

elicited non-voluntary movement in the legs.” With help from a machine, the rats could, in effect, walk again, though they weren’t controlling their own movement. Previous work by Lacour’s co-corresponding author, Grégoire Courtine, suggests that electrochemical stimulation can encourage some of the fibers in the injured spinal cord to connect, promoting voluntary leg movement.

“This work represents a significant advance in the development of bio-compatible devices that can be used for

modulation of the functional properties of the spinal cord and brain,” says Reggie Edgerton, a bioengineer at the University of California–Los Angeles, who wasn’t involved in the work. “It is now apparent that there can be multiple strategies to neuromodulate the spinal cord and brain, ranging from indwelling electrodes within the spinal cord to stimulating transcutaneously. Ideally, each can be developed to include in a clinical toolbox from which the best option for a given patient under a given situation

can be selected.” He adds that the next challenge is to establish the real-world durability of e-dura.

Lacour says her team now has a number of parallel experiments to conduct, including testing the longevity of the device and trying to design a completely implantable system that does not have wires leading out of the patient. If successful, e-dura could have a range of important brain–interface applications, such as the long-term monitoring of epilepsy.

Joseph Bennington-Castro

Ion bonding in organic scaffolding promotes biomineralization

The seashells you pick up at the beach might not seem extraordinary, but they are a source of inspiration for researchers searching for efficient ways to store extra atmospheric carbon. Through a process called biomineralization, organisms like mollusks, clams, and corals crystallize excess carbon in their environment into hard calcium carbonate shells. Understanding on a molecular level the way that inorganic minerals interact with a framework of biological macromolecules is a critical step toward mimicking the process in artificial systems—and one that has proven challenging.

Now, an international team of materials researchers has demonstrated that these organic scaffolds influence the crystallization process by binding clusters of positively charged calcium ions, inducing mineral formation in specific locations. The results, published recently in *Nature Materials*, challenge previous assumptions about the molecular-level mechanisms responsible for biomineralization.

“This work is of great value in the realm of fundamental materials science—in particular in the world of living systems, where soft matter controls hard matter,” said Jim De Yoreo of Pacific Northwest National Laboratory.

De Yoreo and his colleagues used liquid-phase transmission electron microscopy (TEM)—a relatively new imaging technology that visualizes atomic-level

activity in liquid samples—to monitor the crystallization process in real time at nanoscale resolution.

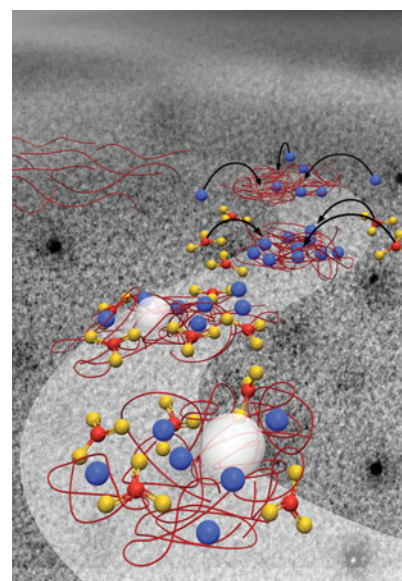
They first observed vaterite and a little bit of calcite, two different calcium carbonate crystal structures, forming in a solution in the TEM.

Then, they repeated the experiment with added polystyrene sulfonate (PSS), an organic polymer with negatively charged side chains that is structurally similar to the macromolecules that guide biomineralization in natural systems.

This time, the mineralization process looked different: Amorphous calcium carbonate (ACC) formed first, then later transformed into vaterite. ACC is a precursor to many biologically based minerals.

To understand how the PSS scaffold interfered with vaterite formation, the researchers mixed the calcium with the macromolecules without the carbonate. The macromolecules clumped together, absorbing the calcium ions to form globules. Once the carbonate was added, ACC crystals only formed within the calcium-PSS globules, and stopped growing once the calcium ran out. The finding suggested to the team that calcium binding to the organic macromolecules mediated how and where the ACC formed.

Having monitored the crystallization process step by step, they concluded that the negatively charged polymer side chains act as a sponge for the positively charged calcium ions (or counterions), concentrating them in specific regions.



Large charged molecules (red) lure in calcium ions (blue), which position carbonate ions (yellow and red) and form amorphous calcium carbonate (white ball).

Biomineralization then readily occurs where the calcium is clustered.

“The sponge makes it possible to locally increase the ion concentration, which makes nucleation easier,” said Nico Sommerdijk, a collaborator in the study from Eindhoven University of Technology in Eindhoven, The Netherlands.

Previous work had suggested an alternate route to crystallization: the scaffold might guide biomineralization by providing a low-energy surface upon which the crystals could deposit themselves in an ordered fashion. The crystals would form



wherever it was most energetically favorable to do so.

These results add to this picture, suggesting that ion binding can sometimes overpower energetic favorability.

“Our experiment shows how important these counterions are to the hard system,” said De Yoreo, referring to the calcium ions that the organic scaffold soaks up. “Even when you make ordered structures out of proteins, the counterions play a huge role.”

Although the idea that ion binding might play a role in the biomineralization process was first suggested by a group of Israeli scientists 30 years ago,

the technology to thoroughly test it was only recently developed.

“Liquid-phase TEM makes it possible to view the whole process—from the binding of calcium ions by the matrix, to the formation of amorphous calcium carbonate and its subsequent transformation to crystalline vaterite—at high resolution, as it proceeds in the reaction solution,” said Fiona Meldrum, a materials chemist from the University of Leeds who was not involved in the research. “In combination with other experimental methods, the work provides new insight into the mechanisms by which organic molecules control crystallization.”

The finding comes at an ideal moment, as concern grows about the impact of excess atmospheric carbon dioxide on the health of the planet. Biomineralization is a natural way to sequester this carbon, removing it from the atmosphere and depositing it elsewhere. Although such technology is a long way from implementation, understanding the process could help researchers recreate it artificially to deliberately remove carbon dioxide from the atmosphere. “Carbon dioxide begs for sequestration,” said De Yoreo. “What we’re looking at here is a way of promoting this process.”

Laurel Hamers

3D-printed structures developed for complex self-evolving deformations

Some technological advances happen by accident. Some happen on purpose. And some are the result of concerted and creative efforts by researchers to explore areas of common interest.

A team of scientists led by Dan Raviv of the Massachusetts Institute of Technology (MIT) has developed a manufacture workflow that combines computationally driven design with printable primitive components, aided by realistic simulations. With this framework, users can design and print non-trivial structures

that bend and stretch in response to their environment. They are not unlike the water-capsule children’s toys that blow up into dinosaurs in water. However, these active structures extend the process to more sophisticated shapes and functionalities that can exhibit controllable responses to a greater variety of external stimuli, including electric fields, temperature, and light. The team’s work is described in the December 2014 issue of *Scientific Reports* (DOI: 10.1038/srep07422).

The design step implemented three basic structural units (or primitives): one bending primitive, and two stretching primitives. These primitives are constituent components of the larger, complex shape being manufactured. The bending primitive relies on differential expansion between fused materials. When stimulated, one side expands at a greater rate than the other side, resulting in a curve. The angle and the plane of the curve are controlled by the dimensions and relative position of the two printed materials.

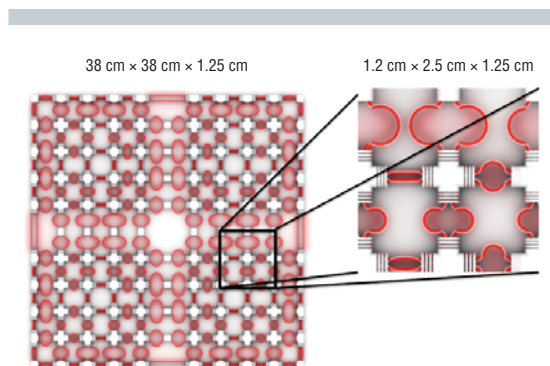
The two stretching primitives use two different schemes. In the first scheme, the mechanism is similar to the bending primitive, except that there is no differential

expansion in the printed object, so the growth is linear. The second stretching scheme uses rings. The rings are printed with different materials on the outside and inside; the inner material expands when stimulated so that the ring elongates, resulting in linear stretching. The mathematical models used in the workflow were developed so the user can design the final form of the active structures, and the computer will print the initial configuration.

The team used a Stratasys Connex 500 multi-material three-dimensional (3D) printer in their work, which enabled them to directly integrate the different materials into the printed structures. The expanding materials were acrylated monomers. When activated—in this case, the materials were hydrophilic, but potentially any stimulus could be used—the monomers assembled into linear chains with a few difunctional acrylate molecules. A hydrogel is created with as much as twice the volume of the original material.

Once they achieved their final form, the printed structures were compared to a simulation. The team used the Project Cyborg design platform, enhanced with Autodesk’s Nucleus system and some additional functionality for modeling the temporal aspect of the deformations. Simulations were restricted to kinematic behavior and did not model atomic movement.

“This was not a one-(person) job. This was truly a multi-author work,” Raviv



A complete example embedding dynamic primitives of stretching and folding on a grid. This grid can accommodate a self-evolving deformation into a complex structure with both convex and concave parts. Reprinted with permission from Nature Publishing Group.