

ratory carbon dioxide, effectively pumping carbon out of the atmosphere to the deep sea (3). Metabolic suppression and anaerobic metabolism, used by some migrators during daytime forays into expansive oxygen minimum zones, may reduce the efficiency of this biological carbon pump in some regions (14). The efficiency of carbon pumping is similarly reduced in the Southern Ocean, where air-breathing mammals and birds are a key component of the food chain. They respire massive amounts of photosynthetically derived carbon back into the atmosphere (13). In contrast, larvaceans increase carbon flux by concentrating particles in their mucus feeding webs that then sink rapidly to depth (15). All these processes depend on the demand for energy, which varies between species by up to three orders of magnitude [see supporting online material (6)].

Despite their potential importance, these and similar phenomena remain

poorly constrained for most oceanic taxa. It is thus difficult to estimate or predict the role of animal function in biogeochemical cycles. The relevant processes must be recognized and quantified, their rates scaled up, and put in the context of global elemental budgets. Wilson *et al.*'s important contribution to our knowledge of the inorganic carbon cycle will hopefully infuse a new appreciation for the role of higher trophic levels in ocean dynamics. Clearly, the field is moving beyond the dismissive viewpoint described by Horne, in which animals were merely a source of "heterogeneity in the sea" [(16), p. 239]. As he noted, "Our element of seawater may well contain an important second phase we have not mentioned—a fish" [(16), p. 3].

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## MATERIALS SCIENCE

# Beyond Biomineralization

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Modern strategies to design advanced materials are often inspired by nature. For instance, during biomineralization, living organisms can impose highly complex shapes and textures with remarkable structural hierarchy upon solid inorganic matter to produce materials that often far exceed the performance of human-made counterparts (1, 2). However, crystallization in purely inorganic systems can also yield smoothly curved forms that resemble those of biomaterials (3). These so-called "biomorphs" are obtained by coprecipitation of barium carbonate (witherite) and silica from alkaline media. A concerted self-assembly process yields nanosized carbonate crystallites that arrange in a highly ordered manner over micrometer lengths, thereby shaping morphologies such as regular helicoids on scales up to millimeters—all in the absence of any complex organic additive or surface scaffold. On page 362 of this issue, García-Ruiz *et al.* use video microscopy to provide insight into several steps decisive for structure evolution and identify a chemical feed-

back process as the driving force for the observed self-organization (4).

A striking similarity between these abiotic biomorphs and most actual biomaterials is their mode of construction, with hierarchical structuring over many length scales and preferential crystallographic orientation. In turn, the chemistry and preparation of the biomorphs are rather simple, thus rendering them excellent model systems to study multiscale interactive self-organizing phenomena.

One of the principles of self-organization explored by García-Ruiz *et al.* is a dynamic, pH-based coupling of equilibria, which induces alternating precipitation of the components. The sensitivity of silicate and carbonate speciation to pH fluctuations in alkaline media, together with pH gradients close to the mineralizing fronts and opposite pH trends in solubility of silica and barium carbonate, are fundamental prerequisites in this context. In other words, an acid and a base (i.e., hydrogen carbonate and silicate) are alternately subject to local neutralization, the latter being directly linked to precipitation. Neutralizing one leads to local conditions under which the other is suddenly out of equilibrium—a situation somewhat reminiscent of the famous

Self-assembly of purely inorganic components can also give rise to complex structures and morphologies once thought restricted to biological materials.

Belousov-Zhabotinsky reaction (5). Silica thereby acts, via precipitation, as an inhibitor for continued carbonate crystal growth first, to stimulate renewed carbonate nucleation later on.

This concept has obvious potential for the design of systems that spontaneously self-assemble to yield highly organized materials. An interesting challenge will be to look for other "acid-base" pairs that would engage in a similar coupled process if conditions are adjusted properly. Simple substitutions such as replacement of barium by one of its alkaline-earth homologs have already been done with success (6, 7). However, the search for alternative reagent pairs should also extend to phenomena beyond those related to pH effects and precipitation; such pairs may be based on a principle analogous to the pH-mineralization feedback. This feedback process teaches us an important lesson: Oscillating precipitation does not necessarily imply periodic structures. The latter arise as a consequence of spatial oscillation, as observed in common banded Liesegang patterns (8). In the present case, oscillation is only of a temporal nature, resulting mainly in encapsulation of carbonate crystallites by silica rather than formation of

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alternating layers. Nevertheless, the oscillatory nature of chemical coupling can become manifest as periodicity in space if initial conditions are chosen appropriately.

The chemical coupling described by García-Ruiz *et al.* nicely explains the origin of the nanocrystals and their uniformity, as well as their sheathing by silica (see the figure, panel A). It also sheds light on the dynamics behind their formation (3). However, details on molecular-scale interactions remain to be clarified, such as how silicate species adsorb or precipitate on the surfaces of growing carbonate crystals.

The circumstances leading to the orientational order of crystallites over mesoscopic

ance of attractive and repulsive forces varies between the tips and the lateral faces of the silica-coated carbonate crystallites, possibly as a result of different charge densities.

Further intriguing questions arise at larger length scales where the global morphology of aggregates evolves. García-Ruiz *et al.* convincingly explain why carbonate undergoes a transition in its mode of growth in the presence of silica, from self-similar branching of one single crystal to continuous formation of nanocrystals toward a polycrystalline assembly. When silica has entirely blocked the initial fractal crystal, new carbonate precipitation is expected to occur as three-dimensional nucleation creat-

ety of complex curved morphologies to a basic mechanism in which the relative directionality of the curling rim segments, as well as their respective growth velocities and height, determine whether helicoids, braids, or worm-like shapes are formed.

But what is the reason for the leaves curling? Is this near-macroscopic curling a consequence of interfacial tension between the medium and the solid surface? Obviously, the crystal assembly starts to turn back at a certain time and grow on itself—which might be an expression of its tendency to minimize overall surface. Or do parameters such as species concentrations or pH change enough in the course of precipita-

tion to favor curved growth? Varying interparticle interactions at lower pH could alter slightly the preferential co-orientation of nanocrystallites in such a way that their assembly inevitably describes a curved surface.

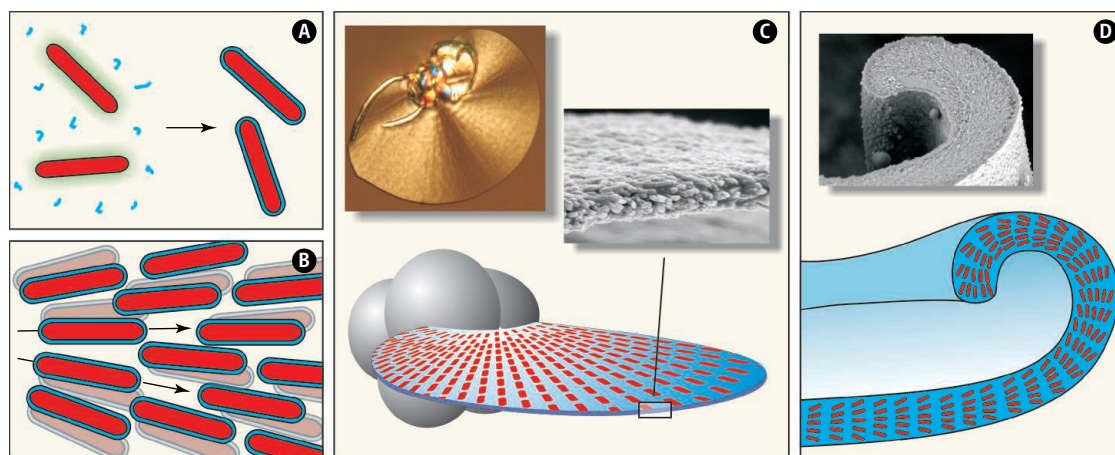
The lessons learned from biomorphs will help to shed more light on the principles nature uses to construct hierarchical architectures. Synergy and intergrowth between components over many length scales are properties innate to both biomorphs and biominerals. Beyond this conceptual similarity, the role of silica as a structure-

inducing additive that itself evolves dynamically during mineralization—rather than being a simple static template—could be the basis for new pathways to fascinating novel materials.

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**Silica-witherite biomorphs.** (A) Rod-like carbonate nanocrystallites (red) become enveloped in a silica skin (blue) as pH gradients around the growing crystallites (green) provoke local silica precipitation. As a result of “chemical coupling” of carbonate and silicate chemistry, nucleation and sheathing occur alternately and coated particles are continuously formed. (B) Coated nanocrystals arrange with an incremental tilt, establishing long-range orientational order throughout their assembly. (C) On global scales, the self-assembly of nanoparticles proceeds at first by developing quasi-2D leaf-like sections. Witherite rods in the leaf describe a radial orientation field, as indicated by distinct interference patterns in polarized optical micrographs. (D) Laminar growth continues until the leaves become scrolled at certain points around their border. The emergent curvature is fueled by propagation of the initial curl along the rim.

lengths remain a mystery: Why do adjacent nanorods arrange with a certain twist with respect to each other (see the figure, panel B), and how is that twist kept constant throughout the assembly? Coated nanoparticles with high aspect ratio, such as rods, have been shown to be versatile building blocks for constructing higher-order superstructures, if the adsorbed layers maintain specific interactions to one another (9). However, the interactions between layers of sheathing silica are by nature quite complicated because of its inherent reactivity. Mutual repulsion results from the negative charges that silica species bear at high pH, whereas attraction can be caused either by hydrogen bonding between protonated groups or direct covalent linking via condensation. The slight misalignment of rods observed in biomorphs suggests that the bal-

ancing numerous crystallites all over the surface (4). Attachment of further nanocrystallites is then, however, observed only along a thin path over the surface, which results in two-dimensional extrusions (see the figure, panel C). This observed two-dimensionality may arise as a result of the sudden precipitation of expanded silica layers on the fractal carbonate crystal and later on the growing leaves. This could effect large-area inhibition of carbonate crystallization, thereby imposing selective growth directions.

The second mystery about the morphological evolution of the crystalline assembly on global scales refers to the actual origin of curvature. According to García-Ruiz *et al.*, leaves continue to grow flat until they curl at certain points around their rim (see the figure, panel D) (4). They describe a physical model that reduces the emergence of a vari-