



Crystallography of Biomimetic Silica Carbonate Precipitates

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In this contribution, we describe the orientational distribution of the carbonate crystallites within some silica carbonate biomorphs. Such precipitates with biomimetic morphologies are formed in alkaline silicate solutions containing barium ions which react with carbon dioxide dissolved from ambient air. We conclude that elucidation of the detailed crystallography and crystallite patterns of a wider range of biomorphs will be vital before any models of their formation can be confirmed.

1. Introduction

Aggregates of astonishingly life-like shapes precipitate from basic silicate solutions that contain alkaline earth metal ions [1]. These biomimetic morphologies (biomorphs) can be so life-like that they may be mistaken for early fossils [2-4]. From the materials-science point of view, these structures are extremely interesting as they can serve as models for the synthesis of new ceramic materials with hierarchical structure and complex form.

It is well documented that these biomorphs comprise amorphous silica and nanocrystalline alkaline-earth carbonate (formed by trapping carbon dioxide from the air) but although structures of biomorphs have been studied [1-10] there is still only limited information about their details and the underlying chemical and physical processes for this remarkable self-assembly. In principle, two models have been put forward: [9] the “top-down” model in which the silica membrane dictates (and templates) the shape [6] and the “bottom-up” model, in which local twist constraints between adjacent nano-crystallites dictate the shape [8, 10] In this contribution, we describe the orientational distribution of the carbonate crystallites of some biomorphs.

The crystal structure of barium carbonate, witherite, consists of a hexagonally close-packed array of Ba ions (compressed along the c-axis) with the carbonate groups laying flat in all octahedra (Fig. 1a and b). In alternate rows along $\langle 100 \rangle$ the carbonate triangles are rotated in opposite directions (accompanied with a shift up or down along the c axis). This lowers the symmetry of the substructure ($P6_3/mmc$) and gives rise to the orthorhombic ($Pmcn$) crystal structure of witherite. The common witherite twinning relates to rows of carbonate groups within the orthorhombic structure being able to lie along one of the three possible $\langle 100 \rangle_{\text{hex}}$ directions resulting in three possible twin orientations. For initial indexing of selected area electron diffraction patterns (SAEDP) of the nanocrystalline witherite of the biomorphs, we ignore the direction of the ordering pattern of the carbonate groups and only use the underlying $P6_3/mmc$ sublattice.

2. Sample preparation

The helical biomorphs were synthesised by mixing 1 ml of a 10 mM BaCl_2 solution with 1 ml of a 17 or 8.5 mM silicate solution (calculated on the basis of monomer) in a plastic cylindrical open container ($\varnothing = 1.5$ cm, $h = 1.7$ cm). Prior to mixing, the pH of the silicate solution was adjusted to 11.3 with 0.1M NaOH.

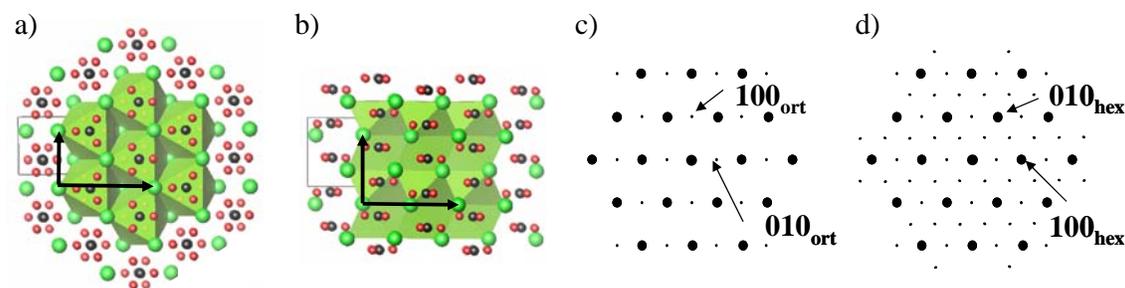


Fig. 1. The crystal structure of witherite shown along a) $[001]_{\text{hex}}$ and b) $\langle 100 \rangle_{\text{hex}}$. The reciprocal lattice of witherite c) indexed in the conventional $Pmcn$ space group and d) showing all three possible witherite twin directions and indexed using the underlying $P6_3/mmc$ subcell.

3. Results

Typical morphologies of some selected biomorphs are shown in Fig. 2. Polarised light micrographs (Fig. 3a) of a thin (ca. 10 micron) section of a worm like biomorph (such as Fig. 2a) confirm orientational order of the carbonate crystallites suggested from scanning electron micrographs [9]. The direction of the black Maltese cross in Fig. 3a relative to the biomorph shows that the crystallites tend to align perpendicular to the biomorph surface. Images from transmission electron microscopy (TEM) in Fig. 3b and c are compatible with this, as the axis of elongation of crystallites lies perpendicular to the edge of the aggregate.

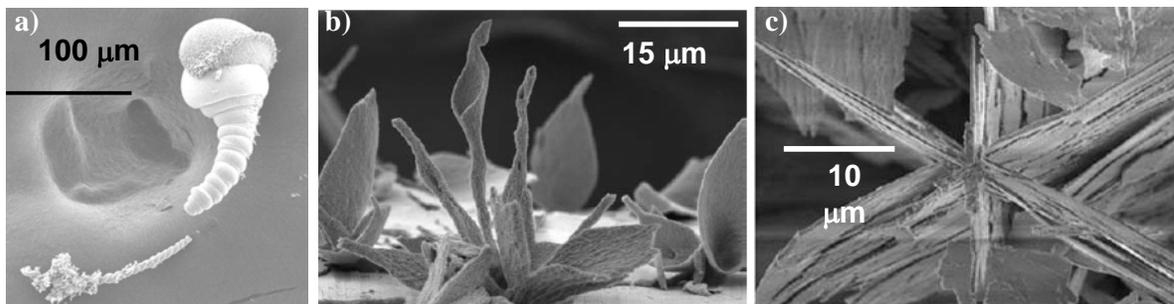


Fig. 2. Examples of biomorphs from a) a standard experiment ($\text{BaCl}_2 = 5\text{mM}$, $\text{SiO}_2 = 8.5\text{mM}$, 298K) b) the standard concentrations 368K and c) low silica concentration (4.2 mM) and 378K.

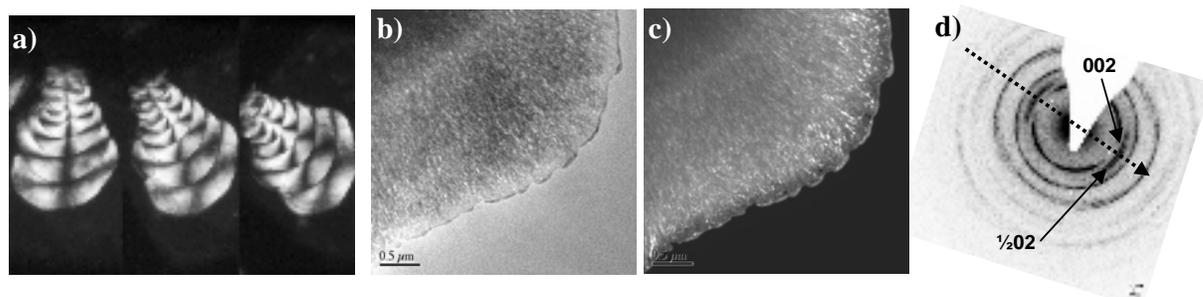


Fig. 3. a) Polarised light micrograph, b) Bright Field and c) Dark Field (from around 002) TEM images of a biomorph such as in Fig. 2. d) SAEDP of the area in b) and c) are indexed in the hexagonal sub cell.

The SAEDP in Fig. 3d confirms that the average c axis is oriented perpendicular to the edge and shows that spread in c -axis orientation is about 50° within the illuminated area. Note also that the reflection $1/2 02_{\text{hex}}$ (equivalent to 012_{ort}) is present confirming that the carbonate groups are at least partially ordered *within* twin domains. It is not trivial to extract more information from these SAEDPs as preparation of thin sections of the tiny aggregates usually destroys some or all of the biomorph external surfaces.



It was found that by increasing the temperature to 70°C, sheet and band like formations thin enough to examine by TEM could be grown directly on carbon-coated copper grids (Figs. 2a, 4a and 4b). SAEDP from the band in Fig. 4b shows a single-crystal-like $\langle 110 \rangle_{\text{hex}}$ SAEDP (Fig. 4c). Upon tilting the band either + or - 30° around the *c* axis, apparent $\langle 100 \rangle_{\text{hex}}$ SAEDPs (Fig. 4d) indicate an average six-fold rotation axis of the sampled area. The weak superstructure reflections (originating in the orthorhombic ordering of the carbonate groups) appear in all $\langle 100 \rangle_{\text{hex}}$ and $\langle 110 \rangle_{\text{hex}}$ zone axis SAEDPs but are always much weaker than in a $\langle 100 \rangle_{\text{ort}}$ or $\langle 010 \rangle_{\text{ort}}$ SAEDP of witherite. This is all compatible with these superstructure reflections in each zone axis arising from only one of the three possible twin orientations. The bands in Figs. 4a and b hence consist of small crystallites collectively oriented essentially as one single crystal with respect to the underlying hexagonal average structure, but with all three twin orientations present.

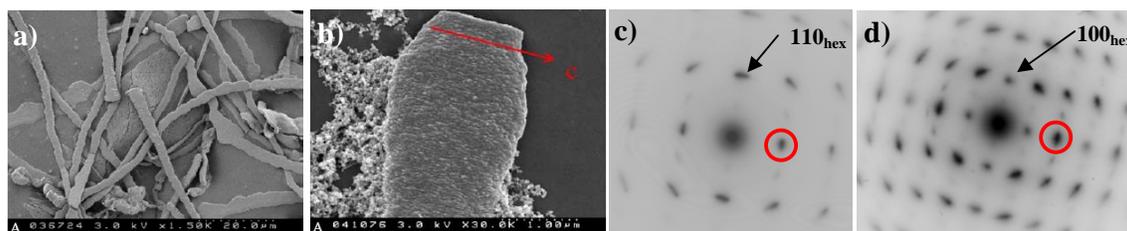


Fig. 4. a) and b) FESEM images of band-like formations from the same sample as Fig. 2b. c) and d) EDPs of the tip of the band in b) with the 002 reflection circled.

If the temperature was increased to 80°, and [SiO₂] lowered from 8.5 to 4.2 mM, further crystallographic ordering of the crystallites was documented. SAEDPs from the “leaves” of crystallites shaped as palm trees (Fig. 2c) reveals that they always consist of two out of the three possible twins.

We conclude that elucidation of the detailed crystallography of a further range of biomorphs will be vital before any models of their formation can be confirmed.

Acknowledgments

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