

A Bright Bio-Inspired Future

Trevor Douglas

Seashells and other biominerals (see the figure) are formed through an intimate association of inorganic materials with organic macromolecules. The macromolecules control the nucleation, structure, morphology, crystal orientation, and spatial confinement of the inorganic phase (1, 2). Materials scientists increasingly use biominerals as an inspiration for new biomimetic materials (3). As shown by Aizenberg *et al.* on page 1205 of this issue (4), such materials can also shed light on biomineralization itself.

The authors suggest a fundamentally new role for the organic architecture in the biomimetic mineralization of large single crystals of calcite, CaCO_3 . They show that an array of organic posts, separated from an engineered nucleation site by relatively large (μm) distances, relieve stress as the mineralization proceeds through a phase change from an amorphous film to a single crystal with millimeter-scale dimensions. Furthermore, the organic posts, embedded in an amorphous layer of CaCO_3 , serve as conduits for the removal of water and impurities from the growing crystal front. This novel model for the role of organic frameworks in biomineralization points to a bright bio-inspired future for materials synthesis.

CaCO_3 is perhaps the most familiar biomineral. It is found in biological systems in a number of polymorphs (crystal structures), including amorphous, vaterite, aragonite, and calcite. However, most biominerals are complex composites of inorganic materials and organic macromolecules (1, 2, 5). The macromolecules also play a role in initiating nucleation and directing crystal growth.

Almost two decades ago, it was shown that acidic macromolecules extracted from a mollusk shell could profoundly influence CaCO_3 mineralization. When attached to a substrate, they would act as a nucleation

catalyst and induce mineralization (6). In model crystal growth experiments (7–9), the ordered polar head groups of organized organic monolayers have been shown to catalyze mineralization of CaCO_3 and control the structure and orientation of the nucleated mineral. This influence results from complementary charge and spatial and stereochemical registry between the inorganic and organic phases.

Furthermore, mineralization underneath modified porphyrin monolayers can induce the formation of an initially amorphous CaCO_3 sheet that subsequently transforms into a crystalline phase (10). As a model for biomineralization, this suggests that an initially deposited amorphous material can undergo a phase change to the final biomineral structure, influenced by interactions at the inorganic-organic interface.

Aizenberg *et al.* (4) have employed self-assembled monolayers (SAMs) on Au or Ag, with disordered head groups, to induce formation of an amorphous CaCO_3 film. A small region of highly ordered SAMs, introduced into the disordered film with the tip of an atomic force microscope, acts

as a nucleation center and catalyzes the phase transition from amorphous to crystalline CaCO_3 . Organic polymer posts are arrayed within the monolayer and have a profound influence on the mineralization process.

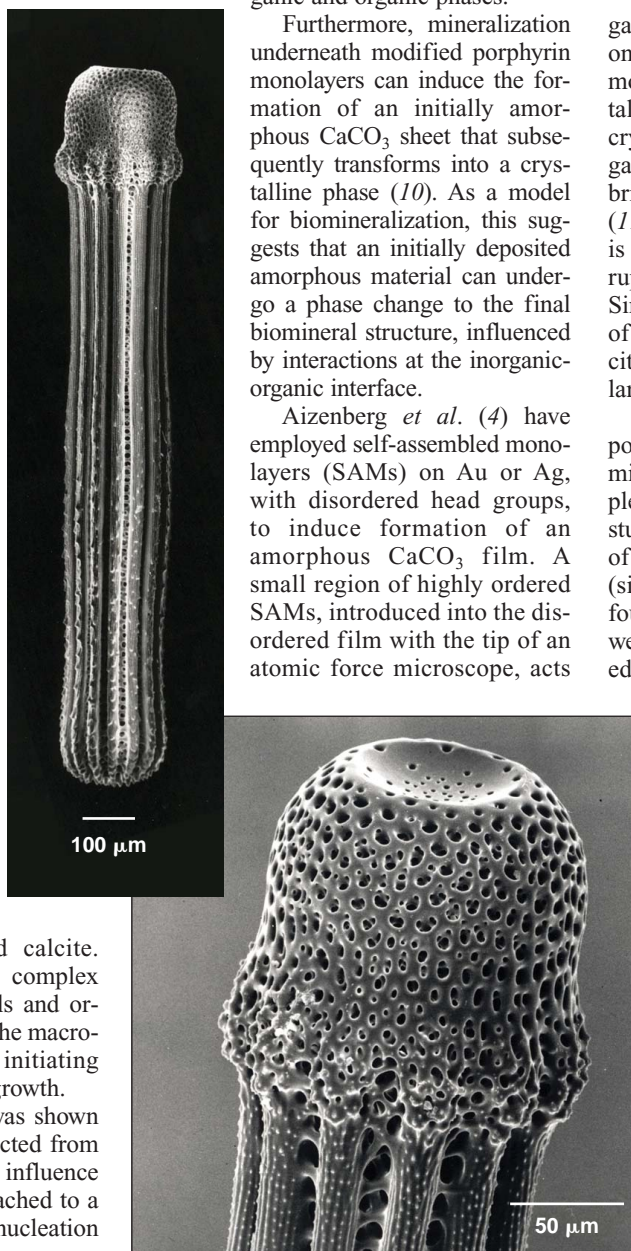
This experimental design is an elegant model for the incorporation of organic macromolecules into an inorganic material, as is often seen in biomineral structures. For example, the nacreous layer of mollusk shells, which gives rise to the mother-of-pearl luster, is composed of crystalline tablets of aragonite arranged into a brick-and-mortar assembly; the mortar is an organic macromolecular layer.

Until recently it was thought that the organic mortar separated the individual aragonite crystal bricks completely. But this model could not explain the perfect crystallographic registry between the aragonite crystals. Schäffer *et al.* showed that the organic layer was porous and that “crystal bridges” could grow through this layer (11). Thus, each stack of aragonite tablets is a single crystal punctuated (but not disrupted) by organic macromolecular layers. Similarly, the end result of the experiment of Aizenberg *et al.* is a single crystal of calcite that is punctuated, but not disrupted, by large organic features.

In other biomineral systems, the incorporation of organic macromolecules into mineral structures remains a source of perplexity. Addadi and Weiner (12, 13) have studied the apparent single-crystal nature of biominerals such as the sea urchin spine (similar to that shown in the figure). They found that it contained up to 0.05% by weight of organic macromolecule, occluded within the inorganic lattice.

Sea urchin spines are composed of Mg-containing calcite. They do not show the preferential cleavage along lattice planes seen in synthetic calcite crystals, but rather fracture conchoidally (like glass). This unusual fracture behavior is a result of the incorporation of proteins, which appear to be adsorbed on specific lattice planes (12) within the crystal. How the large macromolecules are incorporated into these and other biominerals continues to be a puzzle.

Aizenberg *et al.* (4) now show that large organic macromolecules can be incorporated into a crystalline inorganic lattice without disrupting the single-crystal nature of the material. Furthermore, they demonstrate that the large macromolecular posts can act as conduits for the removal of water and impurities as the hydrated amorphous mineral transforms into its final form, and that they are criti-



A porous single crystal. Scanning electron micrographs of a mature sea urchin spine, which is a composite of organic macromolecules and oriented CaCO_3 (calcite).

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cal for releasing tensile stress during the phase transformation. Removal of the organic posts results in the stress-induced formation of polycrystalline films.

The study of biomineralization has influenced a new generation of scientists interested in controlling materials synthesis at both the molecular and macroscopic levels. The understanding that organic macromolecules can facilitate all aspects of the mineral growth and that their incorporation into the material leads to en-

hanced purity and crystallinity (4), as well as increased mechanical strength, will catalyze new enthusiasm for biomimetic approaches to materials fabrication.

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PALEOANTHROPOLOGY

Encore Olduvai

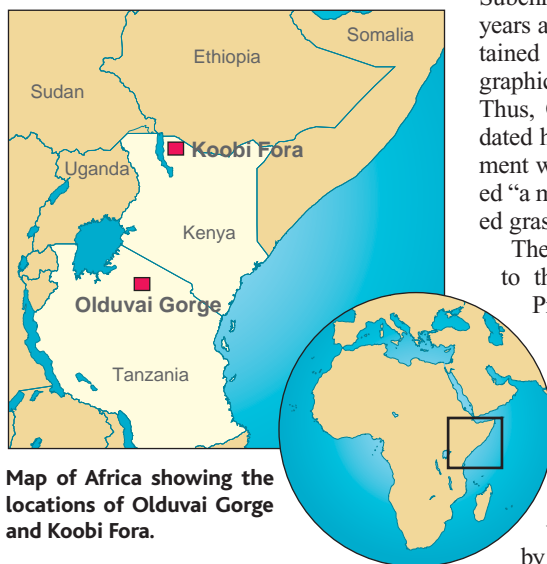
Phillip V. Tobias

On page 1217 of this issue, Blumenshine *et al.* (1) report a new hominin (2) fossil from the Olduvai Gorge in Tanzania (see the first figure). The findings may help to simplify the evolutionary tree of early hominids. The report is particularly welcome in the centennial year of the birth of Louis Leakey, who, with his wife Mary, discovered numerous hominin fossils at Olduvai.

The paleontology of the Olduvai Gorge was first explored in 1911 by Wilhelm Kattwinkel. Two years later, Hans Reck recovered many fossils and a complete human skeleton from the gorge. Although the skeleton still bears the label “Olduvai hominid 1” (OH 1), it was shown later to be a modern human burial into the top of Bed II of the Olduvai sequence. From 1959 to 1976, the Leakeys—especially Mary—did their most productive work at Olduvai (3, 4), discovering hominin fossils OH 4 to OH 56. In 1986, an expedition led by D. C. Johanson and T. D. White found remains of a skeleton, OH 62, and ascribed it to *Homo habilis*. It was the first partial skeleton of this species (5).

About a decade later, Blumenshine and colleagues began to explore the western extension of the Olduvai Main Gorge. Although a few dozen geological localities had been examined there (6), no paleontological or archaeological sites had been recorded. The nearest hominin-bearing site was near the western end of the Main Gorge, where a juvenile parietal bone fragment (OH 25) was found in 1968. West of that site, apart from surface finds of scattered artifacts, no systematic excavation had been carried out and no hominin specimens recovered.

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Map of Africa showing the locations of Olduvai Gorge and Koobi Fora.

The area where the new hominin remains (OH 65) were recovered lies west of the perennial Olduvai Lake shore and northwest of Naisiusiu Hill. Blumenshine *et al.* excavated 11 trenches, taking samples for dating (1). They assign their new specimen to *H. habilis* based on the morphology of the face, upper jaw and palate, dental arcade, and teeth.

In this first report about OH 65, the analysis of face and palate seems to be based largely on anatomical impression. The analysis of tooth measurements could also be more rigorous, given that comparative data are available. For instance, when I calculated “crown areas” of the cheek-teeth, I found a close match between tooth material of OH 65 (751 to 758 mm²), and values recorded (7) for other specimens assigned to *H. habilis* (East African mean 751 mm²). Similarly, shape indices derived from the dental crown diameters of OH 65 cheek teeth reveal a certain degree of elongation and attenuation, a striking feature of *H. habilis*.

It is valuable that the new specimen of *H. habilis* can be placed in a secure geochronological and paleoecological context. The specimen is from the paleomagnetic phase known as the Olduvai Geomagnetic Polarity Subchron, dated to 1.942 to 1.785 million years ago. These dates agree with those obtained by ⁴⁰Ar/³⁹Ar dating for two stratigraphically closely related volcanic tuffs. Thus, OH 65 is one of the most securely dated hominins from Olduvai. The environment was moister than today, and constituted “a mosaic of grassy woodland and wooded grassland” (1).

The authors add an important dimension to the inferred life-style of *H. habilis*. Previous evidence attested that these creatures were terrestrial bipeds, but that they had not thrown off some “evolutionary baggage” that had helped apes and ape-men to adapt to arboreal life. If this applied to West Olduvai hominins, were the trees large enough to bear their weight? If the woodland postulated by Blumenshine *et al.* contained no forest species, then West Olduvai might not have been a favorable long-term environmental niche.

The authors postulate that *H. habilis* made “irregular, seasonal forays to the western basin streams from the ecologically more productive southeastern basin” (1). This idea they find to be consistent with low levels of butchery marking on fossil bones and the use of lava to make artifacts. West Olduvai is at the drier eastern edge of the Serengeti Plain, and Blumenshine *et al.* point out that this area might have supported a resident hominin deme, at least during wetter periods. Such a migratory, resource-, and shelter-based pattern indicates behavioral flexibility and an adaptable life-style of these early *Homo* people. The idea of migratory movements in response to seasonal oscillations recalls the behavioral malleability of *H. habilis* inferred by Isaac (8) from Mary Leakey’s “living floors” at Olduvai. These sites were replete with bones and artifacts, and, famously, in one instance, with a circle of