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Fluid-flow-templated self-assembly of calcium carbonate tubes in the laboratory and in biomineralization: The tubules of the watering-pot shells, Clavagelloidea

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ABSTRACT

We show with laboratory experiments that self-assembled mineral tube formation involving precipitation around a templating jet of fluid — a mechanism well-known in the physical sciences from the tubular growth of so-called chemical gardens — functions with carbonates, and we analyse the microstructures and compositions of the precipitates. We propose that there should exist biological examples of fluid-flow-templated tubes formed from carbonates. We present observational and theoretical modelling evidence that the complex structure of biomineral calcium carbonate tubules that forms the 'rose' of the watering-pot shells, Clavagelloidea, may be an instance of this mechanism in biomineralization. We suggest that this is an example of self-organization and self-assembly processes in biomineralization, and that such a mechanism is of interest for the production of tubes as a synthetic biomaterial.

Statement of Significance

The work discussed in the manuscript concerns the self-assembly of calcium carbonate micro-tubes and nano-tubes under conditions of fluid flow together with chemical reaction. We present the results of laboratory experiments on tube self-assembly together with theoretical calculations. We show how nature may already be making use of this process in molluscan biomineralization of the so-called watering-pot shells, and we propose that we may be able to take advantage of the formation mechanism to produce synthetic biocompatible micro- and nano-tubes.

1. Introduction

In this work we are interested in the fluid-flow-templated self-assembly of calcium carbonate tubes. Self-assembled fluid-flow-templated tubes are found in the physical sciences, in the so-called chemical gardens commonly seen in chemical demonstrations in the laboratory, and also in such geophysical cases as hydrothermal vents on the ocean floor and brinicles under sea ice. All of these examples fall within the field of chemobrionics [1]. We first present the results of laboratory experiments in which we grew self-assembled calcium carbonate tubes in a chemical-garden setup. We describe and illustrate the microstructures found and analyse their compositions.

Biomineral tubes are often secreted around an organism, or part of it, that forms a template about which the tube assembles. One can think of the example of the shipworm, *Teredo*, a bivalve mollusc that bores into wood in a marine environment, and mineralizes the tube it forms about itself, and there are many more instances of biomineral tubes templated around the body of an organism, both in extant species and from the fossil record. One can see the same body-templating biomineralization mechanism operating in another group of bivalve molluscs, Clavagelloidea, the watering-pot shells, which form a biomineral, so-called adventitious tube about their soft body.

This paper puts forward the hypothesis that biology may on occasion use a different method of forming a biomineral tube; that

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of templating mineral tube formation around a liquid jet, as in physical chemobrionic systems. We propose that in contradistinction to the body-templated adventitious tubes of Clavagelloidea, the complex structure of biomineral tubules that forms the 'rose' of their watering pot may be formed through a fluid-flow-templated self-assembly mechanism.

2. Carbonate chemical gardens

In the physical–chemical reaction process dubbed a chemical garden a jet or plume of liquid containing some salt reacts with another metal salt in the surrounding fluid. At the interface between the two reagents, the reaction products precipitate as solids [1]. Chemical gardens are classically grown in three-dimensional containers by placing a solid metal salt seed into another metal salt solution (Fig. 1). When the solid metal salt starts dissolving in the external solution, a semi-permeable membrane forms by precipitation across which water is pumped by osmosis from the external solution, further dissolving the salt. Above a given pressure, the membrane breaks. The dissolved metal salt solution further precipitates in contact with the external solution, producing a collection of mineral forms that resemble a garden, among which tubes that template about the fluid jet or plume are prominent. This growth results from a complex combination of osmosis, buoyancy and reaction–diffusion processes [1]. Here we concentrate on the formation of tubes of calcium carbonate.

Chemical gardens have a long history, and it is convenient to summarize earlier work involving carbonates [1]. In the second half of the nineteenth century, Harting performed a great deal of work on the artificial production of organic forms of calcium carbonate [2]. Subsequently, at the beginning of the twentieth century, Leduc [3] showed chemical-garden tube growth from carbonate solutions. Leduc's tubes used phosphate and sometimes silicate together with carbonate. Copisarow also performed work with carbonates in the early twentieth century [4,5]. Coming now to the recent past, several groups have examined carbonate chemical gardens. Maselko and coworkers have performed experiments with carbonate, often together with hydroxide [6–9]. Ooshima and coworkers [10,11] have reported carbonate tubes growing from membranes. The work of Ibsen et al. [12] involved carbonate chemical gardens grown from a gel. And Haudin et al. [13] have compared carbonate with silicate chemical garden patterns in two dimensions.

Carbonate chemical-garden tubes are also found in geology: some alkaline hydrothermal vents — so-called 'white smokers — precipitate carbonates. In particular the Lost City vent field is formed almost entirely of calcium carbonate in its calcite and aragonite polymorphs, as well as of brucite (magnesium hydroxide) [14,15].

In our experiments reported below we used solutions of sodium carbonate and sodium hydroxide for external solutions and solid polycrystalline seeds of calcium chloride.

2.1. Experimental methods

The solubility of sodium carbonate is much higher than that of calcium carbonate. Besides, the solubility of calcium carbonate decreases drastically when increasing the pH. Thus, when an internal solution of calcium chloride contacts the external solution of sodium carbonate and sodium hydroxide, calcium carbonate can precipitate.

Non-treated lumps of hydrated calcium chloride of analytical purity were used as seeds for the growth of chemical gardens. Sodium carbonate solutions were prepared with bi-distilled water to concentrations of 4 M, 2 M, 1 M, and 0.5 M. These solutions were mixed with another solution of sodium hydroxide <0.15 M. The aqueous solution was poured into the reactor with the salt with care to avoid trapping air bubbles. The growth process at room temperature was followed as long as necessary for the salt to be dissolved completely. When the process finished, the tubes were removed from the solution, washed with water, and dried in air at 45 °C. Micrographs of the samples were obtained using a Phenom scanning electron microscope (SEM) and a FEI Quanta 400 environmental scanning electron microscope (ESEM). Chemical analysis of the micromorphology observed by ESEM was performed in situ in the FEI microscope using EDX analysis. Micro-Raman spectroscopy analysis was performed using a JASCO NRS-5100 spectrometer with a VIS-NIR laser of 532 nm and 30 mW connected to a confocal microscope.

2.2. Experimental results

With a high-concentration solution of 4 M sodium carbonate and 0.12 M sodium hydroxide, the seed of calcium chloride swelled, taking water from the external solution, presumably owing to osmosis. A white membrane was formed; some fingers were observed on its external surface. No tube formed. During the experiment the membrane detached from the floor of the reactor and rose up until reaching the liquid surface (Fig. 2a). With an optical microscope some small tubes were observed at the surface of this membrane (Fig. 2b). After one day of drying, needle crystals were observed on the surface of the membrane (Fig. 2c and d). With a solution of 2 M sodium carbonate and 0.06 M sodium hydroxide a large irregular membrane was formed without tubes.

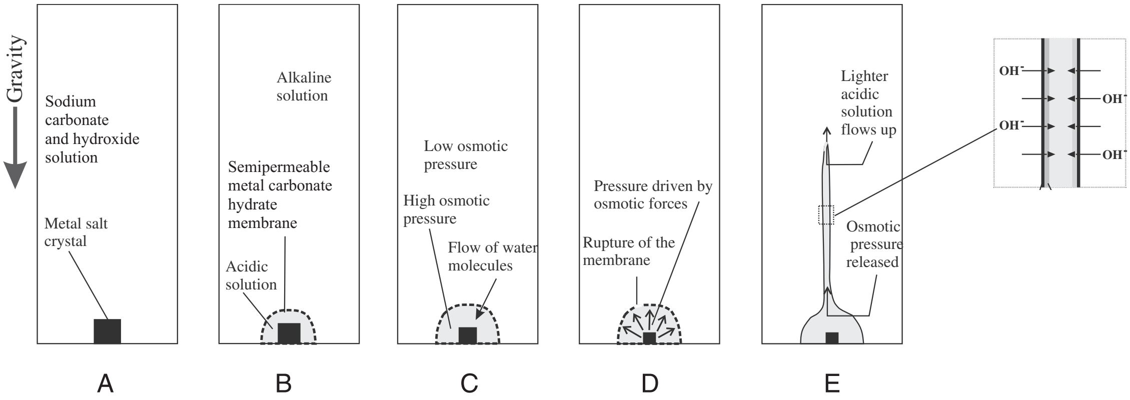

Fig. 1. Chemical-garden growth: (a) setup at start of the reaction, (b) membrane formation between acidic and basic solutions, (c) osmotic pressure is higher within membrane than outside it, so it expands, (d) under osmotic forces the membrane ruptures, and (e) a tube forms [1].