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Starfish Grow Extraordinary Crystals

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The growth and form of crystals in vivo – biomineralization – challenges many ideas about crystalline materials. One typically pictures a crystal as a sterile object with a regular geometric form, but nature frequently challenges this preconception. This is beautifully illustrated by the calcite plates (stereom) of echinoderms, which exhibit complex, sponge-like morphologies and curved surfaces, and yet behave as single crystals. Remarkably, the stereom of certain species is highly ordered. Observations of the sea urchin *Cidaris rugosa* more than six decades ago(*1*) identified a stereom reminiscent of one of the three simplest triply-periodic minimal surfaces (TPMS), the so-called P-surface, that possessed a lattice parameter four orders of magnitude larger than that of calcite. On page XXX of this issue, Yang et al. (*2*) provide a new example of a TPMS at this extreme length-scale, Detected in the knobbly starfish *Protoreaster nodosu*, the stereom resembles another simple TPMS, the D-surface.

TPMS-related structures have been reported in a variety of living and non-living systems, from soft liquid crystalline assemblies to hard wing scales and exoskeletons in insects(*3*). The genesis and stability of TPMS with lattice parameters of up to ~100nm *in vitro* can be understood as a relaxed soft membrane assembly, which is the outcome of competing interactions within the molecular constituents of the membranes, e.g. lipids or copolymers (*4*). The three simplest TPMS geometries are the Gyroid (G), Diamond (D) and the Primitive (P), all of which have cubic symmetry. Microstructures related to the G and D geometries have been found in biological chitin assemblies where they far exceed the 100nm threshold. These form the photonic crystals responsible for the iridescence of butterfly wings and weevil carapaces(*5*). The growth of such structures in the wing

scales of butterfly pupae is associated with a particular cellular organelle known as the smooth endoplasmic reticulum, which folds to give a convoluted membrane whose form is strikingly similar to the G morphology(*6*). Templating of the growing chitin crystal by a TPMS-like soft membrane is thus a plausible, though unproven, mechanism explaining formation of these microstructures.

Yang et al. investigated the structure of the stereom formed by the starfish *Protoreaster nodosus* from the angstrom scale, upwards. In contrast to the sea-urchin *C. rugosa*, plates of *P. nodosus* resemble the D-surface and exhibit a 30 μm lattice parameter, a measurement made on the basis of the types and prevalence of structural defects compared with the ideal D-surface. These defects may explain why the structure responds to loading in a way that is reminiscent of soft materials, avoiding brittle fracture commonly associated with calcite. Some of that data suggests microstructural tuning for biological fitness during evolution. However, given the similar defects in mesoporous and amorphous silica grown within synthetic membranes with G-structures,(*7*) this remains speculative.

Yang et al. reveal an extraordinary interplay between the micron and angstrom length scales of the calcite structure, of cubic and rhombohedral symmetries respectively. Despite its atomic-scale crystallinity, the calcite fractures like a glass, unlike the precise cleavage planes exhibited by geological calcite. This can be attributed to the composite structure of biological calcite, in which organic macromolecules are occluded within the crystal lattice. Further, as proposed as early as the 1960s (*8*), it is now accepted that these calcite biominerals are better described as 'mesocrystals', composed of space-filling arrays of calcite nanoparticles, rather than true single crystals (*9*). This structure is a direct consequence of the crystallization mechanism, where biogenic calcite often forms by way of an amorphous calcium carbonate (ACC) precursor phase. The shape of the constituent ACC nanoparticles is then preserved within the product calcite. It is also conceivable that the mesocrystal ultrastructure enables the crystal lattice to warp and follow the shape of the skeletal surface in some echinoderms (*10*).

These findings confirm the extraordinary control that biology achieves over crystallization.

Traditional models of biomineralization emphasize the role of soluble macromolecules in directing crystal morphologies. The D-type TPMS can be considered as a network of linked four-armed tetrapods, whose morphologies could be controlled using soluble additives. Such a model is consistent with the structure observed in the calcite shells of some dinoflagellates, a type of phytoplankton(*11*), which are reminiscent of non-ordered echinoderm stereom in shape, but comprise multiple crystallites. Instead, the echinoderm stereom is templated by an organic matrix that defines its morphology. This has been demonstrated in studies of sea urchin larvae, where mineralization begins with the formation of a triradiate calcite crystal (spicule). Culturing larvae under conditions that change the shape of the organic compartment in which the spicule forms, yields spicules with morphologies defined by this modified compartment.(*12*) More recently, the shape of larval spicules *in vitro* have been engineered by directing the assembly of cultured cells that then generate the 3D environment in which the spicule forms.(*13*)

It has been widely proposed that biomineralization by way of an amorphous precursor phase – which has no preferred geometry – allows the mineral to be molded into complex shapes by templating. However, as seen in both synthetic systems(*14*) and organisms such as coccoliths(*15*), it is not a pre-requisite. With the ease of forming crystals that far exceed the length-scale of the template, and fairly isotropic crystal morphologies, calcite is a perfect construction material for the stereom, where it can fill a template of any shape without a correspondence between the micron-scale morphology of the crystal and its crystal lattice.

The ultimate question of what determines the ultrastructure remains open, however. Given that lipids can assemble into G-, D- and P-TPMS in vitro, and similar assemblies of soft matter are present in butterfly wing-scales, it is possible that the calcite grows within a sponge-like membrane which templates the calcite. That case is strengthened by the presence of both P and D morphologies in echinoderms. However, current knowledge does not explain how those structures can form with huge lattice parameters (over 10 μm). They may be the result of dynamic and coordinated cellular processes, commonly assumed to control morphologies in living systems. Alternatively, they may result from growth within a porous matrix, analogous to the origin of those

structures in synthetic soft materials.

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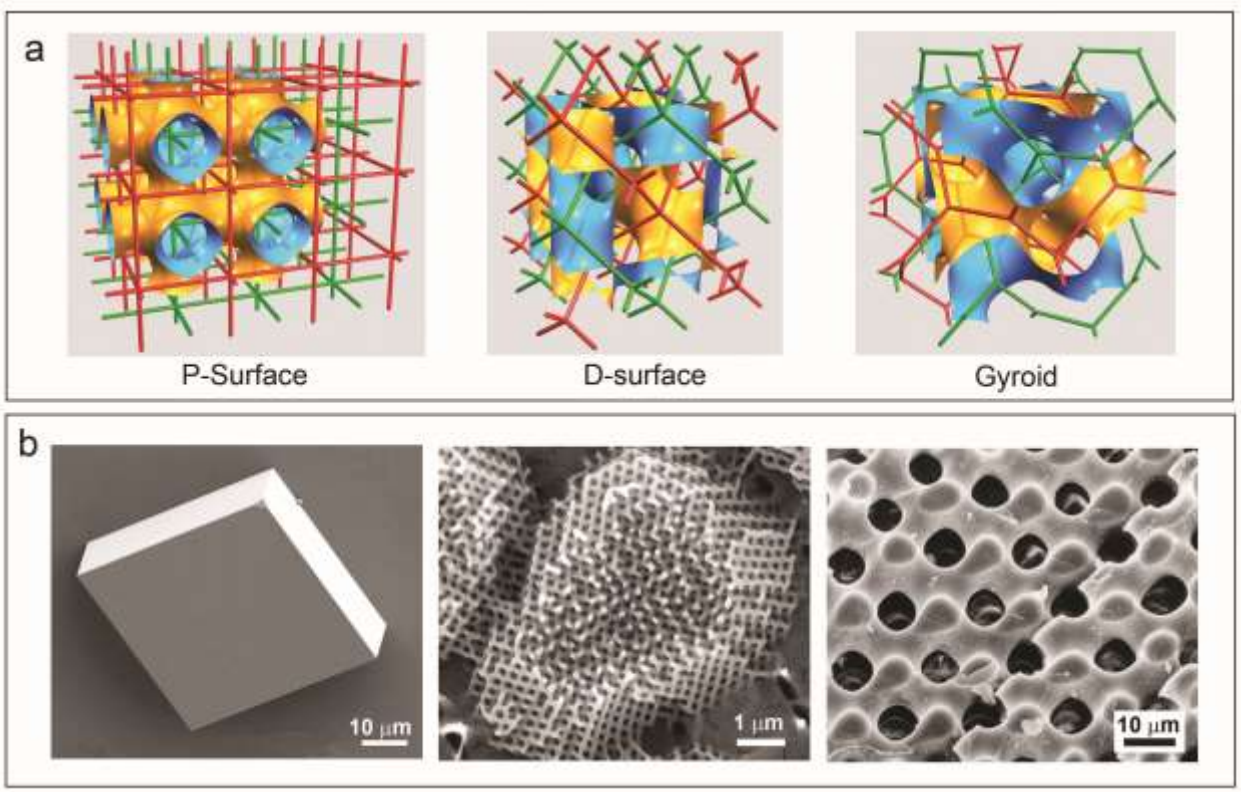

Figure 1: (a) The three simplest triply-periodic minimal surfaces (TPMS): the P(rimitive), D(iamond) and Gyroid surfaces. (b) Scanning electron microscope images of a calcite rhombohedron, chitin gyroid in the green butterfly *Thecla opisena* and a P-surface in the skeletal plate of the sea urchin *Heliocidaris erythrogramma*. We thank Prof Bodo Wilts, Universität Salzburg, for the image of the butterfly scale.