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Effect of inorganic additives on the growth of silica–carbonate biomorphs

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ABSTRACT

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.

1. Introduction

Living organisms have evolved creative crystallization pathways for building inorganic structures with remarkable precision and control [1]. The exploration of abiotic 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 silicate 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 [9–12]. 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 [8,13,14]. The continuous influx of CO_2 into the reaction medium prompts the co-precipitation of $BaCO_3$ and silica, which assemble into a composite structure.

Several studies have reported the synthesis of non-$BaCO_3$ 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 [13,15]. 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 [14,16,17]. 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 [18–21]. 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 this 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 ([$BaCl_2$] = 1–5 mM,

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$[Na_2SiO_3]=8.4$ mM) is placed in a Petri dish (Greiner Bio-One, 35/10 mm) that is open to the air. Different alkaline earth 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 ($[Ba^{2+}]+[M^{n+}]$) 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 h.

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 × 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 Kα 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°, and 110°) results in no appreciable deviation from the reported trends.

3. Results and discussion

3.1. Control morphologies

Fig. 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 (Fig. 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 (Fig. 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, Fig. 1b). These oscillatory features represent topographic modulations that form during biomorph growth [22].

3.2. Morphology characterization

In the following, we consider the morphologies in Fig. 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 $BaCO_3$.

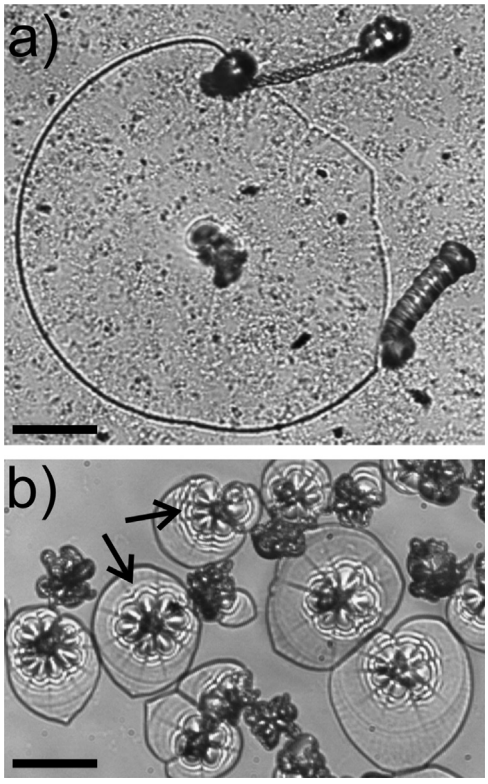

Fig. 1. Optical microscopy images of the control morphologies for the silica–barium carbonate system. (a) Leaf-like sheet, worm-like braid, and twisted helicoid. (b) Flower-and-leaf pattern that forms close to the solution–air interface. The arrows indicate topographic features that are observed as banded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

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 (Fig. 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

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