^{2+}]$ solutions.

3.4 Crystallographic Analysis

We perform powder X-ray diffraction (PXRD) measurements on the crystal aggregates that form when the inorganic dopants are added with a concentration of 1 mM (20 %). Regardless of the nature of the inorganic additive, these samples are dominated by the orthorhombic witherite peaks at 23.9°, 24.3°, 34.4°, 42.2°, 44.9°, 46.9° (Figure 4, bottom black curve). This result proves conclusively that crystalline BaCO_3 constitutes the major portion of the biomorphs at these reaction conditions. In a second set of experiments, we prepare solutions of $[\text{M}^{2+}] = 4 \text{ mM}$ (80 %). The PXRD spectra of the calcium-containing (Figure 4, red curve) and zinc-containing (orange curve) products show no distinct peaks and are

predominantly amorphous aggregates. By comparison, the addition of magnesium ions to the crystallization solution produces a partially crystalline material with the characteristic witherite peaks (green curve). Similarly, the lead-doped aggregates have a crystalline character and are identified as $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ or hydrocerussite (21.1° , 24.7° , 27.2° , 34.1°). Moreover, the strontium-doped biomorphs (blue curve) consist mostly of orthorhombic strontianite (25.6° , 31.2° , 35.9° , 46.2°) and barium strontium carbonate (29.3°). Finally, the solution with silver ions produces highly crystalline silver chloride which is easily identified by the peaks at 28.0° , 32.5° , 46.3° , 54.8° , and 57.6° (grey curve).

The crystallographic analyses yield important insights into the influence of crystal structure on biomorph growth. Recall that the high calcium and zinc concentrations do not produce any distinguishable mesoscale morphologies, which is consistent with the amorphous nature of the depositing material. In the case of lead ions, the precipitation of hydrocerussite results in a radical departure from the biomorph shapes. Note that this mineral forms at highly alkaline conditions that typically favor the assembly of biomorphs. Similarly, the deposition of a thick layer of silver chloride disrupts the normal growth of the witherite crystals. In contrast, the isomorphism of strontianite and witherite affords the substitution of barium by strontium without significantly straining the orthorhombic structure. As a result, the morphologies obtained in Sr-doped biomorphs are almost identical to the additive-free structures. This role of crystallography in pattern selection is not immediately obvious, especially considering that biomorphs display smoothly curved structures as opposed to the euhedral geometries typically associated with crystals.

3.5 Growth Rate

We conduct *in situ* dynamic light scattering (DLS) measurements for crystallization solutions with $[\text{M}^{2+}] = 1 \text{ mM}$ (20 %). Figure 5a shows two representative autocorrelation functions for a strontium-doped (solid, blue curve) and a calcium-doped solution (dashed, red curve) acquired 30 s after initiating the reaction. Using the DLS data, we monitor the evolution of the average particle radius (R_H) in the early stages of the experiment (Figure 5b). The additive-free (open, black circles) and strontium-doped solutions (filled, blue circles) follow similar monotonically increasing trends. Surprisingly, all the other dopant solutions (colored markers) form micrometer-sized aggregates as early as 20 s after initiating the experiment. This effect is confirmed by visual inspection of the crystallization solutions which become turbid almost immediately after mixing. Note that these colloidal particles rapidly grow beyond the range of light scattering techniques and hence further measurements do not provide reliable values.

To delineate the underlying causes of the enhanced growth rates, we perform XRD measurements on the aggregates that form within the first 15 minutes of crystallization. In the case of silver and lead ion dopants, the rapidly growing particles consist of AgCl and $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ respectively. In contrast, the presence of calcium ions induces the rapid formation of mostly amorphous aggregates. A similar result has recently been ascribed to the specific interactions between the silicate and “hard” calcium ions that facilitate the condensation of amorphous silica [16]. Surprisingly, the Mg^{2+} and Zn^{2+} additives play a different role in the growth process. These dopants promote the rapid formation of primarily BaCO_3 crystals at a significantly faster rate than the typical biomorph crystallization.

4. Conclusion

We have investigated the influence of alkaline earth and transition metal ions on the synthesis of silica-carbonate biomorphs. Trace amounts of the dopant metal carbonates lead to significant structural and compositional variations in the deposited aggregates. In the exceptional case of strontium ions, the dopant species are readily incorporated in the orthorhombic crystal lattice with no appreciable effect on the biomorphs. The role of crystal structure in this process is particularly interesting, since the mesoscale biomorph architectures are seemingly not constrained by crystallographic symmetries. This effect is ascribed to nano-sized building blocks in the biomorph structures which are capable of assembling non-euhedral and smoothly curved geometries. In addition, our results highlight three different mechanisms by which the biomorph synthesis is disrupted: the formation of competing crystals (in the presence of Ag^+ and Pb^{2+} ions), the rapid condensation of amorphous silica and carbonate (Ca^{2+}), and the enhanced rate of witherite crystallization (Zn^{2+} and Mg^{2+}). For the reaction conditions that successfully produce biomorphs, the crystal aggregates consist of barium carbonate and silica with only negligible fractions of the dopant species. The structures are hence reminiscent of marine biominerals that assemble magnesium-rich calcites [22,23]. As evident in both the natural and synthetic examples, trace deposition of the dopants can determine the morphology, growth mechanism, and physical properties of the crystal assemblies.

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References

- [1] S. Mann, *Biom mineralization: Principles and Concepts in Bioinorganic Materials Chemistry*, Oxford University Press, Oxford, 2001.
- [2] H. Cölfen, M. Antonietti, *Mesocrystals and Nonclassical Crystallization*, John Wiley & Sons, Ltd., Chichester, UK, 2008.
- [3] L.B. Gower, *Biomimetic Model Systems for Investigating the Amorphous Precursor Pathway and Its Role in Biom mineralization*, *Chem. Rev.* 108 (2008) 4551–4627.
- [4] D. Gebauer, M. Kellermeier, J.D. Gale, L. Bergström, H. Cölfen, *Pre-nucleation Clusters as Solute Precursors in Crystallisation*, *Chem. Soc. Rev.* 43 (2014) 2348–2371.
- [5] J.M. García-Ruiz, J.L. Amoros, *Morphological Aspects of Some Symmetrical Crystal Aggregates Grown by Silica Gel Technique*, *J. Cryst. Growth* 55 (1981) 379–383.
- [6] J.M. García-Ruiz, *On the Formation of Induced Morphology Crystal Aggregates*, *J. Cryst. Growth* 73 (1985) 251–262.
- [7] J.M. García-Ruiz, S.T. Hyde, A.M. Carnerup, A.G. Christy, M.J. Van Kranendonk, N.J. Welham, *Self-Assembled Silica-Carbonate Structures and Detection of Ancient Microfossils*, *Science* 202 (2003) 1194–1197.
- [8] M. Kellermeier, H. Cölfen, J.M. García-Ruiz, *Silica Biomorphs: Complex Biomimetic Hybrid Materials from “Sand and Chalk,”* *Eur. J. Inorg. Chem.* 2012 (2012) 5123–5144.
- [9] W.L. Noorduin, A. Grinthal, L. Mahadevan, J. Aizenberg, *Rationally Designed Complex, Hierarchical Microarchitectures*, *Science* 340 (2013) 832–837.
- [10] J.M. García-Ruiz, E. Melero-García, S.T. Hyde, *Morphogenesis of Self-Assembled Nanocrystalline Materials of Barium Carbonate and Silica*, *Science* 323 (2009) 362–365.
- [11] W. Kunz, M. Kellermeier, *Beyond Biom mineralization*, *Science* 323 (2009) 344–345.
- [12] A.E. Voinescu, M. Kellermeier, A.M. Carnerup, A.-K. Larsson, D. Touraud, S.T. Hyde, et al., *Co-Precipitation of Silica and Alkaline-Earth Carbonates Using TEOS as Silica Source*, *J. Cryst. Growth* 306 (2007) 152–158.
- [13] E. Bittarello, F.R. Massaro, D. Aquilano, *The Epitaxial Role of Silica Groups in Promoting the Formation of Silica/Carbonate Biomorphs: A First Hypothesis*, *J. Cryst. Growth* 312 (2010) 402–412.
- [14] T. Terada, S. Yamabi, H. Imai, *Formation Process of Sheets and Helical Forms Consisting of Strontium Carbonate Fibrous Crystals with Silicate*, *J. Cryst. Growth* 253 (2003) 435–444.
- [15] H. Imai, T. Terada, T. Miura, S. Yamabi, *Self-organized formation of porous aragonite with silicate*, *J. Cryst. Growth* 244 (2002) 200–205.
- [16] J. Eiblmeier, S. Dankesreiter, A. Pfitzner, G. Schmalz, W. Kunz, M. Kellermeier, *Crystallization of Mixed Alkaline-Earth Carbonates in Silica Solutions at High pH*, *Cryst. Growth Des.* 14 (2014) 6177–6188.
- [17] K.J. Davis, P.M. Dove, J.J. De Yoreo, *The Role of Mg^{2+} as an Impurity in Calcite Growth*, *Science* 290 (2000) 1134–1137.
- [18] K.J. Davis, P.M. Dove, L.E. Wasylenki, J.J. De Yoreo, *Morphological consequences of differential Mg^{2+} incorporation at structurally distinct steps on calcite*, *Am. Mineral.* 89 (2004) 714–720.
- [19] L. Fernández-Díaz, J. Astilleros, C. Pina, *The morphology of calcite crystals grown in a porous medium doped with divalent cations*, *Chem. Geol.* 225 (2006) 314–321.
- [20] F. Nindiyasari, E. Griesshaber, L. Fernández-Díaz, J.M. Astilleros, N. Sánchez-Pastor, A. Ziegler, et al., *Effects of Mg and Hydrogel Solid Content on the Crystallization of Calcium Carbonate in Biomimetic Counter-diffusion Systems*, *Cryst. Growth Des.* 14 (2014) 4790–4802.
- [21] E. Nakouzi, Y.E. Ghoussoub, P. Knoll, O. Steinbock, *Biomorph Oscillations Self-organize Micrometer-Scale Patterns and Nanorod Alignment Waves*, *J. Phys. Chem. C* 119 (2015) 15749–15754.

- [22] M.E. Kunitake, S.P. Baker, L.A. Estroff, The effect of magnesium substitution on the hardness of synthetic and biogenic calcite, *MRS Commun.* 2 (2012) 113–116.
- [23] J.J.M. Lenders, A. Dey, P.H.H. Bomans, J. Spielmann, M.M.R.M. Hendrix, G. De With, et al., High-Magnesian Calcite Mesocrystals: A Coordination Chemistry Approach, *J. Am. Chem. Soc.* 134 (2012) 1367–1373.

Figure Captions

Figure 1. Optical microscopy images of the control morphologies for the silica-barium carbonate system. (a) Leaf-like sheet, worm-like braid, and twisted helicoid. (b) Flower-and-leaf pattern that forms close to the solution-air interface. The arrows indicate topographic features that are observed as banded patterns. Scale bars represent 80 μm .

Figure 2. Phase diagram showing the influence of inorganic additives on the morphology of the crystal aggregates. The effect of Ca^{2+} , Mg^{2+} , Zn^{2+} , Pb^{2+} , Ag^+ , and Sr^{2+} is studied at five different concentrations. The percentage values represent the fraction of these inorganic additives relative to the total metal ion concentration ($[\text{M}^{2+}] + [\text{Ba}^{2+}]$). The solid, blue line groups the reaction conditions that show the least divergence from the control morphologies while the dashed, red line indicates the conditions that yield no distinguishable carbonate aggregates. Field of view in each frame: $0.28 \text{ mm} \times 0.28 \text{ mm}$.

Figure 3. SEM images of the crystal aggregates obtained in biomorph solutions doped with 0.5 mM of (a) Ca^{2+} , (b) Mg^{2+} , and (c) Sr^{2+} ions. The highlighted regions are selected for chemical composition measurements using EDS. Scale bars: 20 μm (left panels) and 2 μm (right panels). Bottom right image width: 2 μm .

Figure 4. Powder X-ray diffraction patterns of the precipitate structures obtained from solutions of $[\text{Ba}^{2+}] = 1 \text{ mM}$, $[\text{SiO}_3^-] = 8.4 \text{ mM}$, and $[\text{M}^{n+}] = 4 \text{ mM}$. The additives used are from top to bottom: silver (gray), strontium (blue), lead (purple), magnesium (green), zinc (orange) and calcium ions (red). The bottom, black curve corresponds to a solution of $[\text{Ba}^{2+}] = 4 \text{ mM}$, $[\text{SiO}_3^-] = 8.4 \text{ mM}$, and $[\text{Mg}^{2+}] = 1 \text{ mM}$.

Figure 5. (a) Autocorrelation functions acquired 30 s after initiating the reaction in a solution of strontium-doped (solid, blue) and a calcium-doped solution (dashed, red). The concentrations are $[\text{Ba}^{2+}] = 4 \text{ mM}$, $[\text{SiO}_3^-] = 8.4 \text{ mM}$, and $[\text{M}^{2+}] = 1 \text{ mM}$. (b) Evolution of particle size with time for additive-free solutions (black, open circles) and solutions containing Sr^{2+} (blue, filled circles), Ca^{2+} (red squares), Mg^{2+} (green, upward triangles), Zn^{2+} (orange, downward triangles), and Pb^{2+} ions (purple crosses).

Single column

Figure 1

Double column

Figure 2

Single column

Figure 3

Single column

Figure 4

Single column

Figure 5