

Origin of Life: New Ingredients Suggested

After 30 years of dominance, the traditional recipe for chemical precursors to life is being joined by a serious alternative

Life on Earth probably got its start, textbooks say, when lightning scorched through the noxious primordial atmosphere of methane and ammonia and produced the first complex organic chemicals. This view of chemical evolution has dominated research for 30 years, although most geochemists have seriously doubted that Earth's primitive atmosphere bore much resemblance to the textbook version. Instead, the atmosphere that produced the first building blocks of life may have been similar to today's except that it lacked oxygen. Within the past few years, the geochemists' arguments have begun to be heard. As a result, chemical evolutionists are studying reactions in gas mixtures that geochemists believe more closely resemble the primitive atmosphere.

stroy any prebiotic compounds, evolved.

Stanley Miller, then also at the University of Chicago and now at the University of California at San Diego, immediately demonstrated that the organic life on Earth today might easily have arisen from a highly reducing atmosphere. He passed an electrical discharge through a mixture rich in methane and ammonia, producing copious amounts of the appropriate organic compounds, such as amino acids.

Miller and Urey's proposal of a hydrogen-rich, highly reducing primordial atmosphere prompted numerous new searches for a reasonable path to life. Chemical evolutionists put aside their balky experiments with carbon dioxide atmospheres and eventually produced most of the essential amino acids, linked

was fine work. It was pretty and compelling. It may still be right. But it has tended to dominate thinking in the area." Neither chemical evolutionists nor geochemists have attempted to redress the imbalance, both sides note.

The contradicting geological evidence is fairly strong, up to a point, according to James Walker of the University of Michigan. That point is 3.8 billion years ago. Rocks of that age from Isua, Greenland, the oldest known, contain carbonate minerals that could only have formed if the atmospheric carbon at that time was largely carbon dioxide rather than methane.

Even between 3.8 billion years ago and the formation of Earth at about 4.5 billion years ago, a largely carbon dioxide and nitrogen atmosphere could have been maintained, geochemists say. A trace of hydrogen may have been present, causing the atmosphere to be at most only mildly reducing. Urey's hydrogen-rich, primordial atmosphere either never existed or survived only a short while, according to Walker's interpretation of the rare gas content of today's atmosphere. According to a widely held theory, the carbon, nitrogen, hydrogen, and oxygen in today's ocean and atmosphere were released from Earth as volcanic gases instead of being lingering residues of the presolar nebula. Volcanoes, such as those of Hawaii that draw magma from the mantle at 1300°C, release carbon dioxide, water, and small amounts of hydrogen and carbon monoxide, but no methane or ammonia. At that temperature, the oxidized iron in the mantle allows only traces of reduced gases to be formed.

Earth could have released highly reduced gases early in its history, but only until its core formed. Until then, reduced metallic iron of the mantle, which would eventually form the core, would control the oxidation state of the released gases. But, says Walker, current thinking holds that the mantle's metallic iron fell into the core at or near the time Earth first pulled itself together from the solar nebula. Some chemists suggest that even if a methane-ammonia atmosphere had

A hydrogen-rich primordial atmosphere either never existed or survived only a short while, many geochemists believe.

The proposal of a primitive methane-ammonia atmosphere originally had strong physical and biological rationales. In the early 1950's, Harold Urey of the University of Chicago theorized that conditions at the formation of Earth would have determined the composition of its atmosphere. The solar system is composed mostly of hydrogen, Urey observed. The hydrogen gas that Earth was able to retain after its formation would have kept any gaseous carbon or nitrogen in their most reduced chemical forms, methane (CH₄) and ammonia (NH₃). Their more oxidized forms, carbon dioxide (CO₂) and gaseous nitrogen (N₂), could not have been present in significant amounts. Only the dissociation of water by ultraviolet radiation and the gradual loss of that hydrogen to space would have eventually oxidized the atmosphere, Urey reasoned. In the meantime, life could get its start before an oxidizing atmosphere, which would de-

stroy any prebiotic compounds, evolved. Studies of amino acids in meteorites showed that reactions similar to those forced to occur in laboratory flasks had occurred naturally elsewhere in the solar system. Radio astronomers even found chemicals that would take part in such reactions in interstellar space. The process seemed to be universal.

Such evidence has not impressed most geochemists and cosmochemists. No geological or geochemical evidence collected in the last 30 years favors a strongly reducing primitive atmosphere, they say. Only the success of the laboratory experiments recommends it. "Miller and Urey were in a sense premature [in making their proposal]," says Mario Baur of the University of California at Los Angeles, a thermodynamicist with an interest in chemical evolution. "Practically everything we know about planetary formation has been learned since then. It



Artist Chesley Bonestell's conception of the primitive Earth. According to prevailing geochemical theory, today's atmosphere, minus its oxygen, was released from Earth as volcanic gases (upper left). Lightning (upper right) could have been one of the energy sources that converted some of those gases into complex organic compounds. Once dissolved in ponds and oceans, these compounds could have evolved into the first living organisms. Most chemical evolution studies have been based on an opposing theory, which holds that the primitive atmosphere was a hydrogen-rich residue of Earth's formation.

formed, it may have been short-lived because of the instability of these compounds when exposed to sunlight.

No one is claiming that the geochemists' reasoning in support of a mildly reducing atmosphere is foolproof, only that it deserves greater attention from chemical evolutionists. After nearly three decades of neglect, it is beginning to get that attention. One new advocate of an unfettered approach to the origin of life is Sherwood Chang, a chemical evolutionist at Ames Research Center, Mountain View, California. While not rejecting methane for carbon dioxide, Chang has begun campaigning for serious consideration of both possibilities. Recently, he notes, researchers have been giving more critical consideration to the data. Considering the evidence turned up since Urey first argued for a methane-ammonia atmosphere, "there simply is no compelling justification for methane as the source of carbon."

Chang is among the first to point out that that is not a new idea—it is only once again being forcefully stated. For example, in 1966 Philip Abelson, then of the Geophysical Laboratory of the Carnegie Institution of Washington and now editor of *Science*, argued on geophysical and geochemical grounds against Urey's residual atmosphere; to prove his point, he generated amino acids from mixtures of nitrogen gas, carbon monoxide, and hydrogen. Although Abelson may have managed to reduce the emphasis on ammonia, which he noted is photochemically unstable, his laboratory work was remembered by some as another example of the difficulties of producing suf-

ficient amounts of organic compounds in the absence of methane and ammonia.

An increasing number of researchers believe that the lack of these compounds need not be a barrier to the production of biological precursors. In recent work, John Oró of the University of Houston passed an electrical discharge through a mixture of carbon monoxide, nitrogen gas, and water. Among the products, he says, were amino acids and the two major purines (adenine and guanine) found in nucleotides. Such success, Oró says, supports the hypothesis that the atmosphere was neither too reducing nor too oxidizing, but intermediate in its composition.

Another example of an approach to mildly reducing atmospheres is a computer model developed by Joseph Pinto of the Goddard Institute for Space Studies in New York City and Randall Gladstone and Yuk Yung of the California Institute of Technology. For their model, they assumed that the primitive atmosphere of Earth resembled today's minus all its oxygen. Eight ten-thousandths of an atmosphere of hydrogen, equal to several times the amount of carbon dioxide in today's atmosphere, was assumed to have been built up from volcanic emissions in spite of losses to space and to photochemical reactions. Several thousand times less carbon monoxide than hydrogen would have been present. Such conditions are a far cry from the traditional mixtures of laboratory experiments, where ease of reaction and conveniently high yields have been paramount. Even so, Pinto and his co-workers calculate that sunlight could cause

enough carbon dioxide and hydrogen to form formaldehyde so that 3 million tons of it would rain down on the oceans each year. Within 10 million years, they say, formaldehyde produced at that rate would be concentrated enough for sunlight to polymerize it into more complex molecules.

Baur would like to do without hydrogen entirely. With reduced iron ions as a reducing agent and sunlight as an initiator, carbon dioxide and nitrogen gas could react to form amino acids, according to Baur's thermodynamic calculations. How fast that could happen he cannot yet say. He believes that more research is needed on iron as a reducing agent to answer that question.

A call for more research would be trite in many fields, but chemical investigations of the origin of life have been lopsided for a long time. As Cyril Ponnamperna of the University of Maryland notes, a great deal has been learned about Earth's primitive atmosphere since Urey's 1952 formulation. But even with space-age data in hand, there is no complete answer yet, he says. In light of this uncertainty, Ponnamperna adds, possible chemical beginnings of life cannot be arbitrarily dismissed because conditions are not highly reducing, the reaction rates are slow, or the laboratory yields are not impressive.

—RICHARD A. KERR

Additional Reading

1. R. E. Dickerson, "Chemical evolution and the origin of life," *Sci. Am.* 239, 70 (September 1978).
2. K. Kvenvolden, Ed., *Geochemistry and the Origin of Life* (Academic Press, New York, 1974), vol. 14.