

Life's First Scalding Steps

Biology might have begun in cauldrons at the bottom of the sea

By SARAH SIMPSON

Black clouds of minerals and volcanic gases billow out of seafloor geysers.

NOAA

In a back room at the Carnegie Institution of Washington (D.C.), Jay A. Brandes packs water and powdered rock into a 24-carat-gold capsule not much bigger than a daily vitamin. He injects gases like those spewed by a volcano and then seals the receptacle. Finally, he places the shiny amulet inside "the bomb," a device isolated from the rest of the world by steel panels salvaged from a scrapped battleship. Within, the mixture is besieged with scorching temperatures and bone-crushing pressures, forces like those at work at seafloor geysers. Brandes and his colleagues then look inside the tortured capsule for evidence of the chemical steps that sparked the beginnings of life.

Using no more than the cocktail of chemicals discharged at undersea hydrothermal vents, the researchers are trying to mimic reactions that occur within living cells.

Oceanographer Jack Corliss first discovered these vents in 1977, while exploring a volcanic ridge at the bottom of the Pacific Ocean. Before then, oceanographers had considered the ocean floor cold and mostly barren. Corliss' view outside the tiny research submersible revealed a different world.

Peering out a porthole, Corliss became the first person to witness the biological wonderland of shoe-sized clams, 6-foot tube worms, and blizzards of strange microbes thriving at the vents, which spew out a hellish mix of shimmering brines. If these creatures can subsist in a bath of scorching chemicals and heat from the planet's interior, he reasoned, then per-

haps this is where life got its start.

Corliss' proposal that life sprung from water, gas, and rocks far out of the sun's reach inspired grandiose theories but remained virtually untested for 20 years. Most origins-of-life researchers were still busy pondering the long-held notion that life's precursor chemicals linked up at the surface of a sun-drenched pond or ocean. In this more traditional scenario, the sun simmered a prebiotic soup for millions of years to cook up the first cel-

Hazen/Carnegie Institution of Wash.



Researchers at the Carnegie Institution of Washington (D.C.) test recipes for life inside gold capsules.

lular organisms.

Only in the past few years have scientists such as those at the Carnegie Institution begun to roll up their shirtsleeves and get down to the business of determining what biochemical reactions are possible at hydrothermal vents. In a series of recent experiments, researchers have found that the harsh vent conditions can foster some of the chemical steps thought necessary for early life.

Their results are capturing the attention of a growing group of scientists—and raising belief in the chance of finding life elsewhere in the universe.

The most detailed step-by-step blueprint for how Earth's oldest raw materials could have given rise to the stuff of life came out of the imagination of Günter Wächtershäuser, an organic chemist at the University of Regensburg in Germany. Ten years ago, Wächtershäuser conceived of an assembly-line process at the ocean floor that transforms basic inorganic chemicals into organic chains, the biological molecules that are the building blocks of life.

Wächtershäuser's factory enlists the elements of modern industry—all readily available at vents. The conveyor belt is the flat surface of metal sulfide minerals, such as iron pyrite, abundant in seafloor rocks. The raw materials are carbon- and hydrogen-rich gases from volcanic belches dissolved in the seawater. The workers that drive the assembly line—the keys to the whole process—are metallic ions in the sulfides.

In living cells, complex proteins called enzymes play the role of factory laborers, bringing certain molecules together and splitting others apart. Before enzymes appeared on the planet, Wächtershäuser says that metallic ions filled that catalytic role. Without these mediators, reactions might take months or years, or never happen at all, he adds. New components would never get added to the molecules

passing by on the conveyor.

In Wächtershäuser's theory, the first organic molecule put together on the conveyor belt was acetic acid, a simple combination of carbon, hydrogen, and oxygen that is best known for giving vinegar its pungent odor. Formation of acetic acid is a primary step in metabolism, the series of chemical reactions that provides the energy that cells use to manufacture all the biological ingredients an organism needs.

According to the theory, metabolism came before all else. Once a primitive metabolism evolved, it began to run on its own, and only later were cells' other basic elements, such as a genetic code, invented.

Wächtershäuser focuses on the heart of modern metabolism, the citric acid cycle. All living cells use this series of reactions to extract energy from food. The cycle makes changes in several chemical compounds, but it always begins with acetic acid. Inside a cell, the two carbon atoms in each acetic acid molecule are eventually expelled as carbon dioxide in a reaction that gives off a packet of energy.

Because the citric acid cycle is intrinsic to all modern life, Wächtershäuser guesses that its basic reactions are close to the chemistry with which life began—with one significant variation. In the oxygen-deficient world at hydrothermal vents, heat-loving bacteria operate the cycle backward (SN: 3/29/97, p. 192). Instead of giving off carbon dioxide to make energy, they incorporate carbon atoms to build a succession of more complex organic molecules. Wächtershäuser says life's first chemicals were built the same way.

Around the vents, he theorizes, catalytic metallic ions first enabled the materials around them to fashion acetic acid. In the next step, the ions catalyzed the addition of a carbon molecule to the acetic acid to get three-carbon pyruvic acid, which is another key chemical in the citric acid cycle and also reacts with ammonia to form amino acids, which themselves link up to form proteins.

After writing the blueprint, Wächtershäuser set out to prove each step. He produced the first important component of his assembly process 2 years ago. He and fellow German chemist Claudia Huber, of the Technical University of Munich, reported in the April 11, 1997 SCIENCE that they generated large quantities of activated acetic acid from basic raw

materials at 100°C. This is the temperature typical of the fringe of a hydrothermal vent, where the volcanic brines mix with near-freezing ocean water.

Critics complain that Wächtershäuser's experimental temperature represents a limited zone in the vent environment. Toward the scalding core of a vent system, temperatures are nearer 350°C.

A longtime supporter of the primordial soup hypothesis, Jeffrey L. Bada of the Scripps Institution of Oceanography in La Jolla, Calif., has conducted several experiments showing that certain life-critical chemicals could not survive in their scorching birthplace for more than a few minutes or days. By testing reactions at only a single temperature, Bada says, Wächtershäuser is "not playing with a full deck of cards."

Such a rebuke doesn't apply to other experimentalists, such as the Carnegie Institution team, who are joining the game. The Carnegie researchers at times closely follow Wächtershäuser's blueprint, but they're aiming for results much broader, and perhaps more convincing, than the German chemist has achieved to date.

They are trumping Bada's criticism by testing chemical reactions over a much wider range of temperatures. What's more, with their bomb apparatus, the team can perform experiments at the extreme pressures that are typical under thousands of meters of seawater, a factor Wächtershäuser never explored.

Christopher Chyba of the Search for Extraterrestrial Intelligence (SETI) Institute in Mountain View, Calif., is encouraged by the growing interest in this research. "A variety of ideas, many of them flowing out of Wächtershäuser's hypothesis, are now leading to a kind of renaissance of experiments in the origins of life," he says.

It was another origins-of-life theorist who got the Carnegie team involved. About the same time that Wächtershäuser began considering metabolism as the root of life, a similar idea came to biologist Harold J. Morowitz of George Mason University in Fairfax, Va. He also was drawn to the primitive power of the citric acid cycle. Unlike Wächtershäuser, Morowitz's first ponderings were still steeped in the primordial soup.

It took prodding from his friend Corliss,

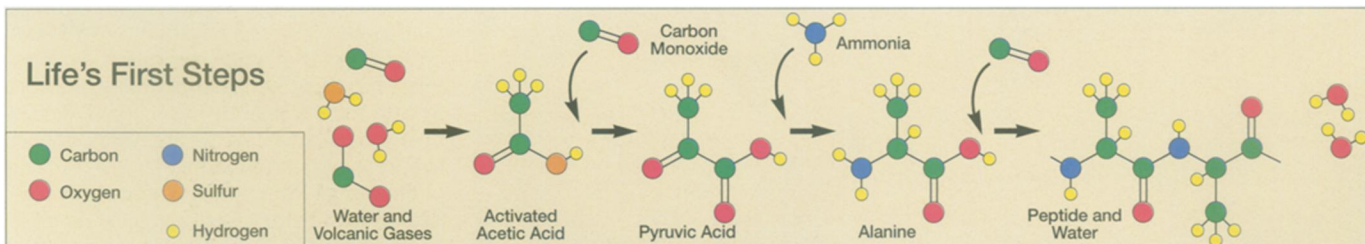
now at the Central European University in Budapest, for Morowitz to move his envisioned birthplace of prebiotic metabolism out of the light and into the ocean depths. That's when he turned to his George Mason colleague Robert M. Hazen, who also holds a position at Carnegie's Geophysical Laboratory. Hazen had long studied what happens to the structures of mineral crystals buried deep inside the Earth, so his high-pressure expertise translated easily into methods for testing what might happen to chemicals at vents.

Hazen and Morowitz assembled specialists, each capable of attacking the origins-of-life question from a different area of expertise, from several institutions. What's more, they are backed by NASA's new Astrobiology Institute, which is exploring where and how life may exist throughout the universe. "We're trying to use a systematic approach to what is a huge and complicated field," Hazen says.

Their approach recently took advantage of Brandes' focus on nitrogen, another important life-building element. Organisms gain nitrogen through reactions involving ammonia, a simple combination of nitrogen and hydrogen. In Wächtershäuser's theoretical assembly line, ammonia is a key player: It helps convert compounds from the citric acid cycle into amino acids. Yet few had expected ammonia to survive the vent inferno.

Brandes led the way to proving that expectation false. In the tiny gold capsules, he mixed water with nitrogen oxides presumed to be present in ancient oceans and added Wächtershäuser's sulfide minerals to jump-start any reactions. Inside the bomb, heating elements and pneumatic pistons subjected the capsules to conditions typical of hydrothermal vents. After only 15 minutes at 500°C and a pressure 500 times that at the planet's surface, the experiment created ammonia—and lots of it. What's more, the ammonia was stable up to a fiery 800°C. The team reported their findings in the Sept. 24, 1998 NATURE.

Once the Carnegie researchers knew that the hydrothermal mix could create ammonia, they turned to the next step, in which ammonia combines with pyruvic acid to build the amino acid alanine. Again, the scientists mixed their ingredients in a gold capsule and heated and squeezed them. Even without a catalyst, as much as 40 percent of the pyruvic



A blueprint describing how biomolecules might have emerged from inorganic chemicals spewing from the seafloor: With a jump-start from sulfide minerals (not shown), each step incorporates raw materials readily available at hydrothermal vents to fashion a more complex molecule.

acid converted to alanine.

Amino acids made at hydrothermal-vent conditions don't impress the researchers who have most enthusiastically promoted the primordial soup hypothesis. They've had amino acids in hand for decades. Back in 1953, chemist Stanley L. Miller of the University of California, San Diego shot a streak of electricity through a laboratory mixture of methane, hydrogen, and ammonia—a replica of the primordial atmosphere. This imitation lightning sent chemicals raining down into a flask of oceanlike water below, which grew red and yellow with amino acids in a week's time.

Research has since drawn Miller's hypothetical atmosphere into question, causing many scientists to doubt the relevance of his findings. Recently, scientists have focused on an even more exotic amino acid source: meteorites. Chyba is one of several researchers who have evidence that extraterrestrial amino acids may have hitched a ride to Earth on far-flung space rocks.

Amino acids from a variety of sources almost certainly seasoned a broth on the planet's surface 4 billion years ago, Chyba says, but he points out that no one has ever satisfactorily explained how the widely distributed ingredients linked up into proteins. Presumed conditions of primordial Earth would have driven the amino acids toward lonely isolation. That's one of the strongest reasons that



Sulfide minerals glitter inside this hydrothermal-vent chimney, which scientists dragged up from the seafloor off the Washington coast last summer.

Wächtershäuser, Morowitz, and other hydrothermal vent theorists want to move the kitchen to the ocean floor. If the process starts down deep at discrete vents, they say, it can build amino acids—and link them up—right there.

Last year, Wächtershäuser and Huber did just that. They reported in the July 31, 1998 *SCIENCE* that at 100°C, they got amino acids to connect into short proteinlike chains called peptides. Even so, Bada won't budge from his surface-soup stance. He sees no reason why amino acids simmering in pools of water on rocky shorelines couldn't link up through just the same reaction. "I guarantee that experiment would work just as well at 25°C," says Bada. "It would take longer, but you'd make the same product."

That may be so, Wächtershäuser says, but the molecular links are broken nearly as fast as they're created in both situations. All the chances lie in the blindingly

quick activity at the vents, he says. "You throw the dice much more often."

Busily throwing the dice in his laboratory, Wächtershäuser is trying to find the right metal catalysts that will get his short peptide chains to lengthen and reproduce themselves, the ultimate criterion of life. Everyone digging around for the origin of life would like to discover the first molecule that learned to make copies of itself.

"That's really what the struggle is all about," Wächtershäuser says, "and so far, it hasn't been found."

Articles appearing regularly in scientific journals claim to have generated self-replicating peptides or RNA strands (*SN*: 8/10/96, p. 87), but they fail to provide a natural source for their compounds or an explanation for what fuels them. Brandes, now at the University of Texas Marine Sciences Institute in Port Aransas, compares this top-down approach to a caveman coming across a modern car and trying to figure out how to make it.

"It would be like taking the engine out of the car, starting it up, and trying to see how that engine works," but Carnegie's approach is from the bottom up, he says. "What we do is start with the block of iron and try to make a car out of that."

The Carnegie team's next refinement to their iron block is to build a laboratory model of a hydrothermal vent. A maze of tubes and flasks will route hot, pressurized gases and water through vent minerals to see whether reactions that take place inside the gold capsules also happen in a more realistic environment. Brandes guesses that one day bottom-up and top-down researchers will together forge a complete chain of events—from the simplest raw materials to a collection of molecules that qualifies as being alive.

Yet even if scientists ultimately find a set of steps for the origin of life in the laboratory, everyone agrees that it may not replicate what occurred on Earth 4 billion years ago.

"I'm optimistic, not that we will ever really know with certainty what happened on Earth but that we will have a plausible account to give," Chyba says.

An account based on hydrothermal forces deep in the sea opens up the possibility of life elsewhere in the solar system. While few places may have had sunlit ponds, more have evidence of geothermal forces. Prime candidates are Mars and Jupiter's ice-covered moon Europa (*SN*: 11/7/98, p. 296). An upcoming mission to Europa will search for a liquid ocean overlying chemical-spewing geysers similar to Earth's hydrothermal vents.

There's an interesting synergy between the experimental results suggesting that life originated on Earth's seafloor and speculation about an ocean on Europa, Chyba says. "To some extent Europa will provide a test of the deep-origins hypothesis." □

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