CHEMISTRY

Prompting Complex Patterns To Form Themselves

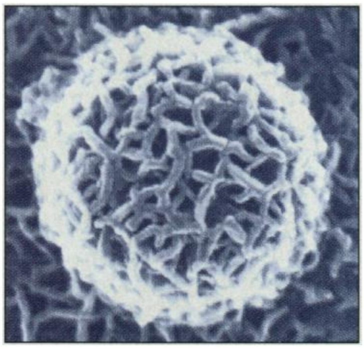
"We've been completely outclassed by nature," laments materials chemist Geoffrey Ozin of the University of Toronto in Ontario, Canada. The objects of his envy are seashells, bones, and other natural structures in which organic molecules, such as proteins, assemble calcium phosphate and other inorganics into complex structures by climbing a hierarchy of size. Atoms align to form crystals, crystals organize to form fibers, and so on, up to features on a scale of millimeters and beyond. Scientists would like to mimic this self-assembling hierarchy, with the eventual goal of creating intricate patterns—such as the circuits on the surface of a silicon computer chip—that put themselves together. But until recently they haven't even come close.

In the past several weeks, however, two separate groups of researchers—one led by Ozin, the other by inorganic chemist Stephen Mann of the University of Bath in England—have made major strides in the mimicry department. The scientists have coaxed inorganic compounds to array themselves around organics, forming a hierarchy of successively larger patterns that runs from the subnanoscopic arrangement of atoms in a crystalline lattice, to larger patterns of inorganic walls surrounding arrays of pores, to groupings of these structures into disks, bowls, and spheres up to 100 micrometers across.

Such structures are still a far cry from a self-made computer chip, but other researchers are hailing these first steps up the ladder of size and complexity. "It's really beautiful chemistry," says Charles Kresge, a self-assembly specialist for Mobil Oil Research in Princeton, New Jersey. Some of the results imply that the formation of these inorganics into large vesicles sets the stage for smaller and more intricate patterns within the vesicle bounds. Adds Pennsylvania State University chemist Tom Mallouk, "It's self-assembled materials synthesis on a new length scale."

Mallouk also notes that these new materials may have practical uses. The porous structures might be used as molecular filters, or as frameworks for holding chemical catalysts. But the initial Toronto materials, at least, may be less suitable as molecular filters, because the pores in these structures have variable diameters, so they can't filter specific molecules by size.

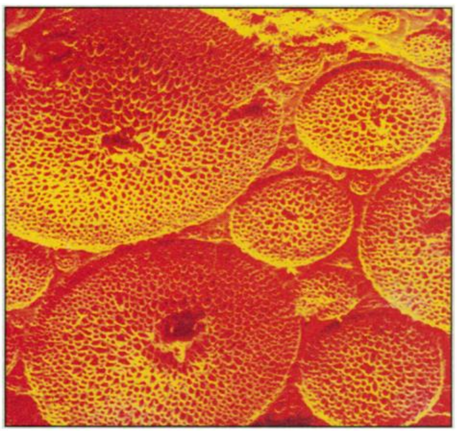
Following nature's lead, both groups enlisted organic molecules as templates to direct the assembly of inorganic molecules. Organics are ideal for this task, explains Ozin, because researchers can precisely design their shapes and charges. In solution, those features cause organics to take on spherical or other configurations and then initiate the assembly of inorganics around these shapes, in effect turning the organic shapes to stone.



D. WALSH AND S. MANN/UNIVERSITY OF BATH

Synthetic skeleton. Calcium carbonate shells, approximately 1.1 micrometers in diameter, assemble into diatomlike skeletons.

Researchers first used a simpler version of this strategy to form porous arrays of crystalline inorganics known as zeolites, which are widely used as molecular sieves in industry (*Science*, 25 March 1994, p. 1698). Typically, zeolites are made by adding positively charged organic template molecules and negatively charged inorganics to water. Attracted by the positive charges, the inorganics cluster around individual organic molecules. Inorganics in these clusters, in an energy-save move known as a condensation reaction, then bond together, creating an array. Washing out the organics leaves an inorganic crystalline material with pores about 10 angstroms in diameter, or about one-thousandth the diameter of a human hair. More recently, researchers have enlisted larger organic templates—groups of organics known as micelles—to create zeolites with pore sizes of up to 100 angstroms.



G. OZIN/UNIVERSITY OF TORONTO

Designer patterns. Organic vesicles prompt the assembly of inorganics into these intricate patterns resembling those found in some marine algae.

Ozin, Scott Oliver, and their colleagues originally set out to construct zeolites with even larger pore sizes by arraying the inorganic building blocks around hollow spheres, or vesicles, made from organic molecules. The Toronto researchers formed their vesicles by mixing an organic surfactant—an alkylamine—with inorganic phosphorus, in the form of phosphoric acid, in a solvent of tetraethylene glycol. They then added aluminum oxide to the solution and heated it, causing the aluminum and phosphorus to react to produce an inorganic layer of aluminophosphate encasing each vesicle.

But the process didn't yield a simple porous array—a zeolite on a larger scale. In the 2 November issue of *Nature* and the November issue of *Advanced Materials*, the group reports ending up with a wide variety of more complex patterns. Among other structures, they saw within the vesicles a maze of tiny dividers, which resemble the patterned silica skeletons of marine algae known as radiolaria. While the jury is still out on exactly why these patterns take shape, Ozin believes it centers within the vesicles. Ozin says one possibility is that the same self-assembly process that creates the large vesicle also creates what amounts to a froth of tiny bubbles within the vesicles. Each bubble has a skin of inorganics, which react to create a maze of inorganic walls within the overall vesicle.

Whatever the explanation, the researchers believe the new structures may ultimately help them understand how organisms such as radiolaria pattern inorganics. It's well accepted that radiolaria use vesicles to pattern inorganic silica, says Mann. And the Toronto experiment shows for the first time that researchers can imitate this large-scale templating, albeit with different molecular building blocks. But he adds that some radiolaria experiments suggest that the natural assembly process may be more complicated, employing proteins and polysaccharides to initiate the growth of inorganics near the inside surface of the organism's cell wall. "We're not necessarily doing it in the same way as nature," admits Oliver. Nevertheless, adds Ozin, "we're using some of the same tools and getting much the same overall shapes."

Whether those shapes will be useful for applications is an open question. The wide variety of architectures and pore sizes in the aluminophosphate skeletons would make it difficult to use the materials as selective molecular filters, says Harvard University chemist George Whitesides. But the Toronto researchers currently have their eyes on other possible applications, such as designing strong yet flexible materials by grading the size of voids from large to small in sheets of their material.

Still, in practical terms, the technique used by Mann and his Bath University colleague Dominic Walsh may be closer to the mark, as it produces porous spheres about 1 micrometer in diameter. The British researchers, who reported their results in the 28 September issue of *Nature*, start by dissolving inorganic calcium carbonate and gaseous carbon dioxide in water. The carbon dioxide converts some of the calcium carbonate into calcium bicarbonate, a more soluble form. The researchers then add oil and a surfactant to ensure a uniform mixture. When the researchers spread this mixture into a thin film and remove some surfactant, two things happen. First, the oil forms droplets in the film, which pack next to one another, forcing the inorganic solution into a meshlike structure surrounding the droplets. Second, this mesh solidifies because the surface-to-volume ratio of the liquid has increased dramatically, causing the CO_2 to quickly diffuse out of solution. As a result, the calcium bicarbonate is converted back into calcium carbonate, which crystallizes out of solution, creating a subnanoscopic crystallization pattern that represents the first layer of the organizational hierarchy.

As this crystallization continues, the calcium carbonate grows to form 15- to 40-nanometer-thick walls surrounding the oil droplets, creating the second level of organization. The Bath team then spread the emulsion over polymer beads 1 micrometer in diameter. When the oil is washed away and the polymer bead is burned out, what remains is the highest level of organization: a branched spherical structure resembling the skeletons of marine algae known as *Thoracosphaera*. And because the holes in these structures are larger than those in conventional zeolites, that may make them useful as filters for large particles such as viruses, says Mann. The overall spherical shape, he adds, may be useful in packing such filters into a chemical separation column.

The final step in the Bath process, of course, isn't quite self-assembly. Although the technique produces porous inorganic spheres all of the same size, such precision is only possible because the researchers layer their emulsion over the plastic beads. So next up for both groups will be to see if they can encourage these systems to take on large uniform shapes without outside help. They're still a long way from self-made silicon chips, but they're getting closer, one pattern at a time.

–Robert F. Service

MEETING BRIEFS

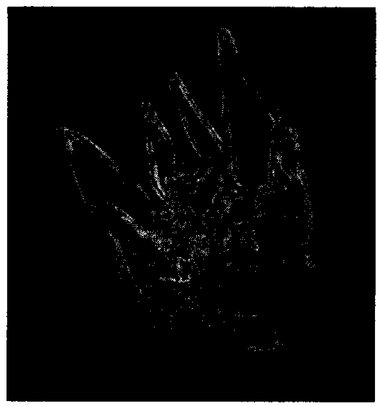
Geologists Debate Ancient Life and Fractured Crust

At the annual meeting of the Geological Society of America (GSA) in New Orleans earlier this month, the juxtaposition of disparate research so typical of earth science gatherings was much in evidence. One day geologists were arguing over how crust under tension could, contrary to theory, break like a layer cake. Two days later paleontologists and developmental biologists were discussing how to disentangle the roots of the animals' family tree, before the first large animal fossils appeared in the record.

Embryos Give Clues to Early Animal Evolution

The Cambrian explosion 530 million years ago raised the curtain on a panoply of different animal forms. Paleontologists, intrigued to know how this dazzling performance was produced, have been trying to peer backstage: They have been searching the fossil record of even earlier times for solid evidence of the key evolutionary steps that led to the debut in the Cambrian Period of animal body plans ranging from arthropods to mollusks. At the GSA meeting, however, developmental biologists had some bad news: The hoped-for solid evidence won't be found.

"It doesn't look good for the traditional paleontologist," says Kevin Peterson of the University of California, Los Angeles (UCLA). "Fossils are not going to help you understand the relationships among the phyla"—the large groups of animals distinguished by their body plans. The reason, he says, is that well before the first fossils were preserved, the diversification took place in "squishy little larvalike things" that would never have been tough enough to show up in the fossil record.


DAVIDSON ET AL.

Rosetta stone? How larvae like this infant sea urchin develop may hold clues to the earliest branchings of the animals' family tree.

The key innovation leading to the current bewildering array of basic body types, say Peterson and his colleagues, was a new scheme of development that allowed microscopic animals to grow beyond a few thousand cells and sculpt themselves in many different ways. The researchers say that those evolutionary steps probably first took place in animals that looked rather like the larvae of modern marine animals: glassy assemblages of cells perhaps less than a millimeter long, which might have lived hundreds of millions of years before the first sizable animal fossils appear in the record.

At the meeting and in a paper on page 1319 of this issue of *Science*, Eric Davidson of the California Institute of Technology (Caltech), Peterson, and R. Andrew Cameron of Caltech argue from work in developmental biology and paleontology that early animals had to overcome a developmental barrier before the many body plans already evident in the Cambrian explosion could evolve. These earliest multicellular animals, the group contends, were limited in size and complexity because their fertilized eggs couldn't divide more than about 10 times before the repeated division hit some limit inherent in the way the embryo controls its development.

The solution to this growth limitation, Davidson and his colleagues say, was the invention of groups of cells, seen in certain kinds of embryos today, that were not immediately committed to developing into a particular type of tissue. These "set-aside cells" could later multiply indefinitely to produce macroscopic animals. To regulate the multiplication and specialization of these cells, the organisms would have had to evolve a complex hierarchy of genetic controls. Evolution, acting on those genetic control mechanisms, could then have produced the variety of body plans that now distinguish one phylum from another.

All this genetic groundwork had to have been laid down in the embryos of larvalike animals that evolved perhaps hundreds of millions of years before the Cambrian explosion. That would put them even earlier than the first fossils of macroscopic animals, the Ediacaran fauna, which appeared by 560 million years ago (*Science*, 27 October, pp. 580 and 598), say Davidson and his colleagues. If