COSMIC BLUE

PRINT OF LIFE

Chemical reactions brewing between the stars may have jump-started biology on Earth, and all across the universe.

By Andrew Grant

In the latest scientific version of Genesis, life begins, paradoxically, with an act of destruction. After 10 billion years of guzzling the hydrogen in its core, a sun-size star runs out of nuclear fuel and becomes unstable. It goes through a series of convulsions and expels a shell of searing-hot atoms—including hydrogen, carbon, and oxygen. The star fizzles into an inert cinder, and its atoms drift off, seemingly lost in the interstellar gloom. ¶ But next the story takes a surprise turn, from destruction to construction. Some of those rogue atoms float into a nearby gas cloud and stick to fine grains of dust there. Even at a frigid –440 degrees Fahrenheit, the atoms bump and crash into each other, merging to form simple molecules. Over millions of years, one relatively dense region of the cloud begins to collapse in on itself. An infant star takes shape at the center. In the surrounding areas, temperatures rise, molecules evaporate from their icy dust grains, and a new round of more intricate chemical reactions begins.

Then comes the most wondrous part of the whole tale. Those reactions weave the simple atoms of hydrogen, carbon, and oxygen into complex organic molecules. Such carbon-bearing compounds are the raw material for life—and they seem to emerge spontaneously, inexorably, in the enormous stretches between the stars. "The abundance of organics and their role in getting life started may make a big, big difference between a giant universe with a lot of life, and one with very little," says Scott Sandford of NASA's Ames Research Center in Moffett Field, California, who studies organic molecules from space.

The notion that the underlying chemistry of life could have begun in the far reaches of space, long before our planet even existed, used to be controversial, even comical. No longer. Recent observations show that nebulas throughout our galaxy are bursting with prebiotic molecules. Laboratory simulations demonstrate how intricate molecular reactions can occur efficiently even under exceedingly cold, dry, near-vacuum conditions. Most persuasively, we know for sure that organic chemicals from space could have landed on Earth in the past—because they are doing so right now. Detailed analysis of a meteorite that landed in Australia reveals that it is chock-full of prebiotic molecules.

Similar meteorites and comets would have blanketed Earth with organic chemicals from the time it was born about 4.5 billion years ago until the era when life appeared, a few hundred million years later. Maybe this is how Earth became a living world. Maybe the same thing has happened in many other places as well. "The processes that made these materials and dumped them on our planet are universal. They should happen anywhere you make stars and planets," Sandford says.

THE FIRST PERSUASIVE HINTS OF LIFE'S POSSIBLE COSMIC ANCESTRY came in 1953, courtesy of a renowned experiment devised by chemists Stanley Miller and Harold Urey. From studies of ancient rocks, geologists had a rough sense of our planet's original chemical composition. Biologists, meanwhile, had uncovered the amazingly complex organic molecules that allow living cells to survive. Miller and Urey wanted to see if pure chemistry could help explain how the former transformed into the latter.

The two researchers prepared a closed system of glass flasks and tubes and injected a gaseous mixture of methane, ammonia, hydrogen, and water—four basic compounds thought to be abundant in Earth's primitive atmosphere. Then Miller and Urey applied an electric current to simulate the energy unleashed by lightning strikes. Within a week their concoction had produced several intriguing prebiotic compounds. Many scientists interpreted this as hard experimental evidence that the building blocks of life could have emerged on Earth from nonbiological reactions.

In many ways, though, the experiment supported the opposite view. Even the simplest life forms incorporate two amazingly complex types of organic molecules: proteins and nucleic acids. Proteins perform the basic tasks of metabolism. Nucleic acids (specifically RNA and DNA) encode genetic information and pass it along from one generation to the next. Although the Miller-Urey experiment produced amino acids, the fundamental units of proteins, it never came close to manufacturing nucleobases, the molecular building blocks of DNA and RNA. Furthermore, it is likely that Miller and Urey erred by simulating Earth's early atmosphere with gases containing hydrogen, which reacts easily, as opposed to carbon dioxide, a gas that is far less reactive but was probably far more plentiful at the time. "Interesting chemicals could not have been made as easily as the experiment made it seem," says astrobiologist Douglas Whittet of Rensselaer Polytechnic Institute in upstate New York.

If life could not so easily have begun on Earth, a few voices argued, perhaps it originated from beyond. The most notable advocate of that hypothesis was the influential British cosmologist Fred Hoyle, who coined the term Big Bang. His 1957 science fiction novel, *The Black Cloud,* envisioned a living, intelligent dust cloud in space; it foreshadowed his later support of panspermia, the theory that life evolves in space and spreads throughout the universe. Starting in the 1960s, Hoyle wrote a series of academic papers describing how bacterial cells could make their way from interstellar dust grains to comets and eventually down to planets like Earth.

Most of Hoyle's peers considered his ideas borderline delusional. Back then, almost nobody thought prebiotic molecules, let alone entire microbes, could survive the harsh vacuum of space. "Everyone assumed space was too cold and too low-density to form molecules," says National Radio Astronomy Observatory (NRAO) astrochemist Anthony Remijan, a leading expert in interstellar chemistry. "That assumption became 'fact' without any evidence behind it at all."

One of Remijan's mentors, astronomer Lew Snyder, then at NRAO, dared to disagree. He did not share Hoyle's vision of bacteria hitching rides across the galaxy, but he thought that interesting molecules might subsist in the alleged desert of interstellar space. Snyder had a strategy for finding them, too. He knew that many chemical compounds are dipolar—they have a positively charged side and a negatively charged one—and that charged particles in motion release energy. If molecules were freely floating as gases, Snyder realized, some of them should spin like batons and create a faint radio-wave signal. Even better, each type of molecule should have its own unique energy signature: It should broadcast at a specific set of frequencies that could be detected and identified by astronomers using radio telescopes on Earth.

Starting in the mid-1960s, Snyder applied for observing time on the main radio telescopes, to no avail. The scientists in charge of the observatories agreed with the consensus view that space could not support complex chemistry. In December 1968, Snyder traveled to Austin, Texas, for a meeting of the American Astronomical Society, where he and a colleague, David Buhl, hoped to change some minds. At the end of their talk, famed physicist Charles Townes (who won a Nobel Prize for his work in the development of the laser) stood up and announced that he

Molecules of hydrogen and carbon glow green in this infrared image of the nebula T942. Previous pages: Stars forming in the Orion nebula.

OPPOSITE: NASA/SPITZER. PREVIOUS PAGES: TONY HALLAS had found ammonia molecules near the center of the Milky Way using the radio telescope at the University of California, Berkeley. "Suddenly the people at NRAO decided we weren't crazy anymore," Snyder says, "and asked us for a list of molecules we wanted to look for."

Early in 1969, Snyder and Buhl set up shop at NRAO's Green Bank Telescope in West Virginia and chose their first target: formaldehyde, an organic molecule made up of two hydrogen atoms and an oxygen atom tethered to an atom of carbon. Sure enough, when they pointed the 140-foot radio dish at a massive cloud of gas and dust near the center of the Milky Way, there was a distinctive dip in the radio signal at 4.8 gigahertz—the music of formaldehyde. The same signal appeared in cloud after cloud. After waiting for more than a year to get observing time, Snyder needed just a few nights at the telescope to demonstrate that complex organic molecules, formaldehyde in particular, permeate the galaxy. He soon found hydrogen cyanide (88.6 gigahertz) in the Orion nebula and isocyanic acid (87.9 gigahertz) in a cloud called Sagittarius B2. "After that, we could have gotten telescope time to do anything," Snyder says. "We could have looked for interstellar flu germs."

Infrared image of RCW 120, a star-forming region harboring organic molecules.

Within a few years, Snyder and other radio astronomers had identified dozens of organic molecules, including formic acid (which causes the sting in ant bites) and methanol (a simple alcohol). Although none of these molecules reached the complexity of Miller and Urey's amino acids, some of them can form proteins and other biologically important compounds when mixed together in water on Earth. Contrary to all expectation, interstellar clouds proved to be very friendly environments for breeding complex chemistry. Now a whole new discipline—astrochemistry—began to emerge, and its emboldened practitioners set out to learn more about what is cooking in those colorful nebulas.

Despite the large and growing catalog of space chemicals coming from the radio observatories, astronomer J. Mayo Greenberg of the University of Leiden in the Netherlands suspected that his colleagues were missing a vital piece of the puzzle. The radio astronomers were searching for free-floating gas molecules in space, but nebulas also contain dust, microscopic grains of carbon and silicon. What would happen, Greenberg wondered, if interstellar gas molecules like formaldehyde collided with frigid grains of dust? They would freeze there instantly, he surmised, creating another kind of environment in which chemical reactions, driven by starlight, could take place. At temperatures just a few degrees above absolute zero, the molecules would still vibrate. These vibrating molecules—just like the rotating dipolar ones Snyder observed—could absorb and emit radiation. The frozen chemicals Greenberg was postulating would show up not in radio, however, but at infrared wavelengths. Starting in the 1970s, Greenberg was vindicated by a team of astronomers at the University of California, San Diego. They pointed a variety of infrared telescopes at interstellar dust clouds and discovered dips at specific frequencies corresponding to molecules includ-

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ing methanol, ammonia, and water ice.

Now that Greenberg knew interstellar space harbored frozen molecules as well as gaseous ones, he wanted to know how these chemicals interact under such extraordinary conditions. Theory alone could not provide the answer; this question called for some hands-on experiments. So in 1976, Greenberg hired Louis Allamandola, a recent Berkeley Ph.D. graduate in low-temperature chemistry, to re-create the kinds of reactions that might take place on microscopic icy grains thousands of light-years away.

ALLAMANDOLA'S SOLUTION WAS TO CREATE AN APPARATUS THAT could replicate the exotic cold depths of space—in essence, an extraterrestrial version of the Miller-Urey experiment. With colleague Fred Baas, he installed equipment to chill a shoebox-size chamber to within several degrees of absolute zero and depressurize it to a near vacuum. Then he set up a plasma lamp to fire beams of ultraviolet light at the chamber, much like the radiation present in planet- and star-forming regions of dust clouds. Finally, in true Miller-Urey fashion, he threw in a gaseous mixture of simple molecules, mimicking what was then known about the composition of interstellar clouds, and watched the results.

Allamandola's simulations, carried out first at Leiden and now at NASA's Ames Research Center, revealed not only that some chemical reactions really do occur at extremely low temperatures, but also that these reactions produce other reactive chemicals, thereby providing the spark for more molecular hookups. Ultraviolet radiation spices things up as well: It heats the grains and breaks up some of the molecules into reactive fragments, which in turn bond with other fragments to form new kinds of molecules.

Once again, nature proved extremely adept at brewing complex molecules. In current versions of Allamandola's experiment, the resulting icy mixtures contain dozens of prebiotic molecules, among them the same amino acids that Miller and Urey found. In fact, Allamandola's nebula-in-a-box has yielded an even richer chemical palette. He has manufactured intricate molecular rings containing carbon, nitrogen, and hydrogen; fatty-acid-like molecules that look and behave like the membranes protecting living cells; and nucleic acids or nucleotides, the primary components of RNA and DNA.

Creating molecules in the lab does not prove that the same molecules exist on dust grains in distant nebulas, but so far Allamandola's technique has an impressive track record. By 1990 he had published a list of simple compounds his group at Ames had created in simulations. By 2000 radio astronomers had found almost all of them in various dust clouds throughout our galaxy, suggesting that the interplay between ice and gas may be one of the most important mechanisms for synthesizing the precursors of life.

Still, Allamandola's research could not explain how compounds moved from the far reaches of space to the surface of Earth, where life actually took hold. Addressing this question meant bridging the gap between diffuse interstellar clouds and the condensed objects that ultimately emerge from them. When dense regions of a cloud collapse, the massive inner part becomes a star while the rest forms a swirling disk of gas and dust that may give rise to planets. (We now know that many, perhaps most, stars produce such planetary systems; see "Is Anybody Out There?" on page 46.) As large planets come together, the process involves such heat and pressure that all traces of preexisting organic matter are destroyed. Not all material in the disk gets treated so brutally, however. Some of it remains nearly intact in comets and asteroids, smaller conglomerations of ice and rock. When bits of these objects struck Earth as meteorites, they could have delivered organic molecules back onto its surface.

Convincing evidence that meteorites could be rich sources of organic molecules came in 1969, when a 200-pound meteorite hurtled to the ground in Murchison, Australia. Analysis indicates that the rock contains millions of organic compounds, including amino acids that could not have come from terrestrial contamination. Two years ago, Zita Martins from Leiden showed that the meteorite contains nucleobases. David Deamer of the University of California, Santa Cruz, even found fatty-acid-like molecules similar to those Allamandola created in the lab. Other meteorites—including Murray, which landed in Kentucky in 1950, and Allende, which made landfall in Mexico in 1969—have been shown to contain similar organic compounds.

Meteorites carrying the same complex chemicals have been striking Earth since it formed 4.5 billion years ago. "The things we see landing on Earth now are probably representative of what was landing on us back during Earth's infancy," says NASA's Sandford, who has traveled the world searching for samples from on high. In 1984 he found a rock from Mars, and in 1989 a piece of the moon, all right here on Earth. During a six-week tour of Antarctica, he slept in a tent under the midnight sun and rode a snowmobile to ice fields littered with meteorites by day.

Gradually, painfully, through some four decades of effort, Sandford and the other scientists have teased out different strands of the story of prebiotic chemistry. Carbon, hydrogen, oxygen, and other atoms knock about in nebulas, sometimes freely and sometimes bound up with ice and dust. They arrange themselves into elaborate molecular structures. Meteorites abound with organic compounds, which rain down on any nearby planets.

ORGANIC SPACE

Since Lew Snyder and David Buhl discovered interstellar formaldehyde in 1969, astronomers have identified more than 150 molecules in deep space, mostly by using radio telescopes to detect the faint radiation the molecules emit. Notable space chemicals found in just the past few years include the sweet (a sugar, glycolaldehyde), the fragrant (ethyl formate, which smells like rum), and the explosive (fulminic acid, used in detonators). Most exciting, some of the molecules resemble those associated with life: In 2007 an international team found amino acetonitrile (NH_2CH_2CN), a molecule structurally similar to glycine—one of the building blocks of biological proteins.

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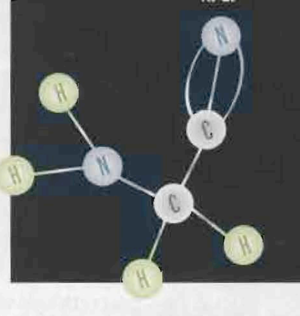

Helping to weave all those strands into a single, elegant narrative is an Emory University astrochemist with a providential name: Susanna Widicus Weaver. Through a series of models and experiments, she has demonstrated that ultraviolet radiation can break chemical bonds and split molecules into highly reactive fragments called radicals. It is difficult for radicals to do much at −440°F, but when the temperature warms even slightly (as when a

Deep space may be the ultimate breeding ground for life, but the greatest enigma remains untouched: How did a collection of organic molecules, whatever their origin, make the leap to life on Earth?

star begins to form), the radicals merge to form larger molecules. "You can take methanol [CH_3OH], break it apart, and make several types of radicals, and then those can all find each other," Weaver says. "In just two or three steps on the grain surface, you can go from a simple mixture to something a lot more complex, like methyl formate [$HCOOCH_3$]." In a major 2008 paper, Weaver predicted an abundance of such radicals in dust clouds. A thorough search of interstellar ice grains by infrared astronomers should determine whether radicals indeed play a primary role in constructing prebiotic molecules. If they do, astrochemists in the lab could see what other complex combinations result from these radicals and then search for those molecules in space.

Weaver's models also demonstrate that once the temperature in the dust cloud reaches about −280°F, most of the molecules evaporate from the ice on dust grains and enter a gas phase, allowing them to react a lot more quickly and to form complex molecules. Molecular players might include acetone (the stuff in nail polish remover), methyl formate, and ethylene glycol (antifreeze), she notes. That explains why radio astronomers have found more complex molecules in the warmer, more active star-birthing regions of dust clouds than in the colder, darker areas.

But then the story becomes less clear. Radio astronomers have yet to identify anything as complex as an amino acid, so astrochemists do not know exactly how complex these gaseous molecules can get. We know that meteorites contain amino acids and even nucleobases, but not whether they scooped up those molecules from dust clouds or created them later, on their interplanetary course. "We really don't know where the chemistry in the dust cloud stops and where the chemistry in meteorites starts up," Weaver says. She notes that the answer has tremendous implications for one of science's most fundamental questions: How common is life throughout the universe?

If meteorites create most of the direct chemical precursors of life, our solar system might be an unusual case. According to Weaver, the size of our sun, the region of the galaxy in which it formed, even how long it took for the planets to form—all these characteristics are different in other star systems and may influence the chemical inventory available to any Earth-like planets orbiting there. But if dust clouds can manufacture these molecules on their own, then life is probably prevalent throughout the universe. "No matter which dust cloud you look at, things look very similar chemically," Allamandola says.

A new generation of sensitive, high-resolution telescopes will help resolve the debate by probing both dust clouds and the protoplanetary disks from which asteroids, comets, and planets form. Remijan and his colleagues are salivating over the scientific potential of the Atacama Large Millimeter/submillimeter Array (ALMA) in Chile, a network of 66 radio dishes that will provide unprecedented resolution and sensitivity when it becomes fully operational in late 2012. And two space-based infrared observatories—the European Space Agency's Herschel Space Observatory, which has been gathering data since last year, and NASA's James Webb Space Telescope, scheduled to launch in 2014—will allow astronomers to search for the infrared signatures of the specific icy radicals that Weaver's model predicts.

As much as astronomers love new instruments to play with, nothing beats seeing extraterrestrial chemistry in action. We cannot yet send probes to the Orion nebula, but we can look for clues closer to home. Europa, a large satellite of Jupiter, is covered with a thick shell of ice crisscrossed with long, brownish or pinkish fractures. Saturn's much smaller moon, Enceladus, features a network of icy volcanoes spewing ammonia, formaldehyde, and other organic molecules. These water-rich moons might have replicated the organic chemistry found within interstellar dust clouds. One clue involves the changing colors of the moons. "Some of the same processes that take place in deep space may occur in these icy bodies in the supercold outer regions of the solar system," Allamandola says.

TAKING THE BIG VIEW, REMIJAN MARVELS AT ALL HE AND HIS COLleagues have achieved. Not so long ago, deep space seemed static and dull; now it looks like the possible breeding ground for a blueprint of life that might be shared all across the universe. Yet the greatest enigma remains untouched: How did a collection of organic molecules, whatever their origin, make the leap to life on Earth?

"The overall goal is to take this chemical inventory, mix it all together, and form a self-replicating molecule like RNA," Remijan says. He has personally helped detect 11 interstellar molecules with the Green Bank Telescope in West Virginia but recognizes that a full list of the organic chemicals out there is only a start. What scientists really need is a snapshot of the chemistry that was happening on Earth 4 billion years ago. That might actually be possible.

Titan, another of Saturn's moons, has a thick, methane-tinged atmosphere that is reminiscent of early Earth's. It even has pools of hydrocarbons on its surface, the only known bodies of liquid on any world other than our own. But Titan's −290°F surface temperature means that all of its chemistry moves in slow motion. Studies of Titan could therefore provide a peek at how complex prebiotic molecules came together on Earth, and potentially on many other worlds too.

In a new study, researchers from the United States and France conducted a new Miller-Urey-style experiment that mixed the organic molecules found in Titan's atmosphere. They ended up with all of the nucleobases that make up RNA and DNA. The study suggests the beginning of a new synthesis that reframes the old questions in a deeper and more meaningful way. It may not be a question of whether life's chemistry began in space or in meteorites or on the surface of a planet (or moon). All three environments may very well have lent a hand.

"When life was forming on Earth, it probably used a large variety of sources, some from the planet and some from the sky," Sandford says. "Life doesn't care about the 'Made in...' label on the molecules." **D**