

# First Life

*Billions of years ago, deep under the ocean, the pores and pockets in minerals that surrounded warm, alkaline springs catalyzed the beginning of life*

Michael Russell

Life is no less wonderful when science solves some of the mysteries of its origin. We understand how birds fly and how diamonds sparkle, yet these sights remain entrancing. Likewise, the mathematics of thermal convection are well known, but their most familiar examples, such as the geysers and hot pools at Yellowstone National Park, continue to delight.

The same force that drives "Old Faithful" drives the planet: Convection—of magma, water and air—is the Earth's engine. Its swirling currents cause volcanoes to erupt, ocean nutrients to mix and trade winds to blow. In effect, it creates fresh surfaces, full of chemical potential. And about four billion years ago—only a few hundred million years after Earth formed—this potential enabled some very important chemical

reactions. Warm springs deep under the ocean's surface brought the Earth's deep heat to the surface and fertilized the new seas with ions from the underlying rock. These conditions, allied with solar energy, enabled life's beginning.

Although scientists don't know for certain how life started, geochemists who study the ancient Earth can make and test hypotheses based on our knowledge of those early conditions. Thus, the question we ask is not "did it happen this way?" but rather, "could it have happened this way?" And if we can say at each step "yes, this is possible," then we can construct a path that stretches from the raw materials of the universe to ourselves. In this article I'll attempt to chart some of the steps along the path from lifeless liquid to living plants.

## A Tale of Two Molecules

At the beginning of this journey, it is helpful to review what we know about living things today. Consider, from a chemical perspective, what life does: At the bottom of every food chain, a bacterium or plant uses hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) to synthesize organic compounds. Some organisms extract hydrogen atoms from molecules such as hydrogen sulfide (H<sub>2</sub>S or HS<sup>-</sup>); others break down water during photosynthesis. All other life forms rely on, exploit and consume those cells that combine hydrogen and carbon dioxide.

Such simple inorganic molecules also existed on the young Earth, and they provided the raw materials and the energy for life's emergence. A dense carbon dioxide atmosphere filled the oceans with high levels of dissolved CO<sub>2</sub>. At the same time, molecular hy-

drogen (H<sub>2</sub>) escaping from the Earth's crust had a strong propensity to convert back to water, a reaction that removes an oxygen from the CO<sub>2</sub> molecule and can produce acetic acid (vinegar) and methane—precursors of more complex organic molecules. Yet H<sub>2</sub> and CO<sub>2</sub> are stable in each other's presence. Indeed, the fact that hydrogen and carbon dioxide do not fuse spontaneously—despite the chemical potential to do so—is the reason life exists. Life is both the catalyst for and the product of this reaction. Here it is at its simplest:



However, this equation neglects the other components required to build a variety of organic molecules. Aside from carbon, hydrogen and oxygen, slightly more complex chemical reactions involve nitrogen (as ammonia), sulfides, phosphates and trace amounts of several transition metals, including iron, nickel, manganese, cobalt and zinc. All of these raw ingredients would have been present in the early ocean, particularly near deep-sea hydrothermal vents, which emit hot water saturated with dissolved minerals.

The equation above also overlooks the major by-products of life, apart from water. Living things—even the simplest—produce an amazing amount of waste. (As an aside, this waste, eventually including oxygen, is the signal most likely to betray the presence of life on other planets.) Many microbes get their names from the wastes they generate—methane producers are called "methanogens," and those that produce acetate (the ionic form of acetic acid) are "acetogens." The latter were probably the

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first organisms, in part because of the energy released by acetate formation, which, as Everett L. Shock of Arizona State University has calculated, would have been considerable. The more complicated equation at the bottom of the page shows the production of a unit of proto-life as well as voluminous acetic acid and waste water. These result from the chemical combination of a salty soup of precursors including  $H_2$ , ammonia and sulfides, and they form within the mounds around high-*pH* (alkaline) hydrothermal springs.

The high ratio of waste to proto-life in the reaction below might appear striking, but note the tremendous amount of hydrogen used. Hydrogen is fuel for life's motor, a motor that generates chemical compounds with a more stable thermodynamic state and greater entropy than their precursors. Our modern visible biosphere uses the same engine, although today's oxygenic photosynthesis by cyanobacteria, algae and plants is a world away from this simple process. But how did it get started?

#### Out of the Box Solutions

To answer this question, one must first imagine the conditions on the planet back when proto-life began. Earth spun more rapidly on its axis—a day lasted only four or five hours. The Moon was much closer, causing strong, frequent tides and storms. Giant meteorites pelted the planet, vaporizing the ocean surface when they struck water and throwing up dust clouds that blocked warmth and light from the Sun when they struck land. Under these conditions of constant, chaotic change, life could not have formed on the Earth's exterior. There was only one place of constancy and nourishment—a warm spring in the relative safety of the deep ocean floor. There, protected from destructive ultraviolet radiation, existed a place that never dried out, never got too hot or too cold, never became too acidic or too alkaline.

My colleague Allan Hall and I suggested in 1988 and 1989 that warm, alkaline (basic) springs at the bottom of the acidic Hadean ocean could have provided the conditions that carefully nurtured life's emergence. The gradients of temperature and *pH* around hydrothermal vents would have provided energy and opportunity, and the minerals dissolved



Scottish National Gallery of Modern Art

Figure 1. Four billion years ago in the Hadean Eon, a choking carbon dioxide atmosphere blanketed the convection-roiled Earth. Beneath sterile waves of a world-spanning ocean, hydrothermal springs seeped hydrogen and sulfides into an acidic brew that contained iron, phosphate and other vital trace elements. At the meeting of these waters, iron-nickel sulfides formed a membranous froth, which catalyzed the formation of nucleic acids and proteins—precursors to the first living organisms. That alien, but ultimately fertile landscape is evoked in the painting *Dehors* by Yves Tanguy (*above*), which was created more than half a century before most origin-of-life research took place. Nevertheless, Tanguy, like other surrealists, was intent on starting from scratch. Thus, his “biomorphs” resonate with the mineral gardens and mounds on the floor of a barren ocean, and pennants streaming from the tips of three distorted axes give a sense of energy flowing and time passing. Scientists now know the chemistry of those primitive organisms (*bottom of this and facing pages*) because the remarkable events behind their origin are manifest in every mote of every living creature today, from viruses to artists. And, like all forms of life, those first organisms produced large amounts of waste—in this case, water and acetic acid, or vinegar. This chemical depiction of life possesses a strong thermodynamic drive, which has led scientists to speculate that this energy propelled the “acetogens” to be the first to evolve and escape the mound.





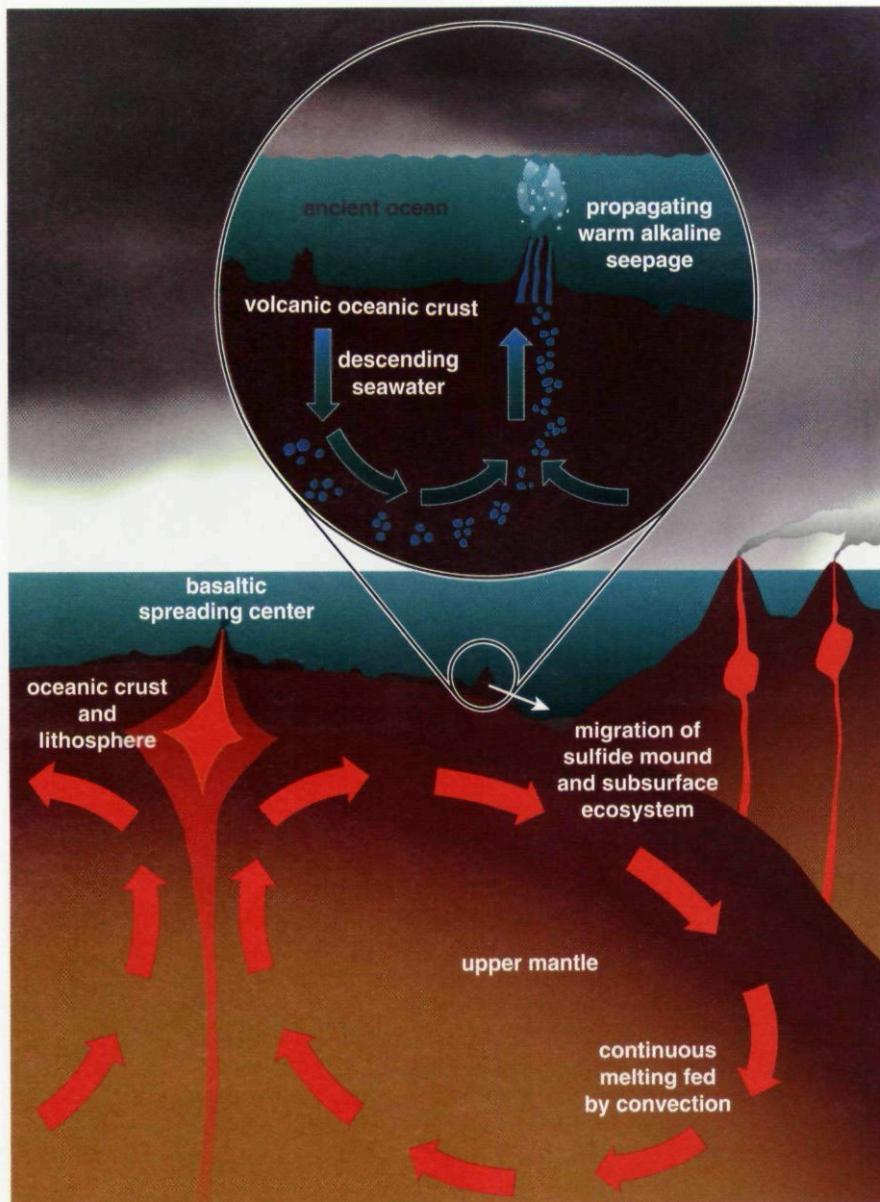


Figure 2. Convection is the Earth's engine. The circulation of rock in the mantle drives the movements of the lithosphere, the upper layer, in which water percolates downward, takes up the heat of radioactive decay and bears a rich burden of elements into the ocean through vents in the sea bottom. The hottest vents, called black smokers, occur at oceanic ridges, whereas milder, alkaline springs are farther away.

in water flowing from such a spring would have provided a constant source of chemical nourishment—a continuously regulated flow reactor, in chemical-engineer parlance. The dissolved compounds would likely have fallen out of solution and formed insoluble solids when mixed with the chemicals in cooler seawater, thereby generating towering mounds of precipitated carbonate, silica, clays and iron-nickel sulfides that surrounded such springs.

The alkaline-spring theory was bolstered in 2000, when a team led by oceanographer Deborah S. Kelley at the University of Washington found structures 800 meters below the ocean surface that

were similar to those we had predicted. Some of those pale, carbonate spires near the Mid-Atlantic Ridge reached 60 meters, earning the site the evocative name of "Lost City." The temperature of the Lost City springs stays around 90 degrees Celsius—much cooler than another type of hydrothermal vent, the so-called black smokers, which form at oceanic ridges and discharge water at about 400 degrees—hot enough to melt lead and incinerate any organic polymers (a characteristic that challenges the candidacy of black smoker vents as sites of organic synthesis in their own right). However, the black smokers were important sources of metal and phosphate ions.

The germ of the alkaline-spring hypothesis came from my son Andy. One evening I entertained him by making some "chemical gardens" from a kit (they're available in toy shops and science museums). The gardens are actually long fingers of silica that form when hydrated crystals of a strong acid and weak base (for example, cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) are immersed in an alkaline solution of sodium silicate. The results are rather beautiful. But the next night, to my consternation, he started breaking them up. Deaf to my pleas to join us at supper, he announced from behind the locked bathroom door, "Hey Dad, these things are hollow!"

Hollow! Suddenly I understood the puzzling mineral patterns I had seen in 350-million-year-old rocks from a lead-zinc mine in Ireland. Those columns, chimneys and bubbles in the stone were made of iron sulfide—they must have once been natural chemical gardens. When I discussed my son's destructive experiment with Allan the next day, we realized that such structures could have acted as an inorganic membrane for the first cells when warm, alkaline-spring water rich with sulfide ions met acidic seawater laced with iron from black smoker vents. We rushed to the laboratory and readily mimicked the fossil shapes by simulating these conditions.

Such experiments show that the iron sulfide precipitate initially forms a gel with pores and bubbles that provide enclosed sites for chemical reactions. The somewhat flimsy membranes between pockets would have trapped and concentrated organic molecules, and the small volume of each bubble would have encouraged less favorable or more complex reactions. For similar reasons, every autonomous life form today utilizes a membrane to contain its contents.

Importantly, the proto-cells that formed at alkaline springs would have experienced a constant stream of  $\text{H}^+$  ions (protons) crossing the membrane from the acidic surroundings. This flow, known as the protonmotive force, does useful work for living cells today—except that now, cells must create their own gradients by actively pumping out  $\text{H}^+$  ions.

Laboratory experiments also demonstrated such iron-sulfide membranes to be semi-permeable: Any larger, "sticky" organic products (amino, fatty and nucleic acids, sugars) were trapped in the



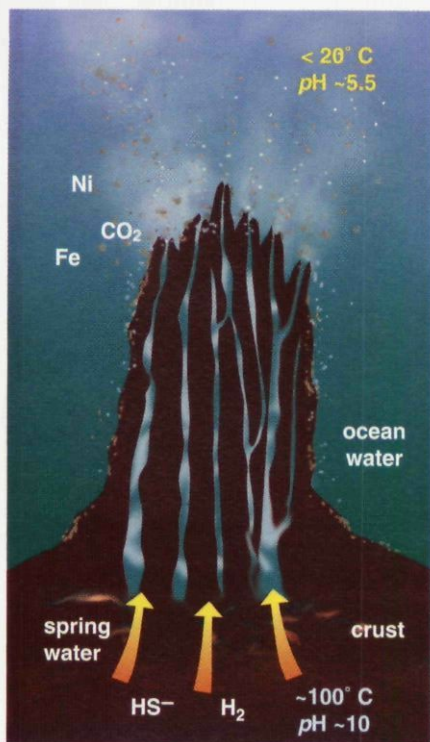


Figure 3. Hydrothermal mounds were key to life's development. Alkaline fluid from such vents carried hydrogen, sulfide and ammonia. The surrounding water was cool, carbonic and oxidized and contained trace metals. In the pores of the mound, organic ions were produced and retained, reacting and self-organizing to emerge as proto-life.

bubbles and pores, but small, unreactive organic molecules (acetic acid, methane) escaped. But how were the organic molecules made in (or delivered to) these inorganic proto-cells in the first place? Even the simplest reactions couldn't just happen. Carbon dioxide and hydrogen, as I noted above, are quite stable in each other's company. They needed a catalyst.

#### What You Get for a Nickel

As Allan and I speculated about possible catalysts, one candidate was the mineral greigite [ $\text{Fe}_3\text{NiS}_4$ ], an iron-nickel sulfide that coprecipitated in those membrane experiments in our lab. I knew from my apprentice days in the organic chemical industry that the nickel it contains could act as an excellent catalyst for organic synthesis, thereby aiding the reaction of hydrogen (dissolved in the vent effluent) with carbon dioxide (dissolved in the ocean water). If greigite was indeed the first catalyst for life, then some remnant of this earliest anabolic process might still exist among the living descendants of those processes: enzymes, life's catalysts.

The importance of iron sulfides in early life was not a recent idea. Back in 1966, Richard V. Eck of the National Cancer Institute and Margaret O. Dayhoff of Georgetown University sug-



Figure 4. The alkaline-spring hypothesis originated with a child's toy. "Chemical gardens" (often sold as "Magic Rocks") result from the immersion of water-soluble salts of a strong acid and weak base in an alkaline solution of sodium silicate. The reaction is similar to that of sulfide and metal ions at the opening of a hydrothermal vent. Both types of precipitates form semi-permeable gelatinous membranes that enclose hollow spaces. (Photograph courtesy of Jimmy Dorff.)

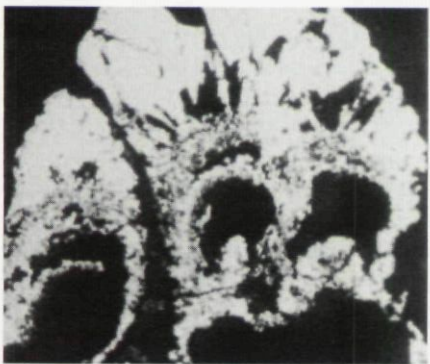


Figure 5. Evidence of natural chemical gardens comes from fossil and contemporary sources. During its years of operation, the Tynagh mine in County Galway, Ireland, yielded 350-million-year-old samples of pyrite ( $\text{FeS}_2$ ) that showed spires (top left) and bubbles (bottom left). The beehive-shaped deposit at right is part of the Lost City site near the Mid-Atlantic Ridge. Its fluid is nearly particulate-free, approximately pH 10 and 90 degrees Celsius. The effluent can be seen shimmering above the cone. (Photograph courtesy of the University of Washington/NOAA.)



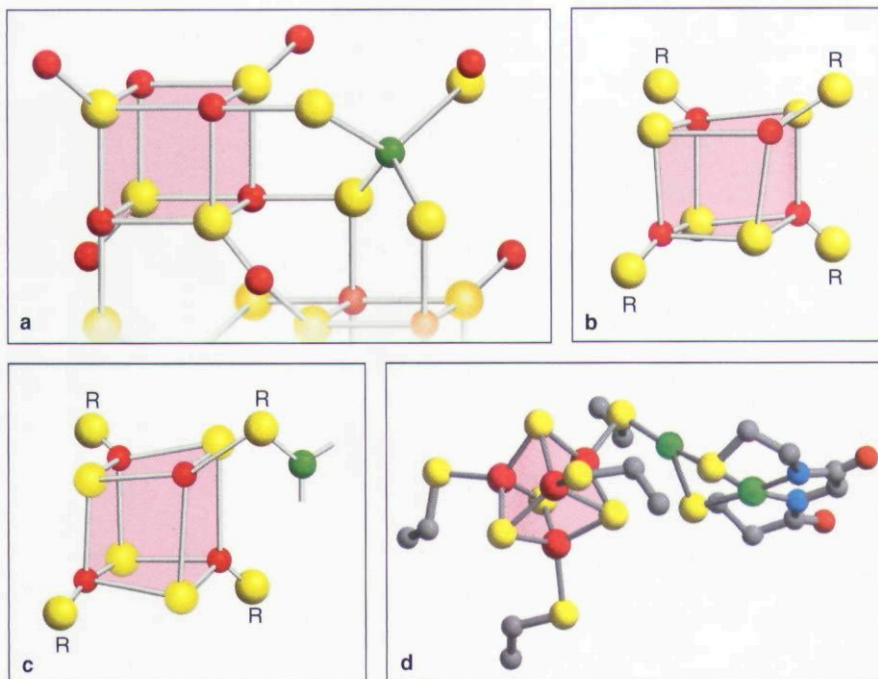


Figure 6. The molecular structure of the mineral greigite (a) is very similar to that of the thiocubane unit (b) of the ferredoxin protein, as well as to the cuboidal complex (c) in the active site of the enzyme acetyl-CoA synthase/carbon monoxide dehydrogenase (shown in schematic form). The x-ray crystal structure (d) for the so-called A cluster of the latter confirms this similarity. Atoms are colored as follows: iron, red; sulfur, yellow; nickel, green; carbon, gray; nitrogen, blue. R signifies links through sulfur to the remainder of the protein. Part d is modified from Darnault *et al.*, 2003.

gested that the oldest types of proteins contained imperfect cubes defined by iron and sulfur atoms on alternate corners. These [4Fe-4S] centers are referred to as *cubanes*, and organisms use proteins incorporating cubanes, such as the protein ferredoxin, to transfer electrons across a membrane or to a site of biosynthesis. Eck and Dayhoff's hypothesized connection between cubanes and early organic chemistry echoed the rather stark view of Nobel-prize winning biochemist Albert Szent-Györgyi: "Life is nothing but an electron looking for a place to rest." Then as now, carbon dioxide can be that resting place: By accepting electrons it is reduced to organic molecules.

In 1999, Juan-Carlos Fontecilla-Camps at the Institute of Structural Biology in Grenoble, France, and Stephen W. Ragsdale at the University of Nebraska demonstrated that enzymes with iron-nickel sulfides could reduce carbon dioxide to carbon monoxide (CO) and water and further catalyze the formation of acetate and more water—the very reactions we were looking for. The active centers of this double-duty enzyme (which is known as carbon monoxide dehydrogenase/acetyl co-enzyme A synthase) has a formula ( $\text{Fe}_4\text{NiS}_5$ ) and structure (cubane-like) strongly reminiscent of greigite

( $\text{Fe}_5\text{NiS}_8$ ). This finding suggested, but did not prove, that inorganic iron-nickel sulfides could have gotten life started.

Another important piece of the puzzle came in 1997, when Claudia Huber of the Technical University of Munich and chemist/patent attorney Gunter Wächtershäuser demonstrated that "a freshly precipitated aqueous slurry of coprecipitated" nickel and iron sulfides (probably greigite) could produce acetate in the presence of carbon monoxide (alas, not carbon dioxide) and methyl sulfide ( $\text{CH}_3\text{SH}$ , which is another product of iron-sulfide catalysis, this time from  $\text{CO}_2$ ). As my collaborator William Martin at Heinrich-Heine University in Düsseldorf and I have suggested, acetate could have subsequently produced other organic molecules with the energy released by its formation. As early as 1992, Remy J.-C. Hennet of the geosciences firm S. S. Papadopoulos & Associates, Nils G. Holm at Stockholm University and Michael H. Engel at the University of Oklahoma used iron sulfides and clays as catalysts to generate simple amino acids such as glycine from basic starting materials. And in 2004, Luke Leman and M. Reza Ghadiri of the Scripps Research Institute, with Leslie Orgel of the Salk Institute for Biological Studies, demonstrated the generation of strings of amino

acids—peptides—using carbonyl sulfide ( $\text{COS}$ ) and metal-sulfide catalysts. Only one link in this chain of inductive reasoning remains to be achieved: demonstration of an inorganic means of reducing  $\text{CO}_2$  to CO.

Even without this keystone, geochemists now have evidence of how iron (nickel) sulfides could have catalyzed organic synthesis and contained some of its products. Over time, it seems plausible that certain peptides engulfed nearby iron-sulfur clusters to yield the ferredoxins of today. E. James Milner-White at the University of Glasgow and I have shown, at least in theory, that a string of simple amino acids can indeed wrap around an iron-sulfide cluster to form a primitive enzyme, rather as Eck and Dayhoff first suggested.

Amino acid polymers not only had the propensity to co-opt catalysts from their surroundings, but in bulk, they also could have lined the inorganic bubbles that enclosed them. And because peptides are generally insoluble, this proteinaceous film could conceivably take over the role of cell wall and membrane. In this way, globules of self-replicating molecules could have finally floated free of the hydrothermal mounds that spawned them.

As the chemistry changed from inorganic to organic, rudimentary metabolism would have become more efficient. However, the most complex chemical reactions would have remained rather arbitrary. No consistent means existed to produce macromolecules with specific properties, thus improvements to their design would have been difficult to perpetuate. For Darwinian evolution to begin there had to be some type of natural selection, which implies genetic control, however crude.

### RNA Ascendance

Genetic information is stored as ribonucleic and deoxyribonucleic acid (RNA and DNA) molecules, which are more complex than a simple peptide. Thus, despite modeling the successful synthesis of proteins from the most elementary precursors, chemists have not yet created nucleic acid polymers from scratch in the lab. However, the reactive components for RNA (which probably came first) were readily available: phosphate from hydrothermal vents, and the sugar ribose and some of the nitrogenous bases (primarily adenine) generated from primitive mate-



rials. When linked together, adenine, ribose and a phosphate are known as *adenosine monophosphate*—one of the building blocks of RNA.

The problem is that one monomer of RNA is useless as a blueprint. RNA must have initially had a different, advantageous role in the not-quite-living cell before nucleic acids began to direct the show. Once established, an RNA code could have been co-opted for information storage. But what was its first use?

The answer is probably adenosine triphosphate, or ATP, the molecule that acts as a universal energy currency in living cells. ATP serves an indispensable function as a source of energy—humans generate more than half their body weight of it every day. Harvesting its energy by breaking one of the high-energy phosphate bonds yields adenosine diphosphate or adenosine monophosphate again, which can link up to form an RNA polymer.

In its polymer form, adenosine may have had another indispensable role to play. Anthony R. Mellersh of the University of Derby in Britain has suggested that a bound chain of RNA would have gripped amino acids and effected the formation of peptide bonds. The process is even specific, in a crude sense, because the sequence of bases in an RNA polymer can select for certain amino acid side chains. This observation accords with the view of Carl R. Woese at the University of Illinois at Urbana-Champaign, who in 1967 posited a scenario in which primeval nucleic acids initially dictated protein sequences through a codon–amino acid pairing. Specificity arose from the variable affinity between certain codons (groups of three adjacent bases in RNA) and amino acids.

In modern organisms, dedicated molecules called *transfer RNAs* link specific amino acids to each codon in an RNA message. But Mellersh has shown that, for example, RNA codons with uracil as the central base tend to attract amino acids with hydrophobic side chains, whereas those with a central adenine favor hydrophilic charged or polar amino acids. These distinctions effect the kind of crude selection envisaged by Woese. With his colleague Alan-Shaun Wilkinson, now of QinetiQ Nanostructured Silicon Sensors, Mellersh demonstrated that poly-adenosine, with a predicted affinity for the amino acid lysine, does indeed select lysine from a dilute aqueous solution of amino acids. Furthermore, “AAA” still encodes lysine today.

Shelley Copley of the University of Colorado, Eric Smith of the Santa Fe Institute and Harold Morowitz at George Mason University suggest yet another step: Perhaps nucleotides didn’t merely *select* amino acids formed elsewhere, but actually began to *assemble* them. Morowitz uses pairs of nucleotides for this chemical trick, but we prefer trimers to preserve continuity with the triplet codons of extant life.

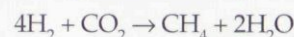
In these models, a mineral (perhaps a sulfide) provides the foundation for an RNA template that selects (or generates) amino acids, then assembles them into peptides. The short proteins accumulate inside the semipermeable iron-sulfide bubbles, where some may sequester precipitated sulfide clusters or provide a non-mineral substrate for the polymerization of other RNAs. The immobile RNA mold repeats the process. This division of labor is an

irreversible first step toward evolution in the proto-cell.

The RNA-world hypothesis does carry some conditions. RNA is fragile, so life was unlikely to have started at temperatures above 50 degrees, and eventually, the more robust, less reactive DNA took over many of the functions of RNA.

### Evolution Brought to Light

As productive as acetate generation must have been for the first organisms, some other means of combining CO<sub>2</sub> and H<sub>2</sub>—to synthesize methane, for example—are even more advantageous in terms of energy release.



But achieving this reaction is not so easy: Substantial barriers exist, although they can be sidestepped by catalysis and jumped with a bit more thermal energy. William Martin and I posit that the or-

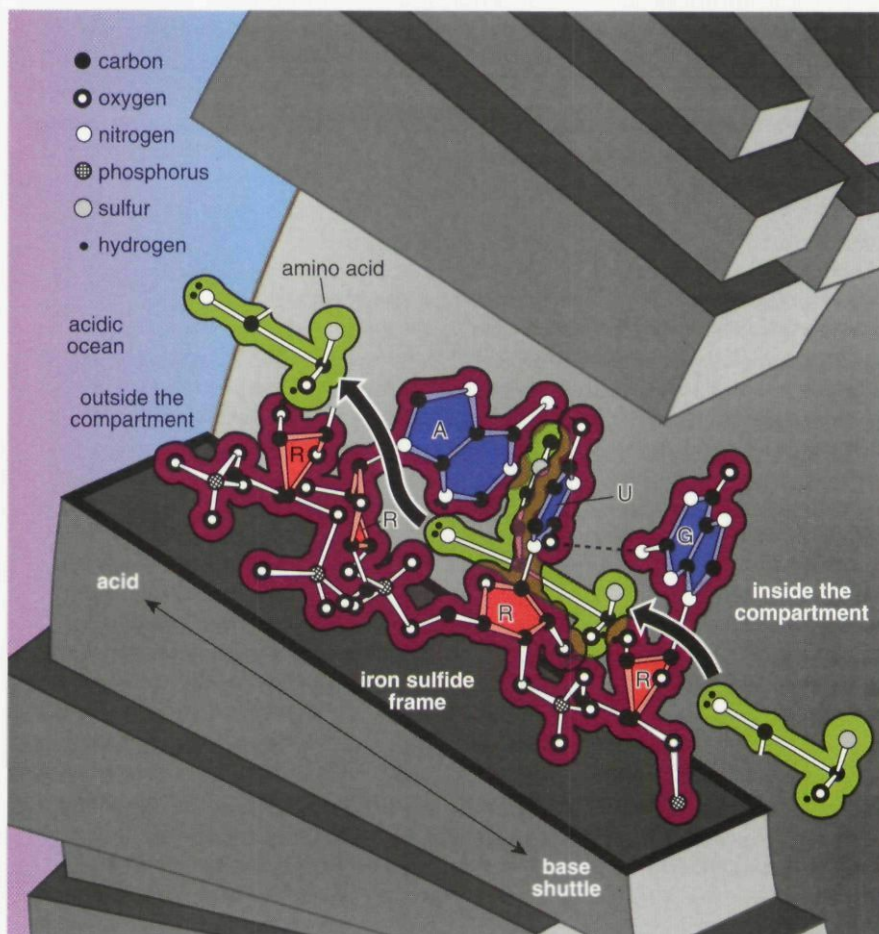
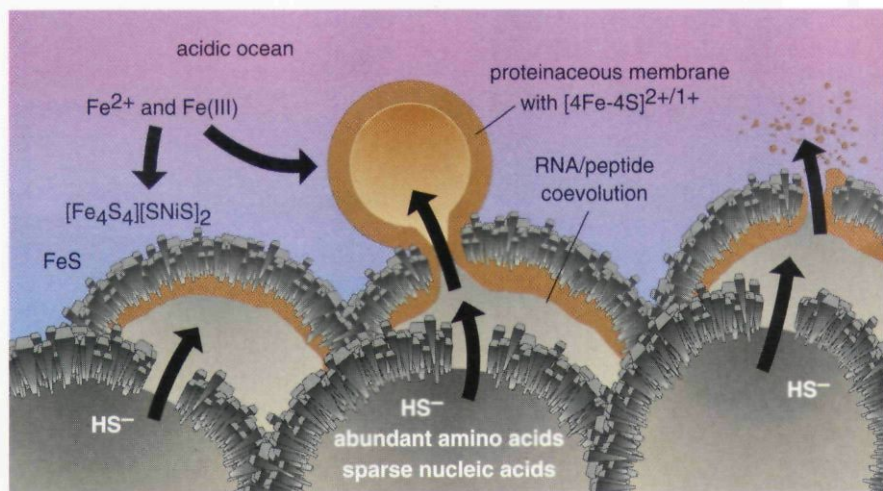


Figure 7. Short pieces of immobilized RNA (such as might form on a mineralized iron sulfide surface, gray) can act as templates for the formation of peptides. The specific amino acid depends in part on the sequence of the RNA, even in the absence of transfer RNA (the mechanism for specificity in modern organisms). Here, an RNA triplet (purple) of adenosine, uridine and guanosine (A, U and G, blue) grips the amino acid methionine (green molecule at center) and offers its nucleophilic amino group to the electrophilic thiocarboxyl group of an adjacent amino acid (green molecule at left). A peptide chain built incrementally in this way would be released by an acid influx from the ocean side of the inorganic membrane. (Based on Mellersh 1993.)





**Figure 8.** In the froth of iron sulfide bubbles around alkaline vents of the Hadean eon, simple organic molecules formed through the catalysis of iron-nickel sulfides would tend to diffuse from their source and bump into one another, accumulating as they became more complex. The result: Gummy, precipitated peptides were likely to have coated the inside surfaces of bubbles with more robust protein synthesis, a process that is believed to have led to the eventual assumption of membrane function by protein. This "organic takeover" represents an early step towards cellular autonomy from the confines of the iron sulfide incubator.

ganisms that achieved this feat, the proto-methanogens, marked the first and most significant fork in the evolutionary tree. In our view, these two different carbon dioxide assimilators, the proto-acetogens and proto-methanogens, quickly specialized and fledged, evolving over time into bacteria and archaea (primitive microbes that are neither bacteria nor eukaryotes). But how did they escape the hydrothermal hatchery?

The roiling ocean at that time was a desert, an ultra-dilute broth irradiated with ultraviolet light. Unfortunate organisms that were blasted into the ocean by hydrothermal exhalations would have died quickly without their accustomed source of hydrogen. The only safe route away from the hydrothermal mound was down—down through the ocean floor and into the warm, underlying sediments and permeable basalts. Dispersed in the crust, organisms could have subsisted on a steady, if meager, diet of hydrogen and carbon dioxide. Thus the deep biosphere was born.

Over millions of years, the convection of rock within the Earth's mantle conveyed the deep biosphere to a meeting with the neighboring tectonic plate. At this destructive junction, as most of the plate slid down into the mantle, some of the ocean floor delaminated and was thrust up to form coastal shallows. A few colonies of bacteria must have found themselves in an optimal position: deep enough to be protected from harmful solar rays, but shallow enough to use radia-

tion at longer wavelength to make more organic molecules from carbon dioxide.

As the emergence of life changed the character of our planet, so too did oxygenic photosynthesis eventually change its face to a blue-green cast. They are the two most extraordinary biological events to date.

### A Breath of Air

Whereas emergent life used hydrogen freed from water by chemical reactions deep in the Earth, oxygenic photosynthesis operates by using solar energy to extract four hydrogen atoms from a pair of water molecules. The hydrogen reacts with atmospheric carbon dioxide in a biosynthetic reaction, and the leftover oxygen atoms are combined and excreted as waste.

It seems likely that photosynthesis, like the first emergence of life, was the product of a mineral catalyst. In this case, the star was a manganese-calcium oxide ( $Mn_4CaO_{24}$ ) rather than an iron-nickel sulfide, although both candidate minerals involve a cubane structure. Unlike iron, manganese atoms are fairly resistant to radiation owing to a greater number of valences. It is possible that the proximity of manganese-containing compounds mitigated the damage to early organisms caused by sunlight. If true, perhaps manganese came to be used as a defense against destructive ultraviolet rays. From that supporting role, it could have been co-opted to play the lead in oxygenic photosynthesis.

One of the minerals expected to be part of this process was ranciéite ( $Mn_4CaO_9 \cdot 3H_2O$ ), which has a formula comparable to that of the oxygen-evolving center, or OEC, of the enzyme that executes photosynthesis. Yet the structure of ranciéite is unlike the structure of the OEC, as recently shown by James Barber and his colleagues at Imperial College London. Rather, the bonds and conformations of the OEC resemble a different manganese-containing mineral called hollandite ( $Mn_8[Ba,K]_{12}O_{16}$ ), according to Kenneth H. Sauer and Vital K. Yachandra at Lawrence Berkeley National Laboratory. How can these observations be reconciled?

The answer may lie in the fact that ranciéite and hollandite are both relatively stable in wet, near-surface conditions and that molecular clusters of either are interchangeable. Thus, it is plausible that a ranciéite cluster near a bacterium could have morphed into a hollandite-like shape. We conclude that a minimum of genetic control would have been required for a membrane protein to bind a hydrated  $[Mn_3CaO_4]$ -Mn complex that released hydrogen in response to light. The nearby cell would have become the lucky beneficiary of a new energy source for biosynthesis. Engulfing this photosynthetic complex in a membrane made the process more efficient. The research groups of John F. Allen (Queen Mary, University of London) and Wolfgang Nitschke (Institute of Structural Biology and Microbiology, CNRS Marseilles) have detailed how the evolution of that first protein led to the emergence of the cyanobacteria. As cyanobacteria became engulfed by other cells to form chloroplasts, the mechanism and shape of the  $[Mn_4Ca]$  center was perpetuated into green plants, where it remains unchanged today.

### The Rest Is History

As shown by its mastery of oxygenic photosynthesis, life has adapted to exploit almost every available energy source on the planet. Yet, this last of life's great metabolic discoveries was made more than 3.8 billion years ago by the geological correlates of iron oxide deposition. Since then, the basics of metabolism have not changed, although the presence of oxygen over the past 2 billion years has allowed cells to achieve ever more complex functions. We humans are one result, different from other life forms only in our semi-reflective consciousness.



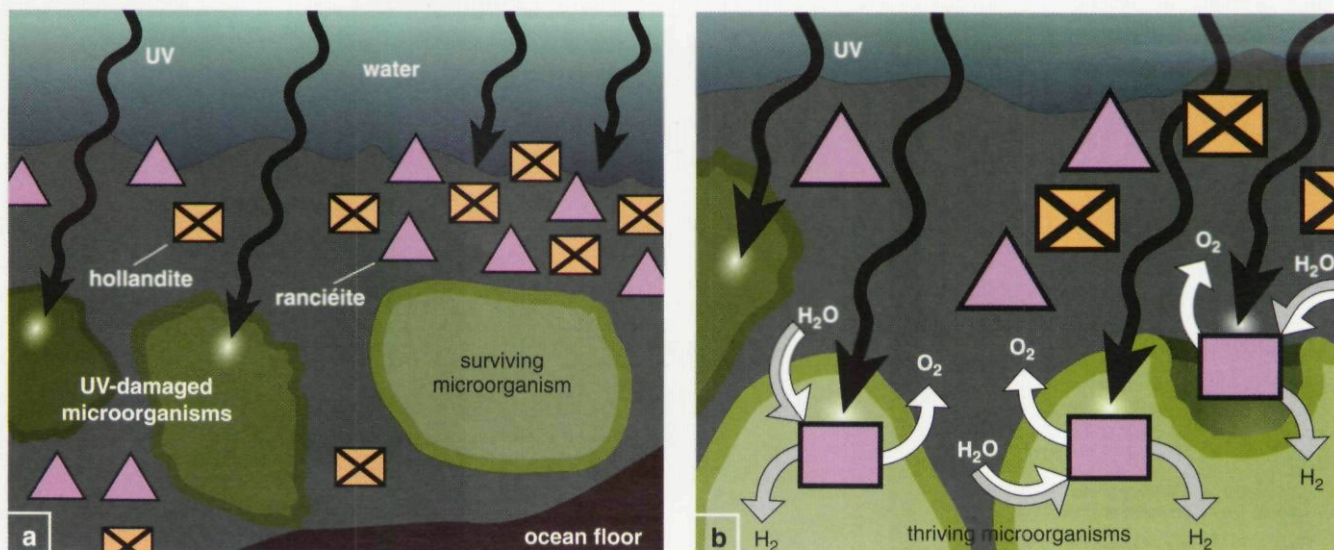


Figure 9. As the Earth changed over millions of years, portions of the ocean floor were lifted into shallow water, bearing microbes from their lightless origins to a new set of challenges and opportunities from the Sun's high-energy photons. The manganese-containing minerals hollandite (orange rectangles) and ranciéite (purple triangles) likely provided some benefit to nearby organisms by absorbing destructive ultraviolet (UV) rays (a). Over time, the coexisting minerals may have encountered something of a structural change, perhaps in conjunction with the surface of a nearby organism, with ranciéite adopting a typical hollandite shape (purple rectangles, b). This novel conformation, in addition to continuing to screen the Sun's rays, would have begun breaking water in two. Any nearby microbe would have been the immediate beneficiary of the readily available  $H_2$  during the process;  $O_2$  waste diffused away. Eventually, the cell engulfed the catalytic molecule (b, far right). Scientists now know that the active component of the oxygen-evolving center of cyanobacteria (and by extension, all plants) has the chemical formula comparable to ranciéite but the structure of hollandite.

Understanding how life started and how it works prods us to realize that we are now responsible for good house-keeping on the planet. But here's the rub: Living at the boundary between order and disorder, and lacking checks and balances, life's imperative encourages us to be profligate and make waste. Consuming resources as fast as we can is natural. That's what we're up against. Maybe a little less mystery and a little more wisdom about the nature of life might prepare us better for what is to come.

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