

[1], [2].

A sequence of bidimensional X-ray diffraction patterns were acquired in transmission mode at regular intervals across the shell thickness. The scattering or degree of preferential orientation of crystals was calculated from the intensity profile along the selected Debye-Scherrer rings (χ -scans).

The degree of crystal orientation was determined from the angular length of the arcs displayed in the Debye rings on the 2D X-ray diffraction patterns. The values of reflection intensities, degree of orientation and crystallinity show progressive variations within during the same shell layer as well as abrupt changes at the transitions between layers with different microstructural organizations. This study provides useful insights into both the mechanisms that control the development of order in mollusc shell microstructures and those that determine the switch between layers with different microstructural organizations.

This information could be of interest to understand the processes of self-assembly that happen in these biomaterials and may be applied to the design of bio-inspired advanced ceramic materials.

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Keywords: mollusk shell, crystallographic orientation, X-ray diffraction

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Oriented nucleation of hemozoin at the food vacuole membrane in *P. falciparum*

Sergey Kapishnikov,^a Allon Weiner,^a Jens Als-Nielsen,^b Michael Elbaum,^a Leslie Leiserowitz,^a ^a*Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot (Israel).* ^b*Niels Bohr Institute, University of Copenhagen, Copenhagen (Denmark).* E-mail: sergei.kapishnikov@weizmann.ac.il

The nucleation of hemozoin (HZ) in the digestive vacuole (DV) of *Plasmodium falciparum* in malaria-infected red blood cells (RBCs) is a topic of current interest. HZ crystals have been reported encased within neutral lipid nanospheres in the DV, which appears inconsistent with the concepts of catalyzed nucleation of HZ at a lipid surface and inhibition of nucleation of HZ via antimalarials that target the HZ crystal surface. To resolve this conundrum, we probed the orientation of HZ crystals in the DV, their position, the site and mechanism of nucleation. HZ crystal clusters in the RBCs were detected and their amount estimated by microfocus X-ray Fe-fluorescence, and their orientations determined by microfocus X-ray diffraction. The diffraction patterns were interpreted in terms of HZ crystals aligned along their needle axes, arranged on a curved surface, exposing their {100} side faces. Using various microscopy techniques, including stain-free cryogenic soft X-ray tomography, freeze-fracture SEM and thin section TEM, we find that nucleation occurs in proximity to the DV inner membrane, where furthermore we find a thickened lipid coating. Morphological evidence supports the {100} orientation facing the lipid, consistent with interpretation of X-ray diffraction results (mentioned above) and *in vitro* nucleation of synthetic hemozoin at various interfaces.

Keywords: biomineralization, malaria, hemozoin

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Single crystal growth and characterization of lead hydroxyapatite

Oratai Saisa-ard, Kenneth J. Haller, *School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.* E-mail: Oratai_phasai@yahoo.com

Calcium hydroxyapatite (CaHAP, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) is the dominant component of human enamel, dentin, and bone. Its structure belongs to space group $P6_3/m$ and is susceptible to ionic substitution in both anion and cation sites. Pb^{2+} can replace Ca^{2+} in the apatite structure resulting in lead hydroxyapatite (PbHAP) which is isostructural with CaHAP. This work reports products from a gel crystallization method used for preparation of larger crystals of PbHAP by controlling nucleation and crystal growth rate by changing the density of the gel medium. Crystals obtained in milli-scale on top of the gel exhibit equant morphology while crystals inside the gel layer exhibit pennant morphology. FT-IR spectra of the products exhibit asymmetric (PO) stretching, symmetric (PO) stretching, and (OPO) bending in the 1002-1047 cm^{-1} , 924-956 cm^{-1} , and 518-600 cm^{-1} regions, respectively, and OH stretching at 3555 cm^{-1} . The FT-IR spectrum of the product on top of the gel also showed NO_3^- bands (NO_3^- from lead nitrate starting material) which are not present in the product formed inside the gel layer.

Keywords: hydroxyapatite, apatite, gel crystallization

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Self-assembly of metallated TPP porphyrin by external dipyrindyl ligands

Arkaitz Fidalgo-Marijuan, ^aGotzone Barandika,^b Begoña Bazán,^a Miren Karmele Urriaga,^a Maria Isabel Arriortua,^a ^a*Department of Mineralogy and Petrology, Universidad del País Vasco (UPV/EHU), Leioa (Spain).* ^b*Department of Inorganic Chemistry, Universidad del País Vasco (UPV/EHU), Vitoria (Spain).* E-mail: arkaitz.fidalgo@ehu.es

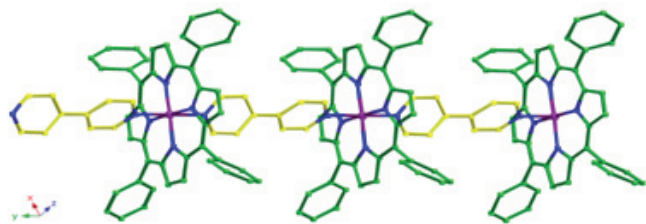
Supramolecular entities based on self-assembly of metalloporphyrins are paradigmatic examples of the great efficiency of the nanodevices used by natural systems in photosynthesis, oxygen transport, electron transfer and catalysis [1]. Therefore, they constitute reference models for the development of new materials that make these, and other yet unexplored, functions.

While metalloporphyrin biosystems operate in solution, the preparation of materials based on these macrocycles moves the problem to the solid state synthesis. Thus, obtaining supramolecular entities may be approached by different strategies of synthetic design. One of them consists on the use of external dipyrindyl ligands to assemble the metallated porphyrin units. In this aspect, the range of compounds that can be used is endless. In this context, our research group is working with different combinations of organic ligands and metalloporphyrins, and the work herein presented corresponds to the compound [FeTPP(bipy)] (TPP=meso-tetraphenylporphyrin and bipy=4,4'-bipyridine), obtained by solvothermal synthesis.

The crystal structure of [FeTPP(bipy)] consists of 1D chains of alternating FeTPP and bipy molecules bonded to the axial positions of the coordination sphere. These chains are sustained by π - π stacking between the phenyl rings at about 5 Å.

So far, very few compounds with TPP and bipy have been described, of which only one [2] is really a 1D coordination polymer, being all others isolated dimers. It is also remarkable that, as far as we know,

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

J. Gómez-Morales,^a S. Veessler,^b I. Rodríguez-Ruiz,^a Z. Hammadi,^b O. Grauby,^b M. Ildefonso,^b N. Candoni,^b J.M. García-Ruiz^a ^a"Laboratorio de Estudios Cristalográficos", IACT/CSIC-UGR, Instituto López Neyra, PT Campus de la Salud, 18212 Armilla (Spain). ^b"Centre Interdisciplinaire de Nanoscience de Marseille" CINaM-CNRS, Marseille (France). E-mail: jaime@lec.csic.es

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

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

M. Sancho-Tomás,^a G. Falini,^b J.M. García-Ruiz,^a S. Goffredo,^c J. Gómez-Morales,^a ^a"Laboratorio de Estudios Cristalográficos, IACT (CSIC-UGR), Granada, (Spain). ^bDipartimento di Chimica "G. Ciamician", Alma Mater Studiorum - Università di Bologna, (Italy). ^cMarine Science Group, Citizen Science Lab, Department of Evolutionary and Experimental Biology, Alma Mater Studiorum - Università di Bologna, (Italy). E-mail: maria@lec.csic.es

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