

PALEONTOLOGY

Earliest Animals Old Once More?

TORONTO—In the past month, the apparent age of the first known animals nearly doubled to a startling 1.1 billion years, then swung back to the conventional figure of 600 million years. And last week at the annual meeting here of the Geological Society of America, the pendulum swung one more time, back toward the extraordinarily early dates claimed a month ago. Paleontologists may have to reckon after all with signs of animals 500 million years earlier than the first known animal fossils.

The first dramatic claim came in the 2 October issue of *Science* (pp. 19 and 80), when researchers said they had found tracks of multicellular animals in 1.1-billion-year-old Indian rocks. Then, paleontologist Rafat Jamal Azmi of the Wadia Institute of Himalayan Geology in Dehra Dun, India, claimed in the *Journal of the Geological Society of India* that he had found tiny fossils, known to be from about 540 million years ago, in rocks just above the purported trace fossils. If so, the tracks might actually be only about 600 million years old (*Science*, 23 October, p. 627). Paleontologist Anshu K. Sinha, director of the Birbal Sahni Institute of Paleobotany in Lucknow, noted that Azmi's finds might be confused with certain kinds of sedimentary structure and that his work had not been replicated. But Sinha and other paleontologists who read Azmi's paper and studied scanning electron microscope (SEM) images of the finds concurred that they were indeed small, shelly fossils (*Science*, 23 October, p. 601).

In a question-and-answer session at the meeting, however, paleontologist Nicholas Butterfield of the University of Cambridge reported that after Azmi visited and gave him a look at actual samples, he believes they are not fossils at all but artifacts. "They're very convincing in black-and-white" SEM images, says Butterfield, "but they're absolutely not biogenic when seen in Technicolor" under a light microscope. Once he could view the objects from any angle and under varied lighting, Butterfield concluded that their ribbed structure was simply a reflection of fine layers in the rock itself. The texture of the rock plus the acid treatment Azmi used to extract any fossils apparently created the oddly shaped bits, Butterfield says.

Others also have doubts. Two other Cambridge experts in Cambrian fossils, Simon Conway Morris and Soren Jensen, studied the samples with Butterfield when Azmi visited Cambridge 2 weeks ago, and they agree that the bits are not fossils. Even one-time supporters, such as paleontologist Mar-

tin Brasier of the University of Oxford, who found the photographs persuasive but hasn't seen the samples themselves, now agrees that, based on the Cambridge experts' views, "it looks doubtful that they are convincing."

Azmi, however, stands by his find, saying that Conway Morris studied unpublished fossils rather than the examples cited in his recent paper. He says that Butterfield's "generalized statement" is "very confusing," be-



In the eye of the beholder. Some say the regular pattern on bits of rock like these make them look like fossils, but others say they are only artifacts.

cause it does not address the issue "specimen by specimen." Azmi concludes: "There cannot be any doubt that these are fossils, for they are not artifacts."

Even if this particular challenge to the claim of billion-year-old animal tracks may be fading, paleontologists at the meeting weren't quite ready to embrace such a startlingly ancient origin of animals. Some critics still aren't sure the tracks are those of living creatures. Confirming the age of the rocks may require new radiometric dates, which will take a few years to complete. The age of the first animals is—still—a question mark. —**RICHARD A. KERR**
With reporting from Pallava Bagla in India.

CATALYSIS

Chemical Accessories Give DNA New Talents

Cells have a strict division of labor: DNA conveys genetic information, while proteins run the chemistry of life. Teams of chemists and biologists are now working to bridge that division by creating hybrid molecules that tack the chemically active functional groups of proteins onto DNA's coiled backbone. The goal is to create molecules that are both chemically adept, like proteins, and easy to copy and vary, like DNA—properties that might enable researchers to "evolve" valuable new catalysts. But this elegant scheme faced a serious hurdle: The enzyme that copies DNA, called DNA polymerase, refused to play along, balking when it encountered a modified DNA building block.

Now two groups have managed to outwit

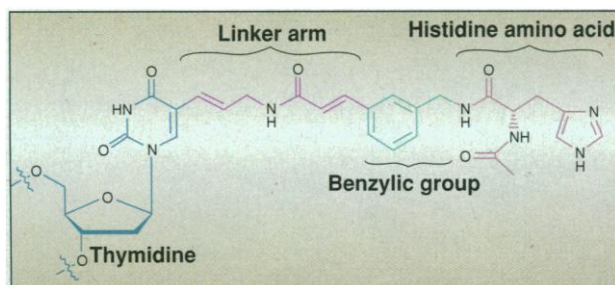
the finicky enzymes, opening the door to a new family of DNA-based catalysts and raising questions of whether such molecular hybrids could have played a role in the evolution of life. In last week's *Angewandte Chemie, International Edition in English*, molecular biologists Kandasamy Sakthivel and Carlos Barbas III of The Scripps Research Institute in La Jolla, California, reported that adding a rigid chemical arm to the side of a DNA building block, or nucleotide, allowed them to tack on a wide variety of functional groups to the molecule. DNA chains containing the altered building block could still be copied by DNA polymerase. And at the American Chemical Society meeting in August, another team led by Steven Benner at the University of Florida, Gainesville, reported going one step further. They too found that specialized DNA polymerases could copy synthetic nucleotides adorned with functional groups. But they also showed that the DNA hybrids could take a first step toward doing chemistry, by binding avidly to a molecular target.

Although neither of the new experiments actually shows that hybrid DNA-protein molecules can catalyze chemical reactions, "they are getting very close," says Michael Famulok, a biochemist at Ludwig Maximilians University in Munich, Germany. And that's exciting, he adds, because it's far easier to generate enormous families of DNA chains, each one slightly different from the others, than it is to create libraries of related proteins. Such libraries are hunting grounds for new catalysts, says Bruce Eaton, a molecular evolution specialist at NeXstar Pharmaceuticals in Boulder, Colorado. "There's a chance to evolve new chemistries no one has ever seen before."

Researchers have long been generating large families of RNA and DNA chains to see if they could isolate individual ones that performed interesting chemistry. But DNA and RNA by themselves are "rather poor catalysts," says Barbas, because their nucleic acid backbones don't contain the diverse chemical groups needed to carry out a wide variety of reactions. Last year, Eaton and his colleagues improved RNA's catalytic abilities by, for example, modifying RNA bases to carry groups known as pyridines, which are well known for binding to catalytically active metals.

Barbas and Sakthivel wanted to see if they could do the same kind of thing with DNA, because it's more stable than RNA and even easier to replicate. But they had to get around the problem that DNA polymerases are far more finicky about copying modified bases than RNA polymerases are. The chemists thought that if they were careful to make each change away from the business end of each nucleotide—the part that faces its nucleotide counterpart on the com-

CREDIT: R. J. AZMI/WADIA INSTITUTE OF HIMALAYAN GEOLOGY



Armed and ready. An amino acid linked to a DNA building block could enable the double helix to catalyze chemical reactions.

plementary strand of the DNA—it might not affect the pairing and duplication.

The scheme worked. After only three tries, they devised a rigid hydrocarbon arm that projected from the back end of a thymidine nucleotide without affecting its ability to be incorporated into DNA chains and duplicated by DNA polymerases. The arm proved to be quite versatile. Barbas and Sakthivel initially found that they could hook numerous functional groups to the end, including a complete histidine amino acid—a common constituent of proteins—and they have added other amino acids since then.

Meanwhile, Benner's team—which included colleagues at Florida and at GenEra Inc., in Alachua, Florida—took a different route: They modified both the DNA and the polymerases. They had spent years designing novel nucleotides that could be incorporated into a DNA strand alongside the four standard building blocks, including one with a hydrocarbon linker and an amino group tacked onto the back of the molecule. They then engineered mutations into a small family of polymerases and tested them all until they found one that would tolerate the odd DNA.

Benner's group used its combination of modified DNA and tolerant polymerase to go a step further and evolve a DNA that could bind to a specific target. Using a polymerase prone to making occasional random errors, they copied a DNA chain containing the modified nucleotide many times over to produce a library of chains, all slightly different. Benner's team then ran the chains through a column containing a molecular target for the DNA: immobilized adenosine triphosphate (ATP) molecules. Most chains passed the target by, but a few stuck. Those that did were later removed and used as the starting material for a new round of replication. After about 12 rounds of this evolution and selection, they found a DNA hybrid that stuck to ATP 100 times more strongly than a similarly evolved but natural DNA strand.

Both groups say they are now working hard to isolate DNA hybrids that catalyze actual reactions. If that works, Benner says, it will confirm that DNA, like RNA and proteins, can carry out the two key functions of life. The prospect that DNA hybrids

can do this, says Benner, raises the question of whether such hybrid molecules might have played a role in early evolution, taking care of both genetics and chemistry, before proteins and DNA went their separate ways. For now, there's more evidence to suggest that RNA was the original single biopolymer, notes Gerald Joyce of Scripps. But he adds that the new work underscores the notion that the chemistry of life may have changed over time. Says Joyce: "The paints on the palette [for life's beginnings] don't have to be the same ones we see in biology today." —ROBERT F. SERVICE

IMAGING

Technique Probes Electrons' Secret Lives

Electrons on the surface of a material can no longer hide from probing instruments, which can track virtually their every move. But physicists can't spy so easily on electrons that lurk below the surface and have only been able to guess at how they behave. Now, however, two groups of researchers have found a way to peer beneath an insulating surface and image intricate patterns formed by the electrons trapped in a thin, two-dimensional semiconductor layer.

At a meeting sponsored by the National High Magnetic Field Laboratory in Tallahassee, Florida, last week, the leader of one group, Raymond Ashoori of the Massachusetts Institute of Technology, showed the latest fruits of the technique, which maps subsurface charges by scanning the semiconductor with a sharp probe. The images, which show enigmatic rings and filaments of electrons, only deepen the puzzle of how electrons behave when they are trapped in a two-dimensional layer. "The experiments contain an incredible amount of information," says Sankar Das Sarma of the University of Maryland, College Park, "but it is still not clear how to absorb that information to make sense of it."

Ashoori and his colleagues, along with a group led by Amir Yacoby of the Weizmann Institute of Science in Rehovot, Israel, have been studying the phenomenon that earned a trio of other physicists the Nobel Prize this year: the quantum Hall effect. Under exacting

conditions—temperatures within a fraction of a degree of absolute zero and strong magnetic fields—the current flowing through a two-dimensional "electron gas" (2DEG) exhibits a series of plateaus where it no longer increases as the voltage is cranked up. The quantum Hall effect has intrigued physicists since its discovery in 1980, and this year's Nobel Prize is the second to be awarded for studies of it (*Science*, 23 October, p. 613). But physicists don't have a clear view of how the electrons behave as they stack up in quantum energy levels—the source of the plateaus. "There are a lot of data on how a two-dimensional sheet conducts electricity," says Ashoori, "and a lot of guessing as to what's going on inside. But nobody has ever looked."

To see what's happening in the 2DEG, Ashoori adapted a technique called scanning probe microscopy, a standard way to map atoms on surfaces. A sharp tip probes the semiconductor surface, but instead of tracing its atom-scale undulations, it picks up tiny charge variations with the help of an ultrasensitive charge detector. To distinguish the subsurface charges from ones sitting on the surface, the team pumps charge in and out of the semiconductor at a frequency of about 100 kilohertz. The tip locks onto a signal of just that frequency, indicating charges moving in the 2DEG, and ignores the unmoving charge at the surface. Yacoby's probe detects static charges instead and relies on other techniques that don't depend on frequency to tease out the subsurface signal.

Both groups are using their techniques to study the current plateaus seen in the quantum Hall effect. Physicists speculate that "incompressible" regions in the 2DEG—places where the electrons are already squashed together as tightly as the laws of quantum mechanics allow—are responsible. These in-

compressible regions can't accommodate any additional electrons, and so they block increased current flow. In between the plateaus, current flows more freely because "compressible" regions open up in the 2DEG.

What Ashoori's team has seen so far confirms that general picture but adds puzzling details. "Imagine dumping charge in [the material] and waiting to see how it spreads," says Ashoori. "To our shock, it

goes into these patterns that are enormously sensitive to field." Ashoori interprets the patterns, which range from long filaments to small droplets to large islands, as variations in the compressibility of electrons. They appear only at the current plateaus, and they change



Electric arcs. A 2-micrometer-square region of an electron layer in a magnetic field shows mysterious rings of compressible charge.