ASTRONOMY

Did Galaxies Bloom in Clumps?

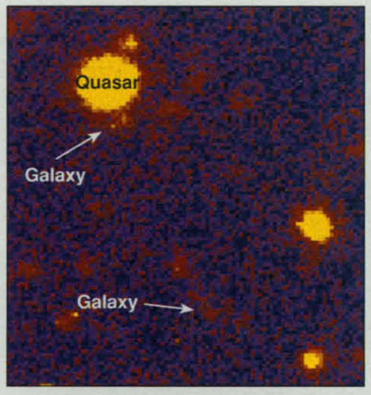
WASHINGTON, D.C.—The beginnings of the great clusters and walls of galaxies seen in today's universe may date back practically to the big bang. By searching the neighborhood of distant quasars—galaxylike objects so bright they can be seen shining from a time when the universe was less than a billion years old, or 10% of its current age—astronomers have found that nearly every one has a fuzzy companion galaxy or two. These small gatherings in the infant universe, says team leader George Djorgovski of the California Institute of Technology in Pasadena, are "the possible cores of future rich clusters of galaxies."

They are also a challenge to the notion that the clumpiness of today's universe emerged fairly recently. If the universe contains as much mass as some theorists believe, the formation of dense clusters would have been retarded by the gravity of the surrounding universe. But the belief in a dense universe has already taken a blow from the discovery of great walls of galaxies when the universe was just 2 billion years old (*Science*, 4 April 1997, p. 36). Now, Djorgovski thinks he can discern large-scale structures even earlier in cosmic history.

Like all astronomers wanting to probe the farthest reaches of the universe, the team had to rely on quasars, because they are so much brighter than ordinary galaxies. At great distances (also referred to as high redshifts because light originating there is drastically reddened by the expansion of the universe), observers have cataloged dozens of quasars. But because only a small fraction of galaxies flare up as quasars, these objects by themselves can't reveal clustering in the early universe. That would be like trying to learn where cities are concentrated by mapping only the ones that have a Q in their name. So Djorgovski's team used the light-gathering power of the 10-meter Keck telescope at Mauna Kea, Hawaii, to search the surroundings of the most distant quasars, at redshifts of between 4 and 5, for neighboring faint galaxies at the same distance.

"This is very much work in progress," says Djorgovski, who presented the preliminary results early this month at a meeting of the American Astronomical Society here. "Only some 10 quasar fields have been studied so far, but in nearly every case, we found at least one companion galaxy at the same redshift as the quasar. This is the first clear detection of primordial large-scale structure at redshifts larger than 4." Djorgovski points out that the quasar companions found by his team are not yet full-fledged galaxies. "There hasn't been enough time [since the big bang] for these things to be anything else than primordial protogalaxies," he says.

Charles Steidel of CalTech, who identified galaxy groupings at redshifts of about 3, when the universe had reached the 2-billion-year mark, isn't sure that Djorgovski's team really has discovered the precursors of the structures he sees. "They're using a different approach, observing only very small fields," he says. And Neta Bahcall of Princeton University is troubled by Djorgovski's finding that the distant quasars seem to have more companion galaxies than quasars at lower redshifts. "This is not what you expect, since further clustering [over time] would only increase their numbers," she says. But Bahcall, who advocates a low-density universe, agrees that Djorgovski has found strong evidence for very early clustering.



S. G. DJORGOVSKI ET AL./CALTECH/KECK OBSERVATORY

Togetherness. Fuzzy protogalaxies cluster near a brilliant quasar.

The observations suggest that only scattered regions of the early universe were dense enough for galaxies to form, so the first galaxies naturally appeared in clumps. "These are very special places in the universe," says Djorgovski. "Chances are that we miss most of them when we observe random spots on the sky." If so, astronomers looking for action in the early universe need to follow the bright lights of quasars.

–Govert Schilling

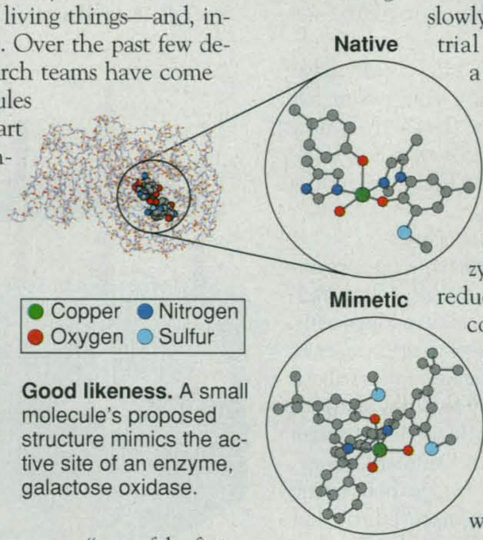
Govert Schilling is an astronomy writer in Utrecht, the Netherlands.

CHEMISTRY

Mimicking an Enzyme in Look and Deed

Making model airplanes and ships look like the real thing requires a delicate touch. But getting those models to actually fly or sail requires another level of sophistication entirely. So it is with efforts to create durable small molecules that look and act like enzymes, the biological catalysts that carry out a multitude of chemical reactions in living things—and, increasingly, in industry. Over the past few decades, numerous research teams have come up with small molecules that resemble the heart of one enzyme or another. But even when these models catalyze the same chemical reactions as the enzymes, they rarely do so in the same way. And those models that faithfully duplicate an enzyme's function rarely resemble their mentor.

Now, a new model catalyst, reported on page 537 of this issue, represents "one of the first good examples to bring together both the structural and reactivity aspects," says Tom Sorrell, an organic chemist and enzyme modelmaker at the University of North Carolina, Chapel Hill. This model, the work of a five-member team at Stanford University led by inorganic chemist Dan Stack and structural expert Keith Hodgson, mimics the active site of an enzyme known as galactose oxidase. Like the enzyme, it works at ordinary temperatures and pressures to transform one set of organic compounds—alcohols—into other compounds called aldehydes, which serve as intermediates for making still other essential compounds. It "is quite an impressive piece of work," says Harvard University inorganic chemist Richard Holm.



Y. WANG AND D. STACK

Good likeness. A small molecule's proposed structure mimics the active site of an enzyme, galactose oxidase.

The new galactose oxidase mimic works too slowly to be useful in industrial processes, where the alcohol-to-aldehyde conversion is a first step in making everything from drugs to perfumes. But Holm and others say it may point the way to other enzyme mimics that could reduce the complexity and cost of many industrial reactions—as well as lower their output of unwanted, polluting byproducts. Properly designed model catalysts could work on a wider range of starting materials and in harsher conditions than enzymes can. And models that have the same basic structure as the corresponding enzymes are most likely to be efficient enzyme mimics, says Stack. "Nature has already solved the problem of how to run certain reactions. All we need to do is copy her."

Key to the function of both galactose oxidase and the new model is a single copper atom at the core of each compound. Copper, like other metals, is good at snatching electrons and giving them up to other atoms. But it excels at doing so only when positioned just right. The metal ordinarily hitches itself to four other chemical groups arrayed in a flat square with the copper atom at the center—a geometry that restricts copper's ability to interact with other compounds, because they can't get close enough. Galactose oxidase gets around this by forcing copper to bind to five other compounds in a pyramid-shaped arrangement—with copper at the center of the pyramid's base—that keeps it a bit unsatisfied, looking for more action.

In this case, the copper is linked to four separate amino acids and a water molecule, which takes up one of the prime reactive spots on the pyramid's base. Alcohols have a strong preference for these baseline positions as well. They kick out the water and take its spot. The copper then wrests electrons and protons—hydrogen nuclei—from the alcohol and transfers them to molecular oxygen, creating a molecule of hydrogen peroxide along with the aldehyde.

To create the same reactive geometry in their model catalyst, Stack and graduate student Yadong Wang designed a set of organic arms that would bind to the copper atom and mimic the role of galactose oxidase's key amino acids. One group, called binaphthol, takes up two of copper's binding sites and warps its bonds into a pyramidal arrangement. Another two arms contain groups known as phenols. Finally, in the activated form of the model, a water molecule inserts itself in the pyramid's base, just as in the enzyme.

The result is a compound that binds alcohols and then goes to work on them, much like the enzyme. In a series of spectroscopic experiments, Stack and Wang found that the compound duplicates the enzyme's reaction steps: After an alcohol molecule binds to the copper, the phenol arms help the copper swipe electrons and protons from the alcohol, producing the aldehyde, which drops off the catalyst. A molecule of oxygen then jumps into the free spot and snags the electrons and protons, forming hydrogen peroxide and regenerating the active catalyst in the process. X-ray structure studies of the model compound frozen in the initial step of this reaction—done by Hodgson, Jennifer DuBois, and Britt Hedman—helped support this picture.

While the new model is one of the first small molecules to truly mimic an enzyme, Stack says it's likely that many will soon follow. X-ray imaging experts are getting ever sharper pictures of the heart of other metal-containing enzymes, giving the modelers crucial guidance. Nitrogenase, which takes nitrogen in the air and converts it to a biologically useful form by tacking on hydrogens, is among the modelers' most hotly pursued prizes. Concludes Stack: "The time is right for rapid progress in this area."

–Robert F. Service

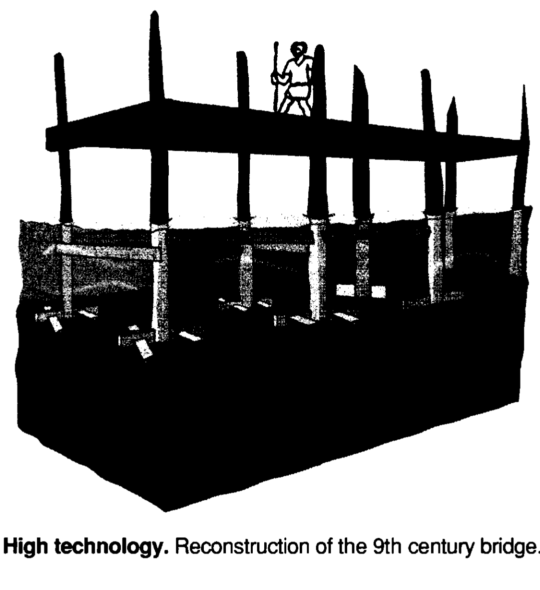
ARCHAEOLOGY

Irish Bridge Sheds Light on Dark Ages

The vaunted engineering skills that the Romans spread across Europe are supposed to have vanished during the "Dark Ages"—from the collapse of the Roman empire in the fifth century until about A.D. 1000. But a new find in the west of Ireland is challenging that assumption. A pair of underwater archaeologists has discovered the remains of a huge wooden bridge across the river Shannon. At 160 meters long, it may be the largest wooden structure from the early medieval period ever found in Europe, and its technical complexity has surprised archaeologists. Researchers now believe that the bridge, dated at A.D. 804, was the work of monks from the nearby town of Clonmacnoise, who kept Roman expertise alive over the centuries.

"The Clonmacnoise bridge fills an important gap," says archaeologist John Bradley of the National University in Maynooth. "There was no evidence of large bridges in Europe between the Roman era and about A.D. 1000." It is unlikely to be the last such discovery, adds Morgens Schou Jorgensen of the National Museum of Denmark, an expert on the large wooden bridges built by the Vikings several centuries later. "I think that other similar bridges will now be found in Ireland, as happened in Denmark after the first Viking long bridge was uncovered in 1932," says Jorgensen. If so, the finding could mean that a sophisticated land communications network may have been in place across Ireland in the 9th century.

Donal Boland and Mattie Graham, divers who specialize in underwater archaeology, had begun their survey of the river Shannon after coming across an intriguing reference to a bridge in the *Annals of Clonmacnoise*, written in 1158. They concentrated on a 500-meter stretch of the river near the remains of the monastery. In 1994, with archaeological guidance from Fionnbarr Moore of the National Monuments Service of Ireland, they found what they were looking for: an ancient oak post sticking out of the muddy riverbed. By last fall, Boland and Graham had discovered a total of 130 timbers, all neatly arranged in pairs 5 meters apart, spanning the entire 160-meter width of the Shannon. They also found nine oak dugout canoes, from which workers may have driven the pilings deep into the riverbed, and the remains of an elaborate horizontal cross-bracing system that once supported a roadway.



L. CARROLL

High technology. Reconstruction of the 9th century bridge.

The line of the posts ran directly into the ruins of a 13th century Norman castle, leading the researchers to suspect at first that the bridge was also a Norman construction. But this theory was ruled out after they sent samples of the oak timbers to Queen's University Belfast for dating by tree-ring analysis. The Belfast researchers, led by Mike Bailie, said the timbers were felled in 804, a full 365 years before Norman invaders arrived from France.

The focus of archaeologists then turned to the thriving 9th century monastic settlement at Clonmacnoise. The town of several thousand inhabitants straddled the point where an east-west route across Ireland known as the Eiscir Riada, or Esker Road, crossed the Shannon. "The bridge was built to attract commerce," says Aidan O'Sullivan, the archaeological director in charge of Clonmacnoise, "and the leadership for the project was probably provided by the monks."

The discovery of the Clonmacnoise bridge has led archaeologists such as Bradley to question whether knowledge was really lost in the aftermath of the fall of Rome, at least in distant parts of Europe that were spared the chaos of the Dark Ages. "We know the Irish preserved Roman texts, and this find suggests that they may also have preserved Roman technology and bridge-building skills," says Bradley. "Perhaps the Dark Ages were not so dark after all."

–Sean Duke

Sean Duke is a science writer in Dublin.