

Air, water and rock were the only raw materials available on the early earth. The first living entities must have been fabricated from these primitive resources. New experiments suggest that minerals—the basic components of the rocks—could have played starring roles in that dramatic feat.

BY ROBERT M. HAZEN

PHOTOGRAPHS BY ROBERT LEWIS

No one knows how life arose on the desolate

young earth, but one thing is certain: life's origin was a chemical event. Once the earth formed 4.5 billion years ago, asteroid impacts periodically shattered and sterilized the planet's surface for another half a billion years. And yet, within a few hundred million years of that hellish age, microscopic life appeared in abundance. Sometime in the interim, the first living entity must have been crafted from air, water and rock.

Of those three raw materials, the atmosphere and oceans have long enjoyed the starring roles in origins-of-life scenarios. But rocks, and the minerals of which they are made, have been called on only as bit players or simply as props. Scientists are now realizing that such limited casting is a mistake. Indeed, a recent flurry of fascinating experiments is revealing that minerals play a crucial part in the basic chemical reactions from which life must have arisen.

The first act of life's origin story must have introduced collections of carbon-based molecules that could make copies of themselves. Achieving even this nascent step in evolution entailed a sequence of chemical transformations, each of which added a level of structure and complexity to a group of organic molecules. The most abundant carbon-based compounds available on the ancient earth were gases with only one atom of carbon per molecule, namely, carbon dioxide, carbon monoxide and methane. But the essential building blocks of living organisms—energy-rich sugars, membrane-forming lipids and complex amino acids—may include more than a dozen carbon atoms per molecule. Many of these molecules, in turn, must bond together to form chain-like polymers and other molecular arrays in order to accomplish life's chemical tasks. Linking small molecules into these complex, extended structures must have been

especially difficult in the harsh conditions of the early earth, where intense ultraviolet radiation tended to break down clusters of molecules as quickly as they could form.

Carbon-based molecules needed protection and assistance to enact this drama. It turns out that minerals could have served at least five significant functions, from passive props to active players, in life-inducing chemical reactions. Tiny compartments in mineral structures can shelter simple molecules, while mineral surfaces can provide the scaffolding on which those molecules assemble and grow. Beyond these sheltering and supportive functions, crystal faces of certain minerals can actively select particular molecules resembling those that were destined to become biologically important. The metallic ions in other minerals can jumpstart meaningful reactions like those that must have converted simple molecules into self-replicating entities. Most surprising, perhaps, are the recent indications that elements of dissolved minerals can be incorporated into biological molecules. In other words, minerals may not have merely helped biological molecules come together, they might have become part of life itself.

Protection from the Elements

FOR THE BETTER PART of a century, following the 1859 publication of Charles Darwin's *On the Origin of Species*, a parade of scientists speculated on life's chemical origins. Some even had the foresight to mention rocks and minerals in their inventive scenarios. But experimental evidence only sporadically buttressed these speculations.

One of the most famous experiments took place at the University of Chicago in 1953. That year chemist Harold C. Urey's precocious graduate student Stanley L. Miller at-

tempted to mimic the earth's primitive oceans and atmosphere in a bottle. Miller enclosed methane, ammonia and other gases thought to be components of the early atmosphere in a glass flask partially filled with water. When he subjected the gas to electric sparks to imitate a prehistoric lightning storm, the clear water turned pink and then brown as it became enriched with amino acids and other essential organic molecules. With this sim-

FELDSPAR: SHELTERS GROWING CHAINS OF MOLECULES

ple yet elegant procedure, Miller transformed origins-of-life research from a speculative philosophical game to an exacting experimental science. The popular press sensationalized the findings by suggesting that synthetic bugs might soon be crawling out of test tubes. The scientific community was more restrained, but many workers sensed that the major obstacle to creating life in the laboratory had been solved.

It did not take long to disabuse researchers of that notion. Miller may have discovered a way to make many of life's

building blocks out of the earth's early supply of water and gas, but he had not discovered how or where these simple units would have linked into the complex molecular structures—such as proteins and DNA—that are intrinsic to life.

To answer that riddle, Miller and other origins scientists began proposing rocks as props. They speculated that organic molecules, floating in seawater, might have splashed into tidal pools along rocky coastlines. These molecules would have become increasingly concentrated through repeated cycles of evaporation, like soup thickening in a heated pot.

In recent years, however, researchers have envisioned that life's ingredients might have accumulated in much smaller containers. Some rocks, like gray volcanic pumice, are laced with air pockets created when gases expanded inside the rock while it was still molten. Many common minerals, such as feldspar, develop microscopic pits during weathering. Each tiny chamber in each rock on the early earth could have housed a separate experiment in molecular self-organization. Given enough time and enough chambers, serendipity might have produced a combination of molecules that would eventually deserve to be called "living."

Underlying much of this speculation was the sense that life was so fragile that it depended on rocks for survival. But in 1977 a startling discovery challenged conventional wisdom about life's fragility and, perhaps, its origins. Until then, most scientists had assumed that life spawned at or near the benign ocean surface as a result of chemistry powered by sunlight. That view began to change when deep-ocean explorers first encountered diverse ecosystems thriving at the superheated mouths of volcanic vents on the seafloor. These extreme environments manage to support elaborate communities of living creatures in isolation from the sun. In these dark realms, much of the energy that organisms need comes not from light but from the earth's internal heat. With this knowledge in mind, a few investigators began to wonder whether organic reactions relevant to the origins of life might occur in the intense heat and pressure of these so-called hydrothermal vents.

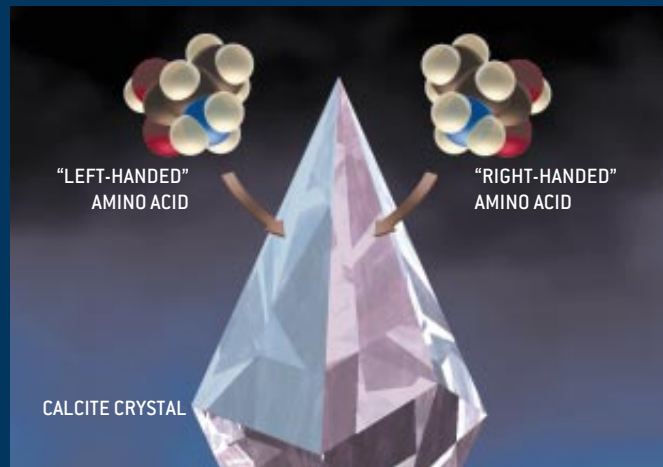


CRYSTAL POWER

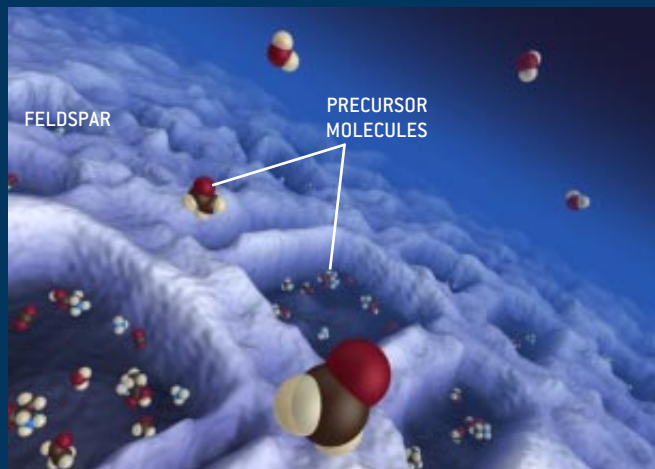
NOTHING COULD BE MORE lifeless than a rock, it seems. So how could rocks—or the minerals that constitute them—have assisted the emergence of life? The answer is chemistry. Minerals grow from simple molecules into an ordered structure because of chemical reactions. By the same token, all living organisms—from bacteria to bats—owe their ability to grow and function to the hundreds of chemical reactions that take place inside cells.

Four billion years ago the earth had no life: chemistry, not biology, altered the planet's surface. In that ancient time minerals—together with the oceans and atmosphere—were the only materials from which the first living entity could have arisen. Chemical reactions, then, must have been the first steps in the origins of life. A sequence of chemical transformations could have reconfigured the simplest components of air, water and rock into primitive collections of carbon-based molecules that could make copies of themselves.

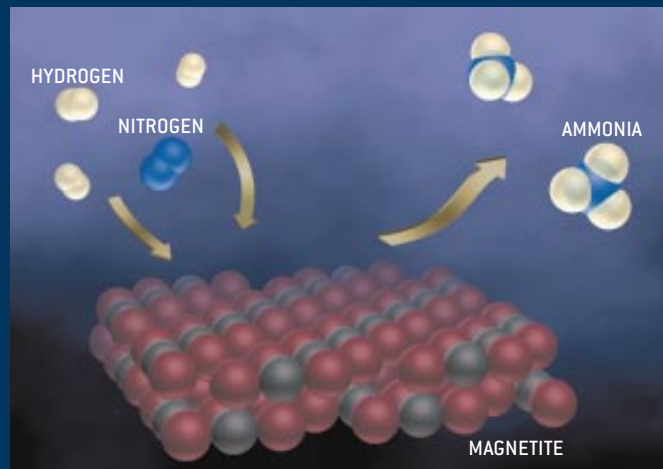
New experiments are revealing that the critical transformations might not have been possible without the help of minerals acting as containers, scaffolds, templates, catalysts and reactants.



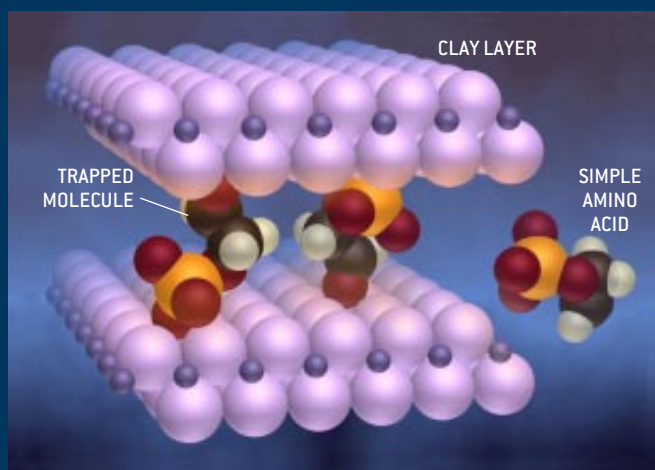
TEMPLATES—The mineral calcite tends to attract left- and right-handed amino acids to different crystal faces. Such a sorting process could explain why life makes use of only the left-handed variety.



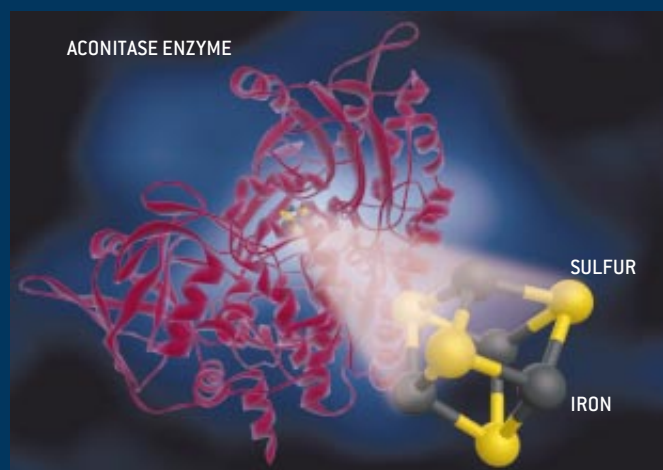
CONTAINERS—Microscopic pits appear in abundance on the weathered surfaces of feldspar and other common minerals. These tiny chambers could have sheltered life's precursor molecules from deadly radiation.



CATALYSTS—Magnetite, an iron oxide mineral, can trigger the recombination of nitrogen and hydrogen gases into ammonia, the essential compound from which living cells acquire nitrogen.



SCAFFOLDS—Layered minerals such as clays can trap stray organic molecules between their rigid sheets of atoms. Held close to one another, simple molecules can react to form more complex compounds.



REACTANTS—Iron and sulfur, the elements that form the active center of certain biological enzymes such as aconitase, can be dissolved from iron sulfide minerals under extreme heat and pressure.

ILLUSTRATIONS BY KENNETH EDWARD Biografix

LAYERED MINERAL: SERVES AS A SCAFFOLD FOR GROWING MOLECULES

Miller and his colleagues have objected to the hydrothermal origins hypothesis in part because amino acids decompose rapidly when they are heated. This objection, it turns out, may be applicable only when key minerals are left out of the equation. The idea that minerals might have sheltered the ingredients of life received a boost from recent experiments conducted at my home base, the Carnegie Institution of Washington's Geophysical Laboratory. As a postdoctoral researcher at Carnegie, my colleague Jay A. Brandes (now at the University of Texas Marine Sciences Institute in Port Aransas) proposed that minerals help delicate amino acids remain intact. In 1998 we conducted an experiment in which the amino acid leucine broke down within a matter of minutes in pressurized water at 200 degrees Celsius—just as Miller and his colleagues predicted. But when Brandes added to the mix an iron sulfide mineral of the type commonly found in and around hydrothermal vents, the amino acid stayed intact for days—plenty of time to react with other critical molecules.

A Rock to Stand On

EVEN IF THE RIGHT raw materials were contained in a protected place—whether it was a tidal pool, a microscopic pit in a mineral surface or somewhere inside the plumbing of a seafloor vent—the individual molecules would still be



Simple molecules could have used RIGID MINERAL SURFACES as the scaffolding on which they reassembled into more complex structures.

suspended in water. These stray molecules needed a support structure—some kind of scaffolding—where they could cling and react with one another.

One easy way to assemble molecules from a dilute solution is to concentrate them on a flat surface. Errant molecules might have been drawn to the calm surface of a tidal pool or perhaps to a prim-

itive “oil slick” of compounds trapped at the water’s surface. But such environments would have posed a potentially fatal hazard to delicate molecules. Harsh lightning storms and ultraviolet radiation accosted the young earth in doses many times greater than they do today. Such conditions would have quickly broken the bonds of complex chains of molecules.

Origins scientists with a penchant for geology have long recognized that minerals might provide attractive alternative surfaces where important molecules could assemble. Like the container idea, this notion was born half a century ago. At that time, a few scientists had begun to suspect that clays have special abilities to attract organic molecules [see box on

page 80]. These ubiquitous minerals feel slick when wet because their atoms form flat, smooth layers. The surfaces of these layers frequently carry an electric charge, which might be able to attract organic molecules and hold them in place. Experiments later confirmed these speculations. In the late 1970s an Israeli research group demonstrated that amino acids can concentrate on clay surfaces and then link up into short chains that resemble biological proteins. These chemical reactions occurred when the investigators evaporated a water-based solution containing amino acids from a vessel containing clays—a situation not unlike the evaporation of a shallow pond or tidal pool with a muddy bottom.

More recently, separate research teams led by James P. Ferris of the Rensselaer Polytechnic Institute and by Gustaf Arrhenius of the Scripps Institution of Oceanography demonstrated that clays and other layered minerals can attract and assemble a variety of organic molecules. In a tour de force series of experiments during the past decade, the team at Rensselaer found that clays can act as scaffolds for the building blocks of RNA, the molecule in living organisms that translates genetic instructions into proteins.

Once organic molecules had attached

cules that would become biologically important. Recent experiments show, once again, that minerals may have played a central role in this task.

Preferential Treatment

PERHAPS THE MOST mysterious episode of selection left all living organisms with a strange predominance of one type of amino acid. Like many organic molecules, amino acids come in two forms. Each version comprises the same types of atoms, but the two molecules are constructed as mirror images of each other. The phenomenon is called chirality, but for simplicity's sake scientists refer to the two versions as "left-handed" (or "L") and "right-handed" (or "D"). Organic synthesis experiments like Miller's invariably produce 50–50 mixtures of L and D molecules, but the excess of left-handed amino acids in living organisms is nearly 100 percent.

Researchers have proposed a dozen theories—from the mundane to the exotic—to account for this bizarre occurrence. Some astrophysicists have argued that the earth might have formed with an excess of L amino acids—a consequence of processes that took place in the cloud of dust and gas that became the solar system. The main problem with this theory

feature of the physical environment selected one version over the other. To me, the most obvious candidates for this specialized physical environment are crystal faces whose surface structures are mirror images of each other [see box on page 80]. Last spring I narrowed in on calcite, the common mineral that forms limestone and marble, in part because it often displays magnificent pairs of mirror-image faces. The chemical structure of calcite in many mollusk shells bonds strongly to amino acids. Knowing this, I began to suspect that calcite surfaces may feature chemical bonding sites that are ideally suited to only one type of amino acid or the other. With the help of my Carnegie colleague Timothy Filley (now at Purdue University) and Glenn Goodfriend of George Washington University, I ran more than 100 tests of this hypothesis.

Our experiments were simple in concept, although they required meticulous clean-room procedures to avoid contamination by the amino acids that exist everywhere in the environment. We immersed a well-formed, fist-size crystal of calcite into a 50–50 solution of aspartic acid, a common amino acid. After 24 hours we removed the crystal from this solution, washed it in water and carefully collected all the molecules that had ad-

Crystal faces of certain minerals could have ACTIVELY SELECTED and concentrated molecules that were destined to become biologically important.

themselves to a mineral scaffold, various types of complex molecules could have been forged. But only a chosen few were eventually incorporated into living cells. That means that some kind of template must have selected the primitive mole-

is that in most situations such processes yield only the slightest excess—less than 1 percent—of L or D molecules.

Alternatively, the world might have started with a 50–50 mixture of L and D amino acids, and then some important

hered to specific crystal faces. In one experiment after another we observed that calcite's "left-handed" faces selected L-amino acids, and vice versa, with excesses approaching 40 percent in some cases.

Curiously, calcite faces with finely terraced surfaces displayed the greatest selectivity. This outcome led us to speculate that these terraced edges might force the L and D amino acids to line up in neat rows on their respective faces. Under the right environmental conditions, these organized rows of amino acids might chemically join to form proteinlike molecules—some made entirely of L

ROBERT M. HAZEN has explored the behavior of minerals under high pressure at the Carnegie Institution of Washington's Geophysical Laboratory since 1976. In the past five years he has designed many of his mineral experiments to mimic the high-pressure environments of deep-sea hydrothermal vents. Rocks and minerals first piqued Hazen's curiosity as a child growing up in northern New Jersey, a region known for its unusual ore deposits. After receiving a doctorate in earth sciences at Harvard University in 1975 and spending a year at the University of Cambridge, he joined the staff at Carnegie. In 1990 Hazen took on a second position, as professor of earth science at George Mason University. He is also a part-time professional trumpeter and the author of numerous articles and books on science, education, history and music.



CALCITE: SELECTS FROM MIRROR-IMAGE MOLECULES

amino acids, others entirely of D. If protein formation can indeed occur, this result becomes even more exciting, because recent experiments by other investigators indicate that some proteins can self-replicate. In the earth's early history, perhaps a self-replicating protein formed on the face of a calcite crystal.

Left- and right-handed crystal faces occur in roughly equal numbers, so chiral selection of L amino acids probably did not happen everywhere in the world at

once. Our results and predictions instead suggest that the first successful set of self-replicating molecules—the precursor to all the varied life-forms on the earth today—arose at a specific time and place. It was purely chance that the successful molecule developed on a crystal face that preferentially selected left-handed amino acids over their right-handed counterparts.

Minerals undoubtedly could have acted as containers, scaffolds and templates that helped to select and organize the molecular menagerie of the primitive earth. But many of us in origins research suspect that minerals played much more

active roles, catalyzing key synthesis steps that boosted the earth's early inventory of complex biological molecules.

Getting a Jump on the Action

EXPERIMENTS LED by Carnegie researcher Brandes in 1997 illustrate this idea. Biological reactions require nitrogen in the form of ammonia, but the only common nitrogen compound thought to have been available on the primitive earth is nitrogen gas. Perhaps, Brandes thought, the environment at hydrothermal vents mimics an industrial process in which ammonia is synthesized by passing nitrogen and hydrogen over a hot metallic surface. Sure enough, when we subjected hydrogen, nitrogen and the iron oxide mineral magnetite to the pressures and temperatures characteristic of a sea-floor vent, the mineral catalyzed the synthesis of ammonia [see box on page 80].

The idea that minerals may have triggered life's first crucial steps has emerged most forcefully from the landmark theory of chemist Günter Wächtershäuser, a German patent lawyer with a deep interest in life's origins. In 1988 Wächtershäuser advanced a sweeping theory of organic evolution in which minerals—mostly iron and nickel sulfides that abound at deep-sea hydrothermal vents—could have served as the template, the catalyst and the energy source that drove the formation of biological molecules. Indeed, he has argued that primitive living entities were molecular coatings that adhered to the positively charged surfaces of pyrite, a mineral composed of iron and sulfur. These entities, he further suggests, obtained energy from the chemical reactions that produce pyrite. This hypothesis makes sense in part because some metabolic enzymes—the molecules that help living cells process energy—have at their core a cluster of metal and sulfur atoms.

For much of the past three years, Wächtershäuser's provocative theory has influenced our experiments at Carnegie. Our team, including geochemist George Cody and petrologist Hatten S. Yoder, has focused on the possibility that metabolism can proceed without enzymes in the presence of minerals—especially oxides and sulfides. Our simple strategy,

MORE TO EXPLORE

Beginnings of Cellular Life. Harold J. Morowitz. Yale University Press, 1992.

Origins of Life: The Central Concepts. David W. Deamer and Gail R. Fleischaker. Jones and Bartlett, 1994.

Emergence: From Chaos to Order. John H. Holland. Helix Books, 1998.

Biogenesis: Theories of Life's Origin. Noam Lahav. Oxford University Press, 1999.

much in the spirit of Miller's famous experiment, has been to subject ingredients known to be available on the young earth—water, carbon dioxide and minerals—to a controlled environment. In our case, we try to replicate the bone-crushing pressures and scalding temperatures typical of a deep-sea hydrothermal vent. Most of our experiments test the interactions among ingredients enclosed in welded gold capsules, which are roughly the size of a daily vitamin pill. We place as many as six capsules into Yoder's "bomb"—a massive steel pressure chamber that squeezes the tiny capsules to pressures approaching 2,000 atmospheres and heats them to about 250 degrees C.

One of our primary goals in these organic-synthesis experiments—and one of life's fundamental chemical reactions—is

ers have harnessed this reaction to manufacture molecules with virtually any desired number of carbon atoms. Our first organic-synthesis experiments in 1996, and much more extensive research by Thomas McCollom of the Woods Hole Oceanographic Institution, demonstrate that F-T reactions can build molecules with 30 or more carbon atoms under some hydrothermal-vent conditions in less than a day. If this process manufactures large organic molecules from simple inorganic chemicals throughout the earth's hydrothermal zones today, then it very likely did so in the planet's prebiological past.

When we conduct experiments using nickel or cobalt sulfides, we see that carbon addition occurs primarily by carbonylation—the insertion of a carbon and

rich variety of complex organic molecules.

Our 1,500 hydrothermal organic synthesis experiments at Carnegie have done more than supplement the catalogue of interesting molecules that must have been produced on the early earth. These efforts reveal another, more complex behavior of minerals that may have significant consequences for the chemistry of life. Most previous origins-of-life studies have treated minerals as solid and unchanging—stable platforms where organic molecules could assemble. But we are finding that in the presence of hot water at high pressure, minerals start to dissolve. In the process, the liberated atoms and molecules from the minerals can become crucial reactants in the primordial soup.

The Heart of the Matter

OUR FIRST DISCOVERY of minerals as reactants was an unexpected result of our recent catalysis experiments led by Cody. As expected, carbonylation reactions produced 10-carbon decanoic acid from a mixture of simple molecules inside our gold capsules. But significant

Minerals could have jump-started CRITICAL CHEMICAL REACTIONS that boosted the earth's early inventory of complex biological molecules.

carbon fixation, the process of producing molecules with an increasing number of carbon atoms in their chemical structure. Such reactions follow two different paths depending on the mineral we use. We find that many common minerals, including most oxides and sulfides of iron, copper and zinc, promote carbon addition by a routine industrial process known as Fischer-Tropsch (F-T) synthesis.

This process can build chainlike organic molecules from carbon monoxide and hydrogen. First, carbon monoxide and hydrogen react to form methane, which has one carbon atom. Adding more carbon monoxide and hydrogen to the methane produces ethane, a two-carbon molecule, and then the reaction repeats itself, adding a carbon atom each time. In the chemical industry, research-

oxygen molecule, or carbonyl group. Carbonyl groups readily attach themselves to nickel or cobalt atoms, but not so strongly that they cannot link to other molecules and jump ship to form larger molecules. In one series of experiments, we observed the lengthening of the nine-carbon molecule nonyl thiol to form 10-carbon decanoic acid, a compound similar to the acids that drive metabolic reactions in living cells. What is more, all the reactants in this experiment—a thiol, carbon monoxide and water—are readily available near sulfide-rich hydrothermal vents. By repeating these simple kinds of reactions—adding a carbonyl group here or a hydroxide group there—we can synthesize a

MAGNETITE: CATALYZES BIOCHEMICAL REACTIONS



MAGNETITE SPECIMEN COURTESY OF LAWRENCE H. CONKLIN



quantities of elemental sulfur, organic sulfides, methyl thiol and other sulfur compounds appeared as well. The sulfur in all these products must have been liberated from the iron sulfide mineral.

Even more striking was the liberation of iron, which brilliantly colored the water-based solutions inside the capsules. As the mineral dissolved, the iron formed bright red and orange organometallic complexes in which iron atoms are surrounded by various organic molecules. We are now investigating the extent to which these potentially reactive complexes might act as enzymes that promote the synthesis of molecular structures.

The role of minerals as essential chemical ingredients of life is not entirely unexpected. Hydrothermal fluids are well known to dissolve and concentrate mineral matter. At deep-sea vents, spectacular pillars of sulfide grow dozens of feet tall as plumes of hot, mineral-laden water rise from below the seafloor, contact the frigid water of the deep ocean and deposit new layers of minerals on the growing pillar. But the role of these dissolved minerals has not yet figured significantly in origins scenarios. Whatever their behavior, dissolved minerals seem to make the story of life's emergence much more interesting.

When we look beyond the specifics of prebiological chemistry, it is clear that the origin of life was far too complex to imagine as a single event. Rather we must work from the assumption that it was a gradual sequence of more modest events, each of which added a degree of order and complexity to the world of prebiological molecules. The first step must have been the synthesis of the basic building blocks. Half a century of research reveals that the molecules of life were manufactured in abundance—in the nebula that formed our solar system, at the ocean's surface, and near hydrothermal vents. The ancient earth suffered an embarrassment of riches—a far greater diversity of molecules than life could possibly employ.

Minerals helped to impose order on this chaos. First by confining and concentrating molecules, then by selecting and arranging those molecules, minerals may have jump-started the first self-replicating molecular systems. Such a system would not have constituted life as we know it, but it could have, for the first time, displayed a key property of life. In this scenario, a self-replicating molecular system began to use up the resources of its environment. As mutations led to slightly different variants, competition for limited resources initiated and drove the process of molecular natural selection. Self-replicating molecular systems began to evolve, inevitably becoming more efficient and more complex.

A long-term objective for our work at the Carnegie Institution is to demonstrate simple chemical steps that could lead to a self-replicating system—perhaps one related to the metabolic cycles common to all living cells. Scientists are far from creating life in the laboratory, and it may never be possible to prove exactly what chemical transformations gave rise to life on earth. What we can say for sure is that minerals played a much more complex and integral part in the origin of life than most scientists ever suspected. By being willing to cast minerals in starring roles in experiments that address life's beginnings, researchers may come closer to answering one of science's oldest questions. 