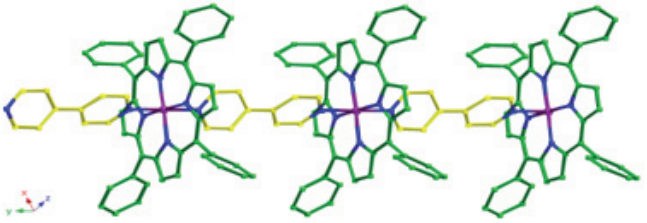
this is the first structure with these ligands based on Fe, one of the most important metals in porphyrin biosystems.



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Confined nanovolumes for the study of calcium carbonate nucleation

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The use of confinement in small volumes is a really helpful method for locating and, thus, observing a nucleation event, as the probability of observing the formation of supercritical nuclei during a nucleation process is very low, due to its stochastic nature [1]. In addition, confinement allows mononuclear nucleation to be reached, which is of great interest for biomaterial science, as controlled biomineralization processes occur in compartmented well defined volumes [2].

A better understanding of nucleation mechanisms could lead to new approaches to crystallization of pharmaceuticals and nanomaterials for instance, as well as mentioned biomineralization studies. In this context calcium carbonate is a good substance model because of its important role in biomineralization [3], [4], and also due to its industrial applications, as filler or pigment in plastics, rubber, drug and food industry [5]. There have been reported many methods to realize confinement (at the nanometer scale) in the literature [1]: controlled-pore glasses or other nanoporous materials and small droplets . Microemulsions are also used to produce confinement in order to measure critical nucleus size via thermal behavior. In order to observe the effect of confinement on the kinetics of crystallization, here we use a droplet microfluidic method [6] in Teflon capillaries and a controlled microinjector that generates micrometer droplets [1].

Here we propose a method for studying the nucleation process of calcium carbonate in microliter to femtoliter range, in order to study the effect of the decrease of volume and depletion of reactants during nucleation and crystal growth. Supersaturation required for nucleation has been reached through direct mixing of equimolar solutions of $CaCl_2$ and Na_2CO_3. The microdroplets were observed at room temperature by optical microscopy, and induction times have been measured for different supersaturations. Kinetic data obtained from measured induction times at different volumes are in agreement with values previously reported in literature [7].

Crystals and precipitates have been characterized using Scanning and Transmission Electron Microscopy, X-Ray diffraction and RAMAN spectroscopy. Preliminary results show the formation of metastable hollow hemispheres at nanoliter range, which transform to faceted calcite crystals and spherulites of polycrystalline vaterite aggregates. The formation mechanism of these hollow hemispheres may be due to the high supersaturation and a template effect of the interface between droplets and oil, however further investigations are being carried out.

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Gelling environments influence on the calcium carbonate precipitation: relevance in biomineralization

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Organisms have been producing mineralized skeletons for the past 550 million years. Much knowledge has been gained over the years on biomineralization processes, however many aspects remain still unclear. One well established issue is that the deposition of calcium carbonate by organisms occurs in a biological confined environment with gelling properties[1]. However, the influence of gels (controlled diffusion) on the deposition of calcium carbonate is still unclear.

In this work, we investigated the role of the degree of entanglement of agarose gel molecules, i.e. different ions diffusion and confined spaces, in calcium carbonate precipitation in the presence of skeletal acidic macromolecules from corals.

Scleratinian coral skeletons are built of aragonite crystals, which are induced to form within a not-well understood organic matrix. It is known that the deposition of calcium carbonate occurs in a biological confined environment with gelling properties. However, it is still a theme of discussion at which level the calcification occurs under biological or environmental control.

The experiments were carried out using a U-tube system following the Counter Diffusion Technique[2]. The U-tube has a column which is accessible to diffuse reagents from two source reservoirs. That is, $CaCl_2$ and $NaHCO_3$ solutions diffused one against the other through a partial gel media (agarose). The agarose was mixed with a different concentrations of soluble organic matrix (SOM) to observe the difference between the $CaCO_3$ crystallization with and without SOM. The organic matrix was extracted from the *Balanophyllia europea*, a solitary Scleratinian coral living in the Mediterranean Sea. The