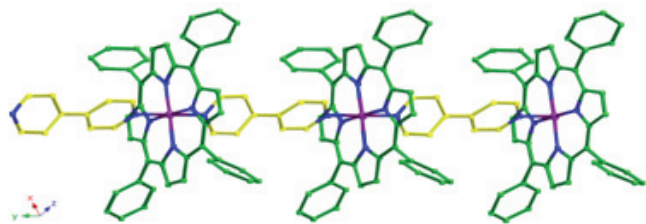


this is the first structure with these ligands based on Fe, one of the most important metals in porphyrin biosystems.



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Keywords: metalloporphyrins, supramolecular chemistry

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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 CaCl₂ and Na₂CO₃. 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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Keywords: nucleation, confinement, biomineralization

MS14.P07

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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, CaCl₂ and NaHCO₃ 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 CaCO₃ crystallization with and without SOM. The organic matrix was extracted from the *Balanophyllia europea*, a solitary Scleratinian coral living in the Mediterranean Sea. The

resulting precipitates were characterized by Infrared Spectroscopy, X-ray diffraction and the morphology of crystals was observed by an optical microscope and a scanning electron microscope.

The results showed that SOM influences not only on the agglomeration, morphology, size and polymorphism of the CaCO_3 crystals but also narrows the range of calcium and carbonate critical concentrations necessary to induce nucleation, the "Crystals-Growing Space". Thus, it appears evident that in gelling environment the SOM is able to select a specific calcium and carbonate concentration. That, respecting the supersaturation laws, confines the nucleation and growth processes.

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Keywords: biomineralization, organic matrix, gelling environment

MS14.P08

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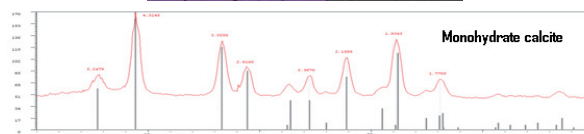
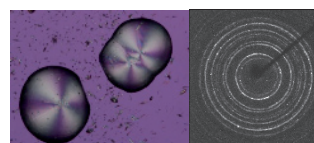
Self-assembled crystalline materials of calcium carbonate and silica

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Biom mineralization is a widespread crystalline phenomenon among living systems which provides superior microscopic and macroscopic material properties, which has aroused a great deal of interest and in vitro studies throughout the past years [1]. Moreover, the self-assembly of alkaline-earth metal carbonates in the presence of silicate is an outstanding example in biomineralization, as purely inorganic precursors cooperate in this case to constitute special structures and shapes strongly reminiscent of biological forms [2]. This kind of completely inorganic, self-assembled silica-carbonate aggregates showing a wide range of non-crystallographic, biomimetic morphologies and sizes from a much simpler system compare to living organisms [3]. However, the precipitation of calcium carbonate (CaCO_3) in basic silica has not produced the similar forms characteristic of biomorphs in the absence of any additives at room temperature until now.

Here we report an experimental study of the crystallization of calcium carbonate in silica gel at ordinary temperature and pressure. The experiments have been performed by diffusion-reaction technique in a diffusion cell, without the presence of organic additives. The concentrations of CaCl_2 and Na_2CO_3 have been varied from 0.05M to 0.2M in equimolar amounts and the gel pH value from 9.0 to 10.5. The crystals have been characterized by XRD, SEM and optical microscopy. After the screening of pH we have specially studied the crystallization at pH=10.5.

At this pH the results are the precipitation of the following crystalline phases with the increase in reagent concentrations: monohydrate calcite, calcite and aragonite. Microscopic observation of these crystalline phases reveals that monohydrate calcite is formed as peanut-like and hemispheric crystals in the liquid part of the system (see figure) whereas calcite (rhombohedral and sheaf of wheat morphologies) and aragonite (flower-like and lamellar morphology) are found out in the gel part. The formation mechanisms and specially the way in which silica interact with calcium carbonate to produce these morphologies is being deeply investigated.



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Keywords: silica gel, monohydrate calcite, calcite, aragonite

MS14.P09

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Coordination polymers of *N,N'*-bis(pyridin-4-ylmethyl)hexanediamide (L): Ligand conformation and the effect of metal to ligand ratio

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The X-Ray crystal structures of four coordination complexes namely: $[\text{Cd}(\text{L})_{1.5}(\text{NO}_3)_2]_n$ **1**, $\{[\text{Cd}(\text{L})(\text{H}_2\text{O})_4](\text{NO}_3)_2(\text{H}_2\text{O})_2\}_n$ **2**, $\{[\text{Zn}_2(\text{L})(\text{H}_2\text{O})_5](\text{NO}_3)_2(\text{H}_2\text{O})_2\}_n$ **3** and $\{[\text{Zn}(\text{L})(\text{H}_2\text{O})_4](\text{NO}_3)_2(\text{H}_2\text{O})_2\}_n$ **4** are described. It was found that the ligand conformation [1] and the metal to ligand ratio [2] play an important role in determining the structure of the resulting complex. By varying the metal to ligand ratio and keeping other experimental factors constant, different coordination complexes were obtained.

Complex **1** was grown from cadmium nitrate and *N,N'*-bis(pyridin-4-ylmethyl)hexanediamide (L) in a metal ratio of 2:1. The complex consists of 2-D networks which are linked by self complementary amide hydrogen bonds. Complex **2** was grown from cadmium nitrate and L in a metal to ligand ratio of 1:1 and it consists of 1-D chains that are interlinked by hydrogen bonding via the nitrate anion. The three independent ligands in complex **2** adopt the AAA (anti-anti-anti) and GAG (gauche-anti-gauche) conformations while the ligands in complex **2** adopt the GAG conformation. Complexes **3** and **4** were grown from zinc nitrate and L in metal to ligand ratio of 1:2 and 1:1 respectively. Complex **3** consists of discrete and dinuclear units that are linked by hydrogen bonding via the coordinated water molecules. Complex **4** consists of 1-D chains that are interlinked by hydrogen bonding via the nitrate counter ions. The ligands in complex **3** are arranged in the AAA conformation while the ligands in complex **4** are arranged in the GAG conformation.

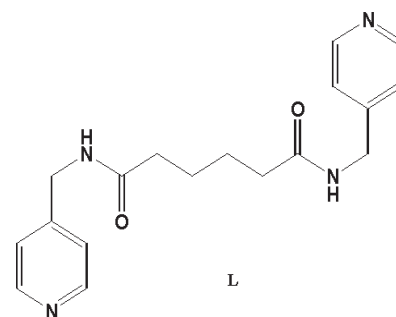


Fig 1. *N,N'*-bis(pyridin-4-ylmethyl)hexanediamide (L).