



# Carbonate-hydroxide chemical-garden tubes in the soda ocean of Enceladus: Abiotic membranes and microtubular forms of calcium carbonate

Silvana S.S. Cardoso<sup>a</sup>, Julyan H.E. Cartwright<sup>\*,b,c</sup>, C. Ignacio Sainz-Díaz<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB2 3RA, UK

<sup>b</sup> Instituto Andaluz de Ciencias de la Tierra, CSIC–Universidad de Granada, E-18100 Armilla Granada, Spain

<sup>c</sup> Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, E-18071 Granada, Spain

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## ABSTRACT

We present the results of laboratory experiments with carbonate-hydroxide chemical gardens designed to reproduce the possible conditions of mineral precipitation at a hydrothermal vent in the alkaline ocean of Saturn's moon Enceladus. We describe the membranaceous and tubular structures that form in this self-organized system. We analyse the resulting material morphology, composition and microstructure using scanning electron microscopy (SEM), micro-Raman spectroscopy, X-ray diffraction (XRD), and energy dispersive X-ray analysis (EDX). We find that, as well as more common minerals such as calcite and vaterite, a significant amount of gaylussite may form under conditions present in Enceladus' soda ocean. We discuss how gravity differences may affect the growth of such chemical-garden structures on Enceladus compared to on Earth.

## 1. Introduction

Enceladus, a moon of Saturn, has an ocean, and that ocean could contain life. This is a premise that is currently provoking a great deal of interest and research (Steel et al., 2017). A leading theory for the emergence of life on Earth is that it emerged at alkaline hydrothermal vents on the ocean floors (Martin and Russell, 2007; Martin et al., 2008; Russell et al., 2014; Sojo et al., 2016). Fleshing out the bones of that hypothesis involves investigating the physics and chemistry taking place at those vents, in which the self-organized growth of membranaceous and tubular structures termed chemical gardens might be key to their being the cradles of life (Barge et al., 2015; 2017). Thus, the possibility of hydrothermal vents in the ocean of Enceladus (Matson et al., 2007; Hsu et al., 2015; Sekine et al., 2015; Waite et al., 2017) — a subsurface ocean on a waterworld that is, moreover, a soda ocean probably of an alkaline pH similar to that of some soda lakes on Earth (Postberg et al., 2009; Hsu et al., 2015; Glein et al., 2015) — likewise raises the question of their putative geochemistry, ultrastructure and composition. This knowledge can then contribute to the debate about whether the moon's ocean might harbour life. Here we present the results of an experimental investigation of chemical gardens grown in the laboratory under conditions similar to those found in Enceladus' soda ocean.

The outline of the paper is as follows. First, we summarize previous research on chemical gardens in general and carbonate chemical

gardens in particular, for those who may not be familiar with such work. Next, we investigate experimentally the various forms of calcium carbonates obtained from a chemical garden produced using sodium carbonate and sodium hydroxide solution and calcium chloride, in which a self-organized chemical pump mechanism forms microtubular precipitates emerging from a vesicular structure composed of an abiotic semipermeable membrane with osmotic properties. Analyses of the material morphology, composition and microstructure have been performed using scanning electron microscopy (SEM), micro-Raman spectroscopy, X-ray diffraction (XRD), and energy dispersive X-ray analysis (EDX). The walls of the tubes are formed by a conglomerate of spheres in a disordered way without a continuous structure and are consequently very fragile. Different polymorphs of calcium carbonate have been found, mainly calcite and vaterite. With high concentrations of Na<sup>+</sup>, a significant amount of gaylussite, hydrated sodium calcium carbonate, has been found in the surface of the vesicles formed. Following this presentation of the experimental results, we discuss them with regard to their interpretation and their application to Enceladus. We complement the experiments with a theoretical exploration of how the different gravitational conditions on Enceladus might affect the growth of hydrothermal vent precipitates. We end with some conclusions.

\* Corresponding author at: Instituto Andaluz de Ciencias de la Tierra, CSIC–Universidad de Granada, E-18100 Armilla Granada, Spain  
E-mail address: [julyan.cartwright@csic.es](mailto:julyan.cartwright@csic.es) (J.H.E. Cartwright).

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## 2. Carbonate chemical gardens

Carbonates are at the frontier of the biotic and abiotic worlds, found in both mineral and biological systems and often linked to biomineralization processes (Lowenstam and Weiner, 1989; Cartwright et al., 2016). Multiple forms of carbonates are found in biominerals formed through sophisticated mechanisms involving organic membranes and biopolymers. These proteins can control the transformation of amorphous calcium carbonate into different crystal polymorphs (Cartwright et al., 2012), and also the morphology of the solid structure, forming composites of carbonate with a small amount of organic matter. Such bio-composites thus make up microstructures possessing particular mechanical properties that are even today still difficult or impossible to reproduce artificially. Biological systems utilize biomineralized forms of carbonates for multiple purposes. In many cases, biominerals are formed templated by a biopolymer around the soft body of an organism for protection; this can be observed in molluscs, for example (Cardoso et al., 2016). In any biomineralization activity many chemical reactions are mediated through enzymes and other biopolymers. However, physical processes also occur involving osmotic and buoyancy forces; these physical phenomena take place also in the abiotic world, such as in chemical gardens.

Chemical gardens are biomimetic plant-like structures formed abiotically by metal-ion salts when immersed in a solution with specific anions. A semipermeable membrane is formed surrounding the salt seed preventing the outflow of ions from the seed but allowing the inflow of water from the external solution driven by osmosis. The internal part swells with more water dissolving the salt seed and increasing the internal pressure. Depending on the properties of the membrane, this increases its volume until it breaks. The internal solution then flows out in a jet reacting with the external solution forming a tube around the fluid flow growing by precipitation. The morphology of the structures formed is a product of the forced convection, driven by osmotic pressure, owing to the semipermeable membrane and free convection from buoyancy, since the ejected solution has generally lower density than the external solution. The final result is a combination of vesicles and tubes of different sizes and shapes, resembling a garden of plants. The self-organized and self-assembled formation of semipermeable precipitation structures has been termed chemobrionics (Barge et al., 2015).

Most effort has been dedicated to research on chemical gardens based on silicate solutions owing to their low solubility and high stability. Less attention has been paid to carbonate chemical gardens. Harting (1872) performed a great deal of work on the artificial production of organic forms of calcium carbonate. Leduc (1911) mentioned using mixtures of carbonates, phosphates and silicates. Copisarow (1927, 1929) also performed work with carbonates. More recently, Maselko and coworkers have performed experiments with carbonate, often together with hydroxide (Maselko and Strizhak, 2004; Maselko et al., 2005; 2014; Kiehl et al., 2015). Takiguchi et al. (2006); Igarashi et al. (2008) have reported carbonate tubes growing from

membranes. The work of Ibsen et al. (2014) involved carbonate chemical gardens grown from a gel. And Haudin et al. (2015) have compared carbonate with silicate chemical garden patterns in two dimensions.

In one of our previous series of experiments to form barium silicate gardens, we were surprised to detect the formation of some precipitates that proved to be carbonate precipitated with the CO<sub>2</sub> adsorbed by the silicate solution as a by-product that was not directly related with the particular reactants being used (Cartwright et al., 2011). This finding gave us the idea to explore the formation of chemical gardens with carbonates. In previous work, we showed that biological self-assembled tube formation involving precipitation around a templating jet of fluids may follow similar physical routes to those involved in the formation of chemical gardens of carbonates (Cardoso et al., 2016).

Here we are interested in carbonate chemical gardens that may be forming at hydrothermal vents in the subsurface ocean of Saturn's moon Enceladus. Our experiments aim to produce similar geochemical conditions to those at such vents (Barge and White, 2017).

## 3. Experimental methods

Solutions of sodium carbonate with NaOH were used as external solutions. Non-treated lumps of analytical grade CaCl<sub>2</sub> hydrate were used as seeds for the generation of chemical-garden structures. In some cases, cylindrical pellets formed of 400 mg of this salt were also used. For preparation of these pellets, the salt was homogenized with an agate mortar and pressed into cylindrical pellets of 10 mm diameter and 1 mm in thickness using a cell at a pressure of 10 bar over 10 min. Several concentrations (aliquots of 4 M, 2 M, 1 M, and 0.5 M) of sodium carbonate were prepared with Milli-Q membrane-purified water. In some instances, this solution was mixed with another solution of [NaOH] < 0.15 M. The aqueous solution was poured carefully into the reactor with the salt seed avoiding trapping air bubbles. The growth process experiments were performed at room temperature and were followed as long as necessary for the salt to dissolve completely. The structures formed were removed from the solution at the end of the process and dried in air at 45°C. The morphology of samples of these materials was studied by means of micrographs obtained using Phenom and FEI Quanta 400 environmental scanning electron microscopes (ESEM). The micromorphology observed by ESEM was analysed chemically in situ in the FEI microscope by using EDX analysis. Micro-Raman spectroscopy was performed with a JASCO NRS-5100 spectrometer using a visible/near-infrared (VIS-NIR) laser of 532 nm and 30 mW connected to a confocal microscope. Powder X-ray diffraction was performed using a PANalytical XOPert PRO diffractometer and Cu wavelength. Identification of the crystallographic phases through diffractograms was performed using the Xpovder program (Martin, 2004).

**Table 1**  
Summary of experimental results.

[Na <sub>2</sub> CO <sub>3</sub> ] (M)	[NaOH] (M)	forms	materials
4.0	0.12	vesicles	halite, gaylussite, vaterite, ACC <sup>a</sup> , calcite <sup>b</sup>
2.0	0.06	vesicles	"
1.33	0.04	vesicles	"
1.0 <sup>c</sup>	0.03	tube + vesicle	-
1.0	0.03	tubes	halite, calcite, ACC <sup>a</sup> , vaterite <sup>b</sup>
0.8	0.02	tubes	"
0.5	0.015	tubes	halite, calcite, ACC <sup>a</sup> , vaterite, Ca(OH) <sub>2</sub>

<sup>a</sup> Amorphous calcium carbonate.

<sup>b</sup> Small amount.

<sup>c</sup> With pellet of CaCl<sub>2</sub>.

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