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Intracrystalline-molecule-induced changes in the crystal structure of biogenic and biomimetic calcium carbonates

Boaz Pokroy, Faculty of Materials Engineering and the Russell Berrie Nanotechnology Institute, Technion Israel Institute of Technology. (Israel). E-mail: bpokroy@tx.technion.ac.il

Nature is replete with materials which are superior to their man-made counterparts. More specifically, in the course of Biomineralization (the formation of minerals in nature) at least 70 biominerals are deposited. The nucleation and growth of these crystals is highly controlled via organic/inorganic interfaces.

These hybrid interfaces are present both between crystallites (intercrystalline) as well as within crystals themselves (intracrystalline). The latter have been found to induce strains in the inorganic crystal which lead not only to deformation of the lattice but also to changes in the crystalline structure, as compared to their non-biogenic counterparts.

Using high resolution synchrotron powder diffraction we were able to measure these strains and changes in crystal structure both in biogenic as well as in biomimetic crystals [1-3]. We found that upon mild annealing we can destroy these hybrid interfaces, leading to relaxation of the strains and to the crystal structure returning to a structure identical to non biogenic counterparts. We also found microstructural changes upon the annealing which are unique to biogenic crystals [4].

It will be shown in addition, that biomimetic crystals which are grown in the lab and contain different biological molecules, exhibit the same structural and microstructural characteristics as those of biogenic crystals.

These results demonstrate that organisms can control not only the polymorph, shape and morphology, but even the crystal structure of their skeletal crystals.

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Control of calcium carbonate precipitation during avian eggshell formation

Alejandro Rodriguez-Navarro,^a Angeles Hernandez-Hernandez,^b Jaime Gomez-Morales,^b Joel Gautron,^c Yves Nys,^c Juan Manuel Garcia-Ruiz,^b ^aDpto. Mineralogía y Petrología, Universidad de Granada, Granada (Spain). ^bLaboratorio de Estudios Cristalográficos, Edificio Instituto López-Neira. Armilla (Spain). ^cINRA, UR83 Recherches avicoles, Nouzilly (France). E-mail: anava@ugr.es

The avian eggshell is a calcified structure which consists mainly of a mineral part (> 95 %) made of calcite crystals and a pervading organic matrix (1 -3.5 %), making a composite material with excellent mechanical properties. The eggshell is a protective barrier for the egg contents that prevents bacterial penetration while allowing the interchange of water and gases needed for the extra-uterine development of the chick embryo. Eggshells have a constant mineralogy and defined microstructure characteristics which are species specific, implying a strict genetic control of this material design [1]. The Eggshell

formation is a simple model of controlled biomineralization processes. Calcium carbonate crystals making the eggshells precipitate out of the uterine fluid which contains calcium and bicarbonate ions as well as the precursor organic components of the eggshell organic matrix. At each stage of eggshell formation, specific organics components are expressed at a given concentration [2]. They are very active and strongly influence calcium carbonate precipitation as has been demonstrated by in vitro crystallization tests [3]. In particular, they affect the nucleation flux, polymorphic phase, crystal size and morphology. Additionally, the characteristic columnar architecture of eggshells and preferential orientation of constituting calcite crystals is the result of a competitive crystal growth process of crystals emerging from pseudoperiodic nucleation centers or mammillary knobs on organic membrane.

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Biodiversity of hierarchical architectures and texture in calcite biomaterials

Wolfgang W. Schmahl,^a Erika Griesshaber,^a Andreas Goetz,^a Klemens Kelm,^b Julia Deuschle,^c Guntram Jordan,^a Alexander Gigler,^a ^aDepartment für Geo- und Umweltwissenschaften, LMU München, (Germany). ^bInstitute for Materials Research, DLR, Köln, (Germany). ^cMPI für Metallforschung, Stuttgart, (Germany). E-mail: wolfgang.schmahl@lrz.uni-muenchen.de

The shell structure of a number of brachiopod species, molluscs, as well as teeth and spines of echinoderms were investigated in high detail and over many length-scales with SEM, AFM, TEM, nanoindentation, micro-Raman spectroscopy and electron backscatter diffraction (EBSD) [1-5]. We are now in a position to identify systematics on the hierarchical architecture of these biomaterials. On the molecular scale the TEM shows that the biocalcite incorporates intracrystalline macromolecules which explains the usual three-to-four-fold increase of hardness of the biocalcite compared to the inorganic mineral as well as the lack of (104) cleavage. With AFM on the nanoscale we always find a mesocrystal architecture which consists of compartments in the 100 nm size-range in the calcite, which are assembled in crystallographic register to form crystals on the higher length scales. In the brachiopod „primary layer“, these crystals form a nanoscale jigsaw-puzzle-like structure of interdigitating dendritic crystals which extend up to 20 micrometers over all branches. The brachiopod „secondary layer“ features mesocrystal fibres which show single-crystal-like coherence over lengths of several hundred micrometers and diameters in the 10-20 micrometer range. The fibres have an axial [0001] texture with the morphological axes perpendicular (sic !) to [0001]. The fibres are separated by organic matrix sheaths. Some molluscs and some brachiopods show layers of columnar calcite, where the [0001] axis is parallel to the columns. The single-crystal columns reach lengths of up to 1mm and widths in the order of 100 micrometers. In the echinodermata the single-crystal-like orientational coherence reaches lengths of several centimeters, covering the length of complete spines, teeth or other skeletal elements. Nevertheless there is a microscale architecture inside these single-crystal-like entities. It leads to a mosaic-spread of crystal orientation in the order of several degrees, however, instead of random mosaic blocks there is an organized fibre- and laminated