

THE ORIGIN OF LIFE IN THE SOLAR SYSTEM: Current Issues

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I can see no other escape from this dilemma (lest our true aim be lost for ever) than that some of us should venture to embark on a synthesis of facts and theories, albeit with second-hand and incomplete knowledge of some of them—and at the risk of making fools of ourselves.

Erwin Schrödinger, *What is Life?*

INTRODUCTION

Progress in the study of the origins of life was dramatic during the decade of the 1980s. Primordial Earth was put more completely into the context of early Solar System history, and as this planetary view provided new insights, other Solar System environments took on greater interest as points of comparison. Work on the energy sources needed to synthesize organic monomers or more sophisticated products on prebiotic Earth expanded widely, with a number of provocative new ideas vying for attention. But most importantly, the elucidation of a putative RNA world held out the hope for resolution of long-standing difficulties in the origin of DNA-protein organisms.

This review is intended to report on some of the current issues in origins-of-life and exobiology research. We therefore cannot hope to present a comprehensive history of the subject. For such reviews, the reader is instead referred

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to Loomis (1988), Oró et al (1990), and Mason (1991). A compilation of key original papers has recently been provided by Deamer & Fleischaker (1994). Finally, Shapiro (1986) offers a skeptical review of just how incomplete our understanding of this subject remains.

The review consists of four sections. To a great extent, the sections are independent of one another and may be read in almost any order. We first examine two areas of general relevance to exobiology: the definition of life, and the existence of possible extraterrestrial environments for life in our Solar System. We then focus on two areas of more specific interest to the origin of life on Earth: possible energy sources for prebiotic chemistry, and the RNA-world hypothesis. We have not hesitated to draw attention to topics that we think require renewed attention, even if these are not now the focus of major research efforts or conference sessions.

DEFINITIONS OF LIFE

There is a kind of ennui that arises over efforts to provide an encompassing definition for life. Many attempts have been made; Sagan (1970) has reviewed physiological, metabolic, biochemical, genetic, and thermodynamic definitions, and there have been many others. It is now a commonplace that the various proposed definitions virtually all fail: One can devise either counterexamples of systems that fit this or that definition, but which are not generally considered to be alive, or counterexamples of organisms that are clearly alive, but which a particular definition seems to exclude. Crystals, fire, automobiles, and mules are well-known examples of these problem phenomena and organisms. A sure indication that this definitional frustration has become part of the zeitgeist was the depiction in the popular novel *The Andromeda Strain* (Crichton 1969) of the futility, if not hubris, of scientists trying to arrive at a complete definition.

Claiming this or that counterexample to be an “unimportant” exception implicitly invokes further criteria in addition to those ostensibly comprising the definition. Either a counterexample falsifies a particular definition, or we need to be willing to say, for example, that a mule is not a living creature, or that a crystal is alive.

Why, then, resume that debate here and now—or for that matter, anywhere or ever? There are two good reasons. There is now one working definition for life that is becoming widely accepted in the scientific community. Moreover, there has been a proliferation of artificial systems, both in the laboratory and in the computer, that come interestingly close to satisfying this definition.

Darwinian Definitions

The definition of life that is becoming increasingly accepted within the origins-of-life community is essentially the “genetic” definition, e.g. “a system capable

of evolution by natural selection" (Sagan 1970). A recent careful formulation, given by Joyce (1994a,b), is: "Life is a self-sustained chemical system capable of undergoing Darwinian evolution." The most important ambiguities in this definition are: What exactly is meant by "self-sustained" and "Darwinian"? Joyce (1994a) explains: "The notion of Darwinian evolution subsumes the processes of self-reproduction, material continuity over a historical lineage, genetic variation, and natural selection. The requirement that the system be self-sustained refers to the fact that living systems contain all the genetic information necessary for their own constant production (i.e. metabolism)." Note that the use of the adjective "chemical" in the definition given above, which we henceforth call the "chemical Darwinian" definition, excludes computer "life" by fiat. The chemical Darwinian definition excludes biological viruses as well, by virtue of the "self-sustained" requirement.

McKay (1994) also accepts the genetic definition, defining life to be "a material system that undergoes Darwinian evolution." This means, he writes, "that it is capable of self-reproduction, and mutation followed by selection based upon stored information." When specificity is required, we refer to this definition as the "material" Darwinian definition. It does not a priori exclude computer "life." Darwinian definitions have become quite influential, shaping not only our views of what life is, but also of how we define its origin. The view that "the origin of life is the same as the origin of (Darwinian) evolution" is becoming commonplace.

The popularity of the chemical Darwinian definition has no doubt been fueled by the breakthrough of the "RNA world" (Gilbert 1986, Joyce 1991; also see the RNA world section below). Prior to the discovery of that possible world, the origin of life was faced with the chicken-or-egg paradox of metabolism vs genetic information, which led some to separate the origins of the two functions. In that sense, adopting the vocabulary of Dyson (1985), there could have been two separate "origins of life," the first of metabolism (possibly capable of reproduction without replication), the second of replication (see also Morowitz et al 1988). With the discovery that one molecule, RNA, could serve both functions, being both phenotype and genotype, the Darwinian definition now seems more certain to embrace the relevant historical phenomena. Of course, Earth's peculiar history need not correspond to the history of life elsewhere.

The metabolic vs genetic dichotomy has led to two disparate approaches to origins-of-life research and to two approaches to life's definition: One path emphasizes the primacy of metabolism, the other of genetic information [Kamminga (1988) has reviewed the history of these approaches]. To the extent that speaking of a "metabolism" carries connotations of compartmentalization (e.g. as in Dyson 1985 or Morowitz et al 1988), the two approaches remain distinct. However, "metabolism" need not require compartmentalization.

What is metabolism? Küppers (1990) defines metabolism in the context of the thermodynamic requirements of life. Because of the Second Law of Thermodynamics, a living system can only remain alive if the production of entropy is offset by an input of energy or energy-rich matter. Metabolism is then no more than the turnover of free energy that makes it possible for a given system, compartmentalized or not, to avoid reverting to an equilibrium state of maximum entropy. In this sense, the chemical Darwinian definition of life includes both genetic and metabolic components.

Compartmentalization

The Darwinian view of life does not require compartmentalization; an evolving system of naked RNA, for example, might well satisfy the definition. However, the emphasis on proteins and nucleic acids has largely overlooked the important role that membrane structures play in life on Earth. The unit of all contemporary life (assuming the exclusion of viruses) is the cell, and an obvious function of the cell membrane is to maintain macromolecular components within an enclosed microenvironment, preventing the diffusion of these components into the surrounding medium while allowing for transport of nutrients and waste products. In a prebiotic setting, compartmentalization could provide a mechanism by which systems of diverse macromolecules could be maintained, leading to encapsulated experiments in the origin of life.

Historically, the origin of bounded microenvironments has received some attention. Oparin (1924) proposed colloidal coacervates as a possible model. Fox & Harada (1958) argued for proteinoid microspheres. However, contemporary cell membranes are not colloidal or proteinoid in nature, but are based on lipids. Deamer and his colleagues (Deamer & Pashley 1989) have shown that amphiphilic molecules (molecules that self-assemble into bilayer aggregates owing to their polar and nonpolar groups; lipids are one type of amphiphile) are present in the Murchison carbonaceous meteorite. Moreover, at least one class of these molecules has the ability to self-assemble into membranous vesicles. It seems possible, then, that such vesicles were available on the prebiotic Earth. For the genesis of primitive cellular life, such vesicles would somehow have encapsulated (Deamer & Barchfeld 1982) both metabolizing and information-bearing molecules. This scenario reminds us that a particular ingredient (in this example, a boundary membrane) might have been essential for the historical terrestrial origin of life, but remain inessential to the abstract definition of life, or even its creation according to that definition.

Never since Darwin

There are important drawbacks to Darwinian definitions of life, as Fleischaker (1990) has emphasized: "Any definition of the living that includes 'the capacity

to evolve' is doubly problematic because such a definition requires not only the future state of a single system but other systems as well." Individual sexually reproducing organisms in our DNA-protein world do not evolve. Worse, from an operational point of view, it may prove impossible to tell whether a candidate system satisfies the Darwinian definition. How long do we wait for a system to demonstrate Darwinian evolution? How do we tell whether it is or is not capable of this, and under what conditions? A positive result is informative; a negative one may provide little information.

These apparent dilemmas can be largely defused by recognizing that we are actually discussing two distinct, though clearly related concepts: "life" and "a living entity." The Darwinian definition refers to a *system* that implicitly contains more than one individual entity. Fleischaker's "system," by contrast, comprises a *single* individual candidate living entity. She presents a definition of an "autopoietic system" that is an operational definition for a living individual. In her words, "Whereas 'autopoiesis' defines an individual living system by its organization at the present moment, 'evolution' characterizes 'life,' a single collective phenomenon that exists over time."

Fleischaker's (1990) proposed definition is determined by three criteria. The living entity must be: 1. self-bounded, 2. self-generating, and 3. self-perpetuating. Without dwelling on the details of her definition, we note that she intends it to allow us to identify either the emergence of life, be it historically in the Archean or experimentally in our laboratories, or the existence of extraterrestrial life. The definition is meant to have operational utility for a single organism, if need be. Fleischaker's definition would acknowledge that Victor Frankenstein (Shelley 1818) created a *living entity* in the lab, but that singular creation was not "life" by the Darwinian definition.

Life in the Laboratory

There are now a number of laboratory systems of self-replicating and "evolving" molecules that come close to satisfying the chemical Darwinian definition of life (see e.g. Achilles & von Kiedrowski 1993, Beaudry & Joyce 1992, Lehman & Joyce 1993, Bartel & Szostak 1993, Joyce 1993, Rebek 1994a,b); Orgel (1992) has recently presented a review. There are at least two respects in which certain of these systems may not yet satisfy the definition.

For example, the RNA systems of Beaudry & Joyce (1992) or of Bartel & Szostak (1993) involve amplification (i.e. replication) via the polymerase chain reaction (PCR) or related procedures. The use of modern biochemical machinery violates the requirement of the chemical Darwinian definition that life be genetically self-sustained. The system does not contain all the genetic information necessary for its own production; rather, one or more enzymes, not coded for by the RNA molecules being replicated, are required in the amplification step. For any particular system, it remains an interesting question,

however, to ask whether the enzymes used merely increase the rate of chemical reaction that would have occurred even in their absence. In that case, it would be less clear that the "self-sustained" requirement was actually being violated.

In Rebek's (e.g. 1994a,b) self-replicating system, on the other hand, no additional enzymes are required. In some of these experiments, a type of selection is driven by irradiation with ultraviolet light (Hong et al 1992). Of course, human intervention was required to set up Rebek's ultraviolet source. For that matter, the components of Rebek's molecules are human-engineered (e.g. the molecules are predesigned to "mutate" upon exposure to the specific wavelength generated by the UV source), and replicate in a thoroughly contrived nonaqueous solvent. But nowhere in the chemical Darwinian definition are limitations placed on the nature of the specialized environment in which the candidate life-form must evolve. These would be additional criteria, extrinsic to the definition, reflecting no more than prejudices about what is "natural." The world is full of organisms with extremely specialized environmental requirements. The Darwinian definition does not care. Rebek's system passes the "self-sustained" requirement, as do von Kiedrowski's (e.g. von Kiedrowski 1986, Terfort & von Kiedrowski 1992, Achilles & von Kiedrowski 1993), which also manage their replication in the absence of an enzyme.

Admittedly, these systems, relying as they do on synthetic chemists to provide the system with specific starting materials, do not provide a realistic simulation for the prebiotic origin of life (and in fact were never intended to do so). But this, too, is an ambiguity for all prebiotic experiments. The Miller-Urey experiment (Miller 1953, 1974), based on a methane-ammonia atmosphere, was once considered to have provided an excellent simulation of the early Earth environment. Now, however, it is suspected (see e.g. Walker 1986) that this reducing atmosphere may never have existed; the early atmosphere may instead have been composed mostly of carbon dioxide. If so, Miller's starting ingredients might also be depicted as artificial. These sorts of assessments may be relevant to a judgment of how accurate a given experiment is as a simulation of early Earth; they are not relevant to the Darwinian definition.

On the other hand, there are clearly ambiguities with the phrase "capable of undergoing Darwinian evolution." For example, von Kiedrowski and his colleagues (von Kiedrowski et al 1991, Terfort & von Kiedrowski 1992, von Kiedrowski 1993, Sievers & von Kiedrowski 1994) argue that the replication exhibited to date by laboratory systems does not satisfy a certain requirement that is implicit in the phrase "Darwinian evolution." Darwinian evolution, which they take to be synonymous with "survival of the fittest," is said to mean in the laboratory that "the most efficient replicator outgrows its less efficient competitors and finally supersedes them in the reaction chamber" (von Kiedrowski 1993; see also Eigen & Schuster 1979). This is distinct from a result in which the most efficient replicator is unable to entirely outcompete

its less efficient competitors in a struggle for common resources, so that all replicators survive (i.e. continue to reproduce) at different but equilibrium levels of concentration ("survival of everybody"; Szathmáry 1991). Szathmáry & Gladkih (1989) have shown that subexponential growth in a system of self-replicating molecules must lead to this type of coexistence (see also Szathmáry 1991). Current laboratory self-replicating systems exhibit only subexponential (typically parabolic) growth (von Kiedrowski et al 1991, von Kiedrowski 1993), so are not yet capable, by this definition, of Darwinian evolution. Further examination of the putative identity of the concepts "survival of the fittest" and "Darwinian evolution" would help clarify this issue.

The Ghost in the Machine

The preceding discussion about contrived laboratory environments for living systems is directly relevant to discussions of computer life. (For reviews of progress in computer life, see Langton 1992 and Levy 1992.) While the chemical Darwinian definition excludes computer life, the material Darwinian definition speaks only of a "material" system, leaving the door open. In a "functionalist" view (e.g. Sober 1992), Darwinian evolution is a process that can be abstracted from whatever particular physical details are necessary to realize this process in a given system. It is not the computer that is said to be alive, but the processes themselves. The material substrate of the computer is a human contrivance that makes these processes possible, but it is a contrivance whose status is no different from the glassware and chemical solutions required for artificial laboratory life. It seems unsurprising that, in this view, "living" systems or ecosystems can be created in a computer (e.g. Rasmussen 1992, Ray 1992).

Is a Complete Definition Impossible?

A complete definition for life would provide criteria that were both necessary and sufficient for an entity to be called "alive." Küppers (1990) has argued that such a definition is inconsistent with a reductionistic, i.e. a physical, basis for biology. The premise that life can be explained completely within the framework of physics and chemistry requires, he asserts, that the transition from the nonliving to the living be a continuous one. A complete definition, one that unambiguously separated nonlife from life, would only be possible if the transition from the first to the second were discontinuous. "However, the definition would then inevitably contain at least *one* irreducible concept, which would express the ontological difference between living and nonliving systems. Since this concept would by definition be life-specific, every holistic definition of 'life' must be inherently tautologous," he states. "It is thus an absolutely characteristic feature of physically oriented biology that it cannot give a complete

definition of the phenomenon 'life.' If such a definition existed, this fact would contradict the premises of the reductionistic program," Küppers concludes.

Whatever its other merits or demerits, it is a virtue of the Darwinian definition that it belies this conclusion. One can imagine, for example, a transition from nonlife to life on early Earth that would have been discontinuous, such as a discrete change in a particular RNA molecule that suddenly gave that particular molecule the ability to self-replicate, initiating a system undergoing Darwinian evolution. The latter concept is "life specific" in the sense that it is central to the definition, but it is not "irreducible"; it is readily elucidated by a behavioral description that need not refer tautologically to life. While there would have been at least some satisfaction in concluding that a complete definition of "life" was impossible, it seems we are denied even that consolation.

EXOBIOLOGICAL ENVIRONMENTS IN THE SOLAR SYSTEM

In the previous section, we discussed possible definitions of "life," and definitions of "a living entity." In principle, an accepted definition of life could be applied to new phenomena discovered during the exploration of extraterrestrial environments, to determine whether this or that newly discovered system was alive. But in the absence of samples returned to Earth for extended laboratory analysis, it is hard to imagine definitions as abstract as those discussed above being of practical use in planetary exploration, even given very sophisticated instruments. This is likely to be true even for Fleischaker's "operational" definition. What is needed is a *remotely* operational definition. Such a definition would make no pretense of being complete or universally applicable, but would have the advantage of utility in a remote-sensing context.

Lederberg (1965) suggested a variety of possible criteria that could be applied remotely to the question of life on Mars, including a search for optical activity and the detection of informational macromolecules. But Lederberg noted the dangers in these approaches; remarking that biochemistry had then only barely reached the point of demonstrating that the ubiquitous antibody γ -globulin had an informational sequence specified by a polynucleotide, he wrote that this ignorance "must evoke some humility in our postulations and experimental efforts concerning macromolecules on another planet."

A decade later, the *Viking* landers on Mars confirmed this dilemma of extrapolation. Results from the *Viking* biology packages (Klein 1978, Margulis et al 1979, Horowitz 1986) were powerful reminders that supposedly unambiguous characteristics of terrestrial biology could crumble in the face of unanticipated extraterrestrial chemistry. Did *Viking* discover biology or only exotic chemistry? Had the *Viking* gas chromatograph-mass spectrometer (GCMS) not demonstrated the absence of organic molecules to the level 10^{-6} to 10^{-9} at the two *Viking* landing sites (Biemann et al 1977), the ambiguity might never have

been resolved (Cooper 1980). Indeed, some members of the *Viking* biology team continued to argue for a biological explanation of certain results, despite the GCMS data (Levin & Straat 1981).

Of course, it is in principle possible to send remote instruments that are less theory-laden in their interpretation than were the experiments in the *Viking* package. A possible example of such an instrument would be a microscope; Lederberg outlined the advantages of that instrument in life remote sensing experiments as early as 1960 (Lederberg 1960). Nevertheless, even this instrument could pose difficult problems of interpretation in a remote sensing context. A number of authors have described the difficulties in distinguishing between terrestrial microfossils and nonbiological structures, and the criteria that may be applied to determine whether putative microfossils are actually of biological origin (e.g. Schopf & Walter 1983, Strother 1992). Making this distinction for living systems, rather than microfossils, could be easier, as living systems might have the advantage of motility or other distinguishing characteristics. But there is no reason why this would necessarily be the case, especially on the time scales available to a practical experiment. Moreover, distinguishing between microscopic life and microscopic nonlife in a thoroughly novel extraterrestrial microworld could provide ambiguities that we cannot now imagine. Again, this is the lesson of *Viking*.

At this stage in the exploration of our Solar System, it may be that all the criteria so far discussed remain too ambitious to be useful in a search for life. McKay (1991) has suggested that, as a matter of practicality, it is wisest to develop criteria for the *possibility* of life "based on a very conservative analysis of terrestrial biology." This analysis notes the importance of an energy source and a handful of common elements, especially, of course, carbon. But the *sine qua non* of life as we know it is liquid water. Even given an abundance of the necessary elements and copious sunlight, terrestrial life absolutely requires liquid water (Mazur 1980, Kushner 1981, Horowitz 1986). This would also appear to be the lesson of the dry valleys in Antarctica, the harshest desert on Earth with virtually no signs of life outside of specific, protected habitats (McKay 1986, Campbell & Claridge 1987).

From an operational point of view, then, McKay (1991) argues that the search for life elsewhere in the Solar System becomes the search for liquid water (see also Chang 1988). We shall apply this criterion to weigh possible habitats for life elsewhere in our Solar System, but first note how this differs from another, well-known perspective in exobiological investigations. The assumption made in McKay's operational definition is that searching for life means searching for life as we know it. Suggestions of drastically different life forms (such as life based on silicon rather than carbon), he asserts, lie in the realm of unconstrained speculation, and therefore have "not made significant contributions to exobiology."

This is quite distinct from the view, most strongly associated with Sagan (e.g. 1961, 1974), that warns that attempts to generalize from the single example of life of which we have knowledge are fraught with danger. "In our present profound ignorance of exobiology, life is a solipsism," he writes (Sagan 1974). "There is no aspect of contemporary biology in which we can distinguish the evolutionary accident from the biological *sine qua non*. We cannot distinguish the contingent from the necessary." Parochialism is the great danger in looking for life as we know it. It is possible life may look nothing like what we know.

Nor are discussions about alternative foundations for biology doomed to no more than speculation. The assumption that extraterrestrial biology would, after all, be based on some form of chemistry allows some speculations to be weighed and found wanting. More than three decades ago, for example, Sagan (1961) noted that "silicates lack the information-carrying properties of variable side chains which characterize such carbon compounds as polynucleotides and polypeptides. Therefore it is doubtful that silicates could be a fundamental constituent of extraterrestrial organisms." Nevertheless, speculations about radically different extraterrestrial biologies are hard-pressed to offer search strategies for life on other worlds. In practice, proponents of both viewpoints would agree that our greatest chance for success is to look where we are most likely to find liquid water. McKay (1994) concludes that "What is needed is more data points, not more imagination."

In lieu of imagination, then, let us examine a range of possible exobiological habitats in our own Solar System, using the requirement that liquid water may now be (or once have been) present as a criterion that has to be met for a location to merit consideration.

Mars—Then and Now

Mars remains the center of attention for those hoping to find life elsewhere in our Solar System. [See Horowitz (1986) for a critical review of the history of these hopes.] The results of the *Viking* biology package seem best explained as the results of oxidant chemistry, not biology (Klein 1978, Margulis et al 1979), and the observed absence of organics at the two landing sites (Biemann et al 1977) may suggest that the surface of the planet is now sterile (Horowitz 1986). The origin of Martian surface oxidants is at least partly understood as a natural result of photochemistry in the atmosphere (Hunten 1979); this in turn implies that the oxidants are globally distributed. Nevertheless, laboratory experiments with terrestrial organisms (Mancinelli 1989) do not support the claim that the Martian surface would therefore be "self-sterilizing" and utterly inhospitable to life. In any case, an oxidizing surface layer would only extend to a finite, possibly quite shallow, depth (Bullock et al 1994). Organic materials reported in a Martian-originating meteorite (Wright et al 1989) suggest that organics may indeed be present on Mars, although subsequent analyses indicate that most or

all of this organic carbon is terrestrial contamination (McDonald & Bada 1995). All the same, liquid water cannot now exist on the Martian surface (Carr 1981, McKay et al 1992), which by McKay's operational criterion suggests we must look elsewhere for life.

If life ever did exist on Mars, it is possible that it retreated to subsurface niches associated with hydrothermal activity, where liquid water may exist. Boston et al (1992) have considered the existence of a deep subsurface microbial ecology on Mars, similar to those known to exist on Earth at several-kilometer depth in oil fields, aquifers, and other locations. More broadly, Gold (1992) has speculated that Earth is home to a "deep, hot biosphere" in the terrestrial crust, not dependent on solar energy, and comparable in biomass to surface life. If life could originate at depth, independently of surface conditions, such deep biospheres could be widespread among the planets and larger moons of the Solar System. (The possibility of an origin of life at terrestrial hydrothermal vents is discussed in the next section.) If, however, life requires specific surface conditions (such as solar energy) to originate, extensive deep biospheres would only exist—if they exist at all—on worlds where the surface was once hospitable. It is hard to see how to pursue these speculations with respect to Mars or other worlds without first better exploring the extent of subsurface life on Earth.

Could life have originated on Mars? There is a great deal of geomorphological evidence that water, in the form of ground ice, exists at or near the Martian surface (Squyres & Carr 1986, Squyres 1989a). Extraterrestrial water in the Mars-originating SNC meteorites provides laboratory evidence for Martian water (Karlsson et al 1992, McSween & Harvey 1993), as does the presence of water-precipitated minerals in these meteorites (Gooding 1992). If Earth obtained a substantial fraction of its oceans from cometary impacts, these collisions should have contributed to the Martian water inventory as well, although this conclusion is complicated by the problem of impact erosion (Melosh & Vickery 1989, Chyba 1990a).

It is also clear from *Mariner* and *Viking* images that this water once flowed at the surface (Carr 1981, McKay & Stoker 1989), probably pooling in lakes (Goldspiel & Squyres 1991). Geomorphological evidence for the existence of early Martian oceans (Baker et al 1991) has been presented, though this claim remains controversial. It appears that Mars began as a wet, but not necessarily much warmer (Squyres & Kasting 1994), world (Squyres 1984, Pollack et al 1987), but then evolved into a frozen desert. Mars' early, more hospitable conditions roughly coincided in time with the origins of life on Earth (McKay 1986, McKay & Stoker 1989), and it appears that liquid water habitats could have been maintained under ice covers on Mars for as long as 700 million years after mean global temperatures fell below freezing (McKay & Davis 1991). It is natural to ask, if life began in liquid water on early Earth, would life have simultaneously evolved in a similar climate on early Mars? Answering this question

requires a search for ancient Martian microfossils. The difficulties associated with demonstrating the biological origin of putative microfossils (Schopf & Walter 1983, Strother 1992)—or fossil stromatolites (Walter 1983)—in terrestrial rocks warn us that this search may prove extremely difficult.

Although the difficulties faced by traditional schemes for panspermia are well known (Davies 1988), it is possible that microorganisms could have migrated between Earth and Mars within debris ejected from the vicinity of large impacts (Melosh 1988, see also Moreno 1988). There is now experimental evidence that impacts can eject a small quantity of lightly shocked material at high velocity (Gratz et al 1993, Melosh 1993). To provide an effective vehicle for panspermia, such ejecta would have to be in the form of boulders large enough to provide shielding from cosmic rays during the transit times of millions of years required to travel between the two worlds (Melosh 1988). If fossil evidence is ever found for life on ancient Mars, it may prove very difficult to determine whether this life originated on Mars independently of Earth, or whether Mars was inoculated by microorganism-rich material from terrestrial impacts. Similarly, it is not out of the question that Mars could instead have inoculated the early Earth.

Jupiter and the Giant Planets

Sagan & Salpeter (1976) have presented possible ecologies for organisms living aloft in the Jovian atmosphere. Similar niches might exist on the other gas giants, especially Saturn. Clearly these ideas are extremely speculative. McKay (1994) has objected that there are no known airborne ecologies on Earth, a planet whose atmosphere is, he states, more clement and energy-rich. (Note, however, that the reducing atmospheres of the giant planets ensure a continual production of organic molecules.) Why aren't the clouds green? Perhaps airborne environments on Earth are simply too short-lived, with fallout times too short to permit colonization by microbes. Similarly, on Jupiter, organisms would face the peril of descending to levels where pyrolysis would occur. Even if buoyancy mechanisms to avoid this fate can be envisioned (Sagan & Salpeter 1976), the chances for originating life under such conditions are very difficult to assess.

Europa

The Galilean satellite Europa may be the most intriguing potential exobiological environment in the Solar System. Tidal heating calculations indicate that Europa could have a deep (> 100 km) ocean of liquid water beneath its fractured (but, judging by the virtual absence of impact craters, very young) icy surface (Squyres et al 1983). If such an ocean exists, calculations based on Antarctic microorganism analogues show that there could be regions on Europa with physical conditions lying within the range of adaptation of terrestrial organisms (Reynolds et al 1983, 1987). The key question remains whether Europa

does or does not have oceans of liquid water; radar sounding (Squyres 1989b) or the upcoming *Galileo* spacecraft's exploration of the Jovian system could possibly settle this issue. Observations of geysers of ice crystals and vapor would provide dramatic evidence for a second liquid water ocean in our Solar System.

Titan

Titan, the large moon of Saturn, presents a prebiological organic chemistry laboratory on a planetary scale. With its N₂ atmosphere containing several percent CH₄, production of complex hydrocarbons and other organic molecules occurs through the action of ultraviolet light and radiation chemistry (Sagan et al 1992). However, the low surface temperatures preclude the existence of liquid water, which argues against the presence of life. Nevertheless, recent work on the formation of transient liquid water environments by impact cratering (Thompson & Sagan 1992) suggests that prebiological "experiments" involving high concentrations of organics in the presence of liquid water have occurred on Titan throughout its history. The crater-floor pools of liquid water resulting from these impacts are calculated to have characteristic lifetimes of ~10³ years.

Comets

Spacecraft missions to comet Halley have confirmed preencounter suggestions that comets are rich in organics; Halley appears to be ~25% organic by mass and perhaps 40–50% water ice (Delsemme 1991). With cosmic abundance ratios of most elements, all the ingredients for life are certainly present. In the absence of liquid water, however, comets appear to be poor environments for life (Bar-Nun et al 1981). The lack of life on Earth's Polar Plateau and Greenland ice sheet suggests to Huebner & McKay (1990) that the far-less-hospitable environment of comet ice should be similarly lifeless. Nevertheless, Hoyle & Wickramasinghe (1987, 1988a,b) and Wallis et al (1989) have argued, on the basis of comparisons of the 3.4 micron spectral feature in comet Halley with that of mixtures of viruses and bacteria, that comets are rich in microorganisms. These cometary organisms, they believe, are responsible for the outbreak of various epidemics in human populations (Hoyle & Wickramasinghe 1979, 1991). These claims have been countered by any number of specialists in the various relevant fields (see Marcus & Olsen 1991 for a review). In particular, the 3.4 micron feature in cometary spectra is readily explicable by the presence of abiological organics (Chyba & Sagan 1987, 1988). Both that feature and its predicted heliocentric evolution (Chyba et al 1989) are increasingly well understood as a combination of gas-phase and solid-state features (Mumma et al 1993).

The possibility of life on comets turns on whether liquid water cores exist in cometary nuclei. Our progress in answering this question has recently been summarized by Podolak & Prialnik (1994). The key requirements for melting

to occur at the center of a cometary nucleus are a large nuclear radius, a low thermal conductivity, and the initial presence of sufficient aluminum-26 to provide substantial heating through radioactive decay. Recent observations make it clear that many giant comets (radii > 100 km) exist (see Weissman 1994 for a summary); ^{26}Al -heating could possibly sustain liquid cores in comets of this size for as long as 10^9 years (Irvine et al 1980, Wallis 1980). If life could originate in the absence of solar radiation, such cometary environments would be excellent candidates for extraterrestrial habitats. However, our knowledge of the cometary nucleus remains too poor for any firm conclusions to be reached concerning the existence of liquid cometary interiors (Podolak & Prialnik 1994), much less about "deep" cometary biospheres.

Asteroids

Speculation about the origin of life on planetesimal-sized bodies has focused on comets, perhaps because they are so water- and organic-rich, but also perhaps in part because they remain sufficiently poorly explored and mysterious that speculation faces few constraints. In this context, it is striking that so little current attention focuses on asteroids as potential sites for extraterrestrial life, especially since we have in our collections numerous meteorites (most of whose presumptive parent bodies are asteroids) that show direct evidence of having experienced organic synthesis in the presence of liquid water.

Perhaps one reason for the relative lack of attention now given to meteorite parent bodies as potential abodes of life is the acrimonious history surrounding early published claims for discoveries of microfossils and other biogenic materials in meteorites. This debate began in the early 1960s and continued for about a decade; reviews of this controversy include those by Urey (1966), Rossignol-Strick & Barghoorn (1971), and Day (1984). There seems to be a consensus that the "organized elements" found within certain carbonaceous chondrites are a combination of terrestrial contaminants and nonbiological mineral or organic structures (Day 1984), providing no persuasive evidence for extraterrestrial life.

Yet by the operational criterion suggested at the beginning of this section—the presence of liquid water—certain meteorites (and their presumptive parent bodies) provide us with the only extraterrestrial examples, besides ancient Mars, where this criterion is, or once was, fulfilled. There is ample evidence for preterrestrial aqueous alteration in meteorites, both from mineralogy (Zolensky & McSween 1988, Grimm & McSween 1989) and from the amino acid and hydroxy acid profiles of carbonaceous chondrites, which suggest that they formed by the Strecker mechanism, requiring liquid water (Peltzer et al 1984, Cronin 1989, Kerridge 1991).

The liquid water environment on the parent body of the CI chondrite Orgueil is constrained by strontium isotopic evolution to have occurred very early, certainly within 10^8 yr, and possibly within 10^7 yr, of its formation (Macedougall

et al 1984). Models of the thermal history of asteroids suggest that ~ 100 -km radius asteroids could have maintained liquid water interiors for several hundred million years (DuFresne & Anders 1962, Scott et al 1989), reasonably consistent with the empirical results. However, Peltzer et al (1984) determined that the time required for the Strecker synthesis on the Murchison meteorite parent body could have been as short as 10^4 yr.

It is tempting to use carbonaceous chondrites as indicators of the extent of chemical evolution that can occur in the liquid water interior of a planetesimal-sized object. Time scales of $\sim 10^8$ yr for the duration of liquid water environments in meteorite parent bodies are comparable to the time scales thought to have been available on early Earth for the origin of life, given the likely constraints imposed by impact "frustration," i.e. sterilization of the surface (Sagan 1974, Maher & Stevenson 1988, Oberbeck & Fogleman 1989, Sleep et al 1989, Chyba 1991). If the Orgueil parent body had in fact contained liquid water for 10^8 yr, that meteorite could present a prima facie case that prebiotic organic evolution in planetesimal interiors simply does not go very far. Unfortunately, it is unclear that this conclusion applies to the more organic- and water-rich interiors of comets. Given the uncertain time scale of Orgueil's liquid water history, it is even unclear to what extent this conclusion applies to other asteroids, and in any case the meteorite sample available to us appears not to be representative of the overall asteroid population (Lipschutz et al 1989).

The monomers for biomolecular synthesis and potentially catalytic clay minerals have been identified in carbonaceous chondrites, where evidence of liquid water also exists. Organic components that form membrane-like vesicles have also been extracted from Murchison (Deamer & Pashley 1989). Yet abiotically produced polypeptides or oligonucleotides have not been reported. Cronin (1976), searching for small peptides in Murchison, concluded that no more than 9 mol% of the total acid-labile amino acid precursors in the meteorite were peptides. The relevant reaction rates or production efficiencies in this environment may be so low that even a Murchison-size meteorite does not contain detectable amounts of abiotically produced biomacromolecules. Perhaps this means that liquid water, prebiotic monomers, and mineral catalysts are together insufficient for further progress toward the origin of life in a time span of 10^7 – 10^8 years. If so, what additional crucial ingredient did Archean Earth have that the sampled meteorite parent body environments did not? Surely this is a question of great interest for understanding the origin of life on Earth (and, perhaps, its possibility on comets). Still, it may be premature to conclude that chemical evolution in meteorite parent bodies has not progressed past the monomer stage until a thorough search of meteoritic samples for prebiotic macromolecules has been made, ideally using modern high-sensitivity methods.

Nonetheless, if the search for life in the Solar System is the search for liquid water, we have found it, or at least its dry remains. Although the sample size

is far too sparse to draw general conclusions, our first limited experience with extraterrestrial liquid water environments, possibly of substantial duration, so far does not reveal progress far down the road towards life.

Earth

So far we have discussed possible Solar System environments for life, as well as criteria for recognizing life should it inhabit any of these. However, the only place in the Solar System where we know that the origin of life has actually occurred is on Earth. We now turn to two current issues in the study of the origin of life on Earth: the sources of energy available to drive prebiotic organic synthesis and the possible role of nucleic acids or their analogs as the first biomacromolecules.

ENERGY SOURCES FOR PREBIOTIC CHEMISTRY

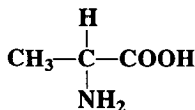
The importance of various energy sources to prebiotic organic synthesis in a planetary environment is intimately related to the oxidation state of that environment. For the early Earth this is uncertain, and arguments based on cosmochemical and geochemical principles for both reducing and nonreducing environments have been reviewed extensively (Chang et al 1983, Walker et al 1983, Walker 1986, Hunten 1993, Kasting 1993, Kasting et al 1993). In this section we discuss recent work on several possible sources of energy for prebiotic organic chemistry on the Archean Earth. We focus on the production of several basic prebiotic molecules: nitriles such as hydrogen cyanide (HCN), aldehydes such as formaldehyde (H₂CO), amino acids, purine/pyrimidine bases, and carboxylic acids (Figure 1).

Atmospheric Energy Sources

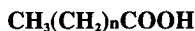
Atmospheric organic chemistry on the early Earth has been one of the major thrusts of origin-of-life research during most of its history, and the relative importance of the several available energy sources (ultraviolet photolysis, electric discharges, shock synthesis from thunder or bolide impacts, and charged particle radiation) in prebiotic atmospheres of varying compositions is relatively well understood. A review of the theoretical and experimental work in this area is beyond the scope of this article; the reader is referred to recent reviews of this subject (Chang et al 1983; Ferris & Hagan 1984; Oró et al 1990; Chyba & Sagan 1991, 1992; Chang 1993).

Exogenous Delivery

The origins of life on Earth coincided with the final throes of the heavy bombardment of the inner Solar System by comets and asteroids (e.g. Chyba 1993).



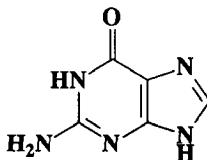
Amino acid (Alanine)



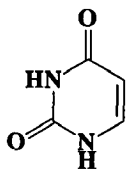
Carboxylic acid



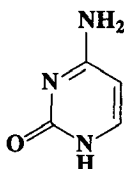
Adenine



Guanine



Uracil



Cytosine

Figure 1 Structures of a typical amino acid, a carboxylic acid, and the four bases present in RNA—the purines adenine and guanine and the pyrimidines cytosine and uracil.

The diameter-frequency distribution of lunar craters makes it clear that the bulk of mass collected by Earth during the heavy bombardment was concentrated in the largest impactors. Of these, comets are by far the most organic-rich bodies, containing HCN and H₂CO at a level $\sim 10^{-3}$ – 10^{-2} relative to H₂O (Mumma et al 1993). Simulations of cometary collisions with Earth strongly suggest that organic molecules would not survive these collisions (Chyba et al 1990), although a large cometary collision could lead to a transient, hot atmospheric environment with a high abundance of excited chemical species whose subsequent quenching could favor synthesis of organics (Oró 1961, Oberbeck & Aggarwal 1992). Experimental simulations of such syntheses (Mukhin et al 1989) have not unambiguously distinguished between surviving organic fragments of the original material and post-vaporization recombination, and are therefore difficult to interpret (Chyba & Sagan 1992).

Interplanetary dust particles (IDPs), which are ~10% organic by mass, are another possible important exogenous source of prebiotic organics (Anders 1989). In an intermediate oxidation-state atmosphere, IDPs could have been the dominant source of organics on prebiotic Earth (Chyba & Sagan 1992). However, the organics in IDPs are poorly characterized and seem likely to consist primarily of kerogen-like material. Laser microprobe techniques have recently demonstrated the presence of polycyclic aromatic hydrocarbons, or PAHs (Clemett et al 1993). The relevance of IDPs to early prebiotic syntheses will remain unclear until further compositional analysis can be carried out, a task that is difficult because of the small quantities of material involved (Gibson 1992).

The most dramatic data point for the exogenous delivery of prebiotic organics to Earth is the discovery of two extraterrestrial amino acids, α -aminoisobutyric acid and racemic isovaline, immediately above and below the clay layer marking the Cretaceous-Tertiary (K/T) boundary (Zhao & Bada 1989). If these amino acids are truly exogenous in origin, they would appear to be material that somehow survived the K/T impact, were synthesized from meteoritic organics in the post-impact fireball (Oberbeck & Aggarwal 1992), or were delivered to Earth by interplanetary dust evolved off the K/T impactor (Zahnle & Grinspoon 1990). Any of these mechanisms would be relevant to early Earth. Further exploration of the amino acid profiles of other K/T boundary sites is essential for evaluating possible explanations for the origin of these apparently extraterrestrial amino acids. (The Zhao & Bada results are for only one site, Stevns Klint, Denmark.)

Photo-Oxidation of Aqueous Fe²⁺

A possible nonatmospheric mechanism by which ultraviolet photolysis could have acted as an energy source for prebiotic organic chemistry is the photo-oxidation of aqueous Fe²⁺ to generate electrons and/or H₂ and thus provide reducing power. H₂ can be generated from near-UV irradiation of aqueous ferrous hydroxide at pH 6–8 (Borowska & Mauzerall 1987), and the presence of banded iron formations in Archean rocks has been cited as evidence that Fe photo-oxidation occurred on the early Earth (Braterman et al 1983, Braterman & Cairns-Smith 1987).

The coupling of Fe photo-oxidation to organic synthetic reactions and protometabolism has been postulated (de Duve 1991) but not shown experimentally. Formaldehyde formation by UV irradiation of aqueous CO₂/Fe²⁺ solutions has been reported (see Chang 1993 for a review), although the synthesis of HCN or carboxylic acids by coupling to Fe photo-oxidation has not been reported. Even if this phenomenon occurs in an ocean, it would be limited to the photic zone. Hartman (1975, 1992) has suggested a scheme for fixation of inorganic carbon and nitrogen by ferrocyanide photo-oxidation in

conjunction with self-replicating clay mineral systems, but this system has not been investigated experimentally.

Hydrothermal Systems

Submarine hydrothermal vents (Corliss et al 1979, Von Damm et al 1985) have been suggested as sites for the origin of life on the early Earth (Corliss et al 1981, Baross & Hoffman 1985). Attractive features of vent environments for prebiotic activity include energy from thermal gradients, the presence of chemical reducing power in the form of minerals, and possible protection from the effects of large bolide impacts (Maher & Stevenson 1988, Sleep et al 1989, Holm 1992).

It has been proposed that amino acids and other organic molecules could be synthesized in vent systems (Shock 1990a), and that condensation reactions to form amide and ester bonds (such as those in proteins and lipids) could also take place in vent waters (Ferris 1992, Shock 1993). These suggestions are based on the concept that the approach to equilibrium among C-, H-, O-, and N-containing compounds is kinetically inhibited under hydrothermal conditions, which prevents the system from reaching true thermodynamic equilibrium and allows organic species to exist in metastable equilibrium states (Shock 1990a). The calculated equilibrium constants K of reactions resulting in polymerization of amino acids to peptides, however, all have values of $K \leq 1$ in such metastable equilibrium systems, indicating that the equilibria lie in the direction of the free amino acids rather than polypeptides (Shock 1992b, 1993). The metastable equilibrium activities of most prebiotically relevant species predicted by these studies are 10^{-5} or less (Shock 1990a, 1992a), indicating steady-state concentrations of questionable value for further organic synthesis.

Some evidence for a possible hydrothermal contribution to prebiotic organic chemistry does exist in the synthesis of long-chain carboxylic acids. Schulte & Shock (1993) have calculated equilibrium constants of 10^4 – 10^5 for the oxidation of aldehydes to acids, including six- and eight-carbon acids, under hydrothermal conditions, and Shock (1990a) has calculated activities of organic acids as high as 10^{-2} in vent systems. The production of carboxylic acids in this manner would, of course, be dependent on the supply of aldehydes to hydrothermal systems from external sources such as the atmosphere. The possibility of Fischer-Tropsch synthesis of molecules such as long-chain carboxylic acids from CO and H₂ in vent environments remains controversial (Miller & Bada 1988, Ferris 1992).

Attempts to test predictions of hydrothermal organic synthesis experimentally have been hampered by the lack of access to natural submarine vents and the technical difficulties involved in laboratory simulation of hydrothermal systems. The data of Miller & Bada (1988) are somewhat difficult to interpret because absolute concentrations are not reported, but they suggest that the stability of amino acids other than glycine is low in vent waters with temperatures

of 250°C or more [but see Shock (1990a,b) for critiques of these experiments]. Hennessey et al (1992) reported the synthesis of glycine and small amounts of a few other amino acids in an experimental mineral-buffered hydrothermal system. These experiments were carried out with HCN, H₂CO, and ammonia (NH₃) as starting materials. However, there may have been sources of these molecules available on the early Earth, e.g. the photochemical production of ammonia (Summers & Chang 1993) and perhaps atmospheric or exogenous sources. Because the maximum duration of these experiments was 54 h, the stability of amino acids over longer times in such a system remains to be explored. Marshall (1994) has reported synthesis of amino acids from NH₄HCO₃, CaC₂, Ca, and H₂O₂ in aqueous solution at 200–275°C. The possibility of biogenic amino acid contamination in these experiments cannot be excluded, unfortunately, because the analysis technique used was not capable of full chiral amino acid resolution and adequate control experiments were not carried out.

Exergonic Mineral Formation

Wächtershäuser (1988a,b; 1990a,b) has proposed that synthesis of organic molecules on the early Earth could have occurred by reduction of aqueous dissolved CO₂ to organic compounds on pyrite mineral surfaces. The energy for these reductions would be provided by the exergonic formation of pyrite (FeS₂) from FeS and H₂S. The negatively charged organic acids produced would be electrostatically held on the positively charged pyrite mineral surface, where a surface protometabolism would develop. Organic molecules would exist in solution only at extremely low concentrations; once they diffused away from the surface they would not return and thus would play no part in further reactions on the pyrite surface.

The mechanisms of the initial reduction of CO₂ to organic compounds, especially the mechanisms of carbon-carbon bond formation, are not clearly defined in this hypothesis (see de Duve & Miller 1991). The equilibrium between water-soluble organic molecules bound to the mineral surface and the enormous volume of an essentially organic-free ocean should lie in favor of desorption and solution of the organics, although this may be less of a problem for hydrothermal interstitial waters in contact with mineral surfaces. The equilibrium between adsorbed molecules on a surface and molecules in the surrounding solution should result in a decrease in surface density of adsorbed molecules as the solution concentration of the molecules decreases (Lahav & Chang 1976). The electrostatic binding of organic acids to the pyrite surface must be strong enough to retain the molecules on the surface, while still allowing the molecules to migrate along the surface and interact freely with each other in a protometabolism. That this is in fact the case in such systems has not been demonstrated.

The formation of FeS₂ from FeS and H₂S has been shown to generate H₂ under laboratory conditions (Drobner et al 1990). Blochl et al (1992) have

reported the reduction of carbon-carbon and carbon-oxygen bonds (alkynes and aldehydes to alkenes and alkanes) in such a system, and Kaschke et al (1994) have reduced cyclohexanone to a variety of dithiols in nonaqueous solvents by this method. However, the central claim of the hypothesis, the fixation of inorganic carbon to organic carbon by FeS₂ formation, has not yet been demonstrated experimentally.

Internal Radioisotope Decay

Radionuclide decay would contribute an amount of energy to a planetary crust comparable to electric discharges (Oró et al 1990), but in a differentiated body the crust would probably be relatively free of reactive organics. Internal radiogenic heating may, however, be important for the synthesis of amino acids on small bodies such as asteroids through the generation of liquid water (Peltzer et al 1984). The decay of ²²²Rn, a short-lived daughter product of ²³⁸U, has been suggested as an energy source for prebiotic chemistry in groundwaters (Martell 1992). One- and two-carbon organic acids have been produced in the laboratory by the self-irradiation of ¹⁴C-containing CaCO₃ (Albarran et al 1987), and ionizing radiation can convert these molecules to longer-chain acids in aqueous solution (Negrón-Mendoza & Ponnampertuma 1982).

Remaining Problems

The relevance of laboratory yields from prebiotic experiments to the actual origin of life in a planetary environment is difficult to assess because the minimum aqueous concentration of simple organics necessary for the synthesis of biomacromolecules has not been firmly established. Most prebiotic chemists would probably agree that, in the absence of surface catalysts or other concentration mechanisms, millimolar steady-state concentrations of simple organics (nitriles, aldehydes, etc) in a prebiotic ocean would probably be sufficient for the synthesis of biomonomers such as amino acids, whereas concentrations below one micromolar would probably be insufficient.

It is possible that surface catalysts such as clays or other mineral surfaces (Cairns-Smith 1982; Ferris & Ertem 1992, 1993), or vesicles formed abiotically from nonpolar molecules (Morowitz et al 1988), could function as concentrating agents for prebiotic organics and thus lower somewhat the bulk oceanic concentrations necessary for the origin of life. Until our knowledge of the oxidation state of the early Earth's environment is better constrained by available geological and geochemical data, however, prebiotic chemists will be left to wander through a maze of possible prebiotic chemical environments and energy sources while the relative importance of each to the actual origin of life on Earth remains unclear.

THE RNA WORLD

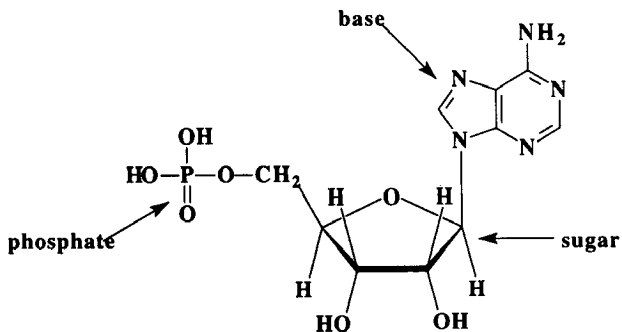
The Chicken-and-Egg Paradox

In modern biochemistry, there is a clear division of the two fundamental functions necessary for life: coding of genetic information and catalysis of chemical reactions. The former is the exclusive domain of the nucleic acids DNA and RNA, while the latter is performed almost exclusively by proteins. This clear division of labor in the contemporary cell historically led to a chicken-and-egg paradox regarding the origin of life: Which biomolecules, proteins or nucleic acids, came first? And how did the earliest organisms perform both the genetic and catalytic functions with either nucleic acids or proteins alone (Dyson 1985, Orgel 1986a)?

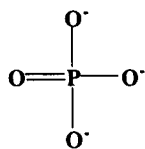
The discovery in the early 1980s by T Cech, S Altman and colleagues that certain RNA sequences could exhibit limited catalytic activity resulted in (in addition to the 1989 Nobel Prize in Chemistry) the emergence of a possible solution to the nucleic acid vs protein problem in the origin and early evolution of life. The "RNA world" (Gilbert 1986) was conceived as an early stage of evolution in which RNA functioned as both genetic material and catalyst, without the aid of protein enzymes as we know them today. The subsequent characterization of the catalytic abilities of self-splicing ribosomal RNA introns (Zaug & Cech 1986, Cech 1990), the RNA subunit of RNase P (Altman et al 1989), and ribosomal RNA (Noller et al 1992) have shown that RNA functions catalytically in significant areas of contemporary biochemistry. The directed expansion of these catalytic abilities through test-tube evolution (Beaudry & Joyce 1992, Lehman & Joyce 1993) and the amplification of inherent catalytic ability in pools of random RNA sequences (Bartel & Szostak 1993, Prudent et al 1994) have led to a consensus that RNA is capable of enough catalytic diversity and power to have served as the enzymatic workhorse of a primitive metabolism.

Lost in the Sugar Forest

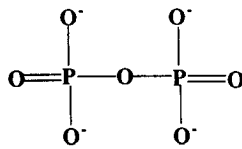
When attention turns to the plausibility of the prebiotic synthesis and survival of RNA, however, problems emerge. RNA is composed of three chemical moieties: the four bases adenine, guanine, cytosine, and uracil (Figure 1), the sequence of which makes up the genetic information; the sugar ribose that forms the backbone of the molecule; and the phosphate group, which links each base-ribose unit to its neighbor. If RNA is to be accepted as a plausible prebiotic molecule, all three of these components must be readily synthesized under reasonable early Earth conditions. Once these building blocks have been made, they must then be joined into base-sugar-phosphate units known as nucleotides (Figure 2). The nucleotides must then be polymerized, again under plausible prebiotic conditions, into oligonucleotides long enough to serve as



Nucleotide (adenosine monophosphate)



Orthophosphate



Condensed phosphate (pyrophosphate)

Figure 2 Structure of a typical ribonucleotide, with components indicated, and the structures of orthophosphate and a condensed phosphate

both catalysts and information carriers. Finally, these oligonucleotides must be capable of catalyzing self-replication through the template-directed formation of complementary strands. The difficulties faced by these processes in the prebiotic environment have been discussed in detail elsewhere (Shapiro 1988, Joyce 1989, Joyce & Orgel 1993, Schwartz & de Graaf 1993); they are briefly summarized here.

The prebiotic syntheses of the purine and pyrimidine bases of RNA are the least problematic. The demonstration of adenine synthesis by aqueous polymerization of HCN was one of the early contributions to experimental origin-of-life research (Oró 1960; Oró and Kimball 1961; Voet & Schwartz 1983). Pyrimidine bases have also been synthesized under plausible prebiotic

conditions (Sanchez & Orgel 1970). These experiments (reviewed in Ferris & Hagan 1984) share the problem of low to moderate yields (typically a few percent) common to prebiotic synthesis experiments. In addition, these experiments were done by heating dry samples. Dry heating scenarios may not be relevant to an ocean-covered Archean Earth, which lacked large areas of exposed land to contain isolated bodies of water that could undergo evaporation and dry heating. Volcanic island arcs may have provided such exposed land in the absence of continental crust, however. Both purines and pyrimidines have been reported in extracts of the Murchison carbonaceous chondrite (see Cronin et al 1988). Impact delivery to the prebiotic Earth is therefore a possible source of nucleic acid bases, although the survival of such organics in large impacts seems unlikely (Chyba et al 1990).

The synthesis of ribose, the five-carbon sugar that forms the backbone of RNA, is even more problematic in the prebiotic environment. The most widely known geochemically plausible method of synthesizing sugars is the formose reaction, which involves the alkali-catalyzed polymerization of an aqueous formaldehyde solution to produce a wide variety of sugars (for a review see Shapiro 1988). Ribose, however, is only a minor component of the product mixture, and both D- and L-enantiomers of ribose are synthesized in equal amounts (the implications of this racemic mixture are discussed below). The ribose peak in a gas chromatogram lies amidst the many other products of the formose reaction (Shapiro 1988): It becomes lost in the sugar forest.

The concentration of formaldehyde needed for ribose synthesis (>0.1 M) is higher than that likely to have been available in the oceans of the early Earth, and the high pH (>8) of the alkali-catalyzed reaction may be higher than that of a prebiotic ocean in equilibrium with a CO_2 -containing atmosphere (Grotzinger & Kasting 1993). Some common minerals such as clays have been found to catalyze the formose reaction at neutral pH (Schwartz & de Graaf 1993), but the other difficulties remain. Furthermore, ribose is prone to decomposition on time scales of at most a few years in the geochemical environment (Larralde & Miller 1994).

A more selective synthesis of ribose has been reported by Muller et al (1990). This involves the preferential formation of ribose diphosphate from glycolaldehyde phosphate in an aqueous NaOH solution (again with a pH probably higher than that of the prebiotic ocean). The suggested prebiotic precursors to glycolaldehyde phosphate are aziridine carbonitrile and oxirane carbonitrile (Wagner et al 1990, Eschenmoser 1993). Although these molecules may exist in the interstellar medium, their stability in a planetary environment is open to question and the ribose diphosphate produced in this reaction is also racemic.

Inorganic phosphate was no doubt present on the early Earth. The concentration in the ocean, however, would have been limited by solubility to approximately the current oceanic value of 0.07 ppm (Pinet 1992). More importantly,

this would have been almost exclusively orthophosphate, PO_4^{-3} , with no high-energy bonds available to drive further reactions. To participate in the polymerization of nucleotides to oligonucleotides, phosphate must be in the form of condensed phosphates (phosphates containing high-energy phosphodiester bonds) such as meta- and polyphosphates (Figure 2). Pyrophosphate can condense from orthophosphate in aqueous solution in the absence of condensing agents, with yields of up to 50% at 160°C (Rabinowitz et al 1968) but <0.1% at 37°C (Hermes-Lima 1990). With thioesters added as condensing agents, yields of several percent based on orthophosphate can be obtained (Weber 1981, 1982), but the availability of prebiotic thioesters is unclear. Urea can also function as a phosphate condensation catalyst, but only at temperatures around 100°C (Osterberg & Orgel 1972). The high temperatures and the acidic form of orthophosphate needed for these reactions may cast doubt on their plausibility in an early Earth environment, although some early Earth models imply very dense CO_2 atmospheres with surface temperatures of 85–110°C (Kasting & Ackerman 1986). Laboratory simulations and analyses of collected volcanic gases indicate that some polyphosphates can be produced by partial hydrolysis of P_4O_{10} in magma (Yamagata et al 1991).

Putting the Pieces Together

Even if we assume that the three major components of RNA—bases, ribose, and condensed phosphates—were available on the prebiotic Earth, there are more hurdles to leap to make RNA. RNA is a polymer composed of monomer nucleotide units, which consist of one base, one ribose molecule, and one phosphate anion. Nucleosides (nucleotides minus the phosphate) have been produced by heating dry mixtures of bases and ribose (Fuller et al 1972) as well as from ribose, cyanamide, and cyanoacetylene in the presence of UV irradiation (Sanchez & Orgel 1970). Much of the product yield in these experiments, however, was in the form of nonbiological isomers of the nucleotides, and the prebiotic plausibility of dry heating in the presence of a possible global ocean is open to question. Adenosine (adenine nucleoside) has also been reported as a product of UV irradiation of adenine/ribose solutions (Ponnamperuma et al 1963).

Nucleotide synthesis from nucleosides and inorganic phosphate under possible prebiotic conditions has been achieved to some degree. Lohrmann & Orgel (1971) generated nucleotides, including 2'-3' cyclic nucleotides, by dry heating a mixture of nucleosides, urea, and inorganic phosphate on hydroxylapatite at 65–100°C. Lohrmann (1975) reported synthesis of nucleoside polyphosphates from dry heating of nucleoside monophosphates and trimetaphosphate. Cyclic nucleotides and nucleoside polyphosphates are particularly important because they contain high-energy phosphate bonds and can polymerize into oligonucleotides without additional condensing agents (Verlander et al 1973). Catalysis of nucleotide polymerization reactions by clay minerals has also been

investigated (Ferris 1993; Ferris & Ertem 1992, 1993) and may have played a role in oligonucleotide formation on the early Earth, but the requirement for activated nucleotides is not eliminated by the use of clays.

The final and most important step on the road to the RNA world is the use of spontaneously polymerized oligonucleotides as templates, in the absence of protein enzymes, to achieve replication and information transfer, i.e. to serve as a genetic material. Here, more serious problems emerge. The efficiency of nonenzymatic template-directed oligonucleotide synthesis is heavily dependent on the base sequence of the nucleic acid used as the template (see Orgel 1986a, b). The complementary strand to the template can be synthesized with relative ease in these experiments, but the subsequent use of that complementary strand to synthesize a copy of the original template is severely restricted. This problem can be overcome at least in simple laboratory systems, as shown by recent work using double-stranded DNA complexes as templates for self-replication (Li & Nicolaou 1994) and other work demonstrating self-replication in a system of self-complementary and cross-complementary oligonucleotides (Sievers & von Kiedrowski 1994).

In addition, the experiments done so far (e.g. Joyce et al 1984, Acevedo & Orgel 1986) have used nucleotides activated with imidazole or included condensing agents such as carbodiimides, molecules that may not have been readily available on the early Earth (however see Ferris & Hagan 1984). Perhaps most critical is the observation that the use of a mixture of D- and L-ribonucleotides in template-directed polymerization experiments results in a severe inhibition of oligonucleotide synthesis (Joyce et al 1984). Since no unambiguous compelling mechanism for the abiotic origin of chirality has been demonstrated (Bonner 1991), and since no prebiotic synthesis of ribose or any other sugar is known to result in an excess of one enantiomer over the other, chiral inhibition of nonenzymatic RNA formation may be the single most daunting obstacle to the use of RNA as the first biomacromolecule.

Alternatives to RNA

The problems with the prebiotic synthesis and stability of RNA are well known in the origin-of-life community, and several possible alternatives to the modern RNA structure have been proposed and investigated. The most conservative of these involve structural isomers of RNA in which the bases are linked to the ribose at different positions in the base ring structure from those in modern nucleic acids. As mentioned above, it has been observed (Sanchez & Orgel 1970, Fuller et al 1972, Maurel & Convert 1990) that synthesis of nucleosides from bases and ribose under prebiotic conditions results in higher yields of structural isomers such as N⁶-ribosyladenine, and some catalytic activity has been reported in these isomers (Maurel & Decout 1992). Nucleoside analogs containing modified bases such as 8-hydroxymethyladenine or urazole

(Schwartz & Bakker 1989, Robertson et al 1994, Kolb et al 1994) have also been suggested as possible components of the first nucleic acids.

More radical ideas for nucleic acid analogs involve substitution of another sugar for ribose in the molecular backbone. Three- and four-carbon molecules such as glycerol, acrolein, and erythritol could fill the chemical role of ribose in nucleic acid analogs and might have been more easily synthesized on the early Earth (Joyce et al 1987, Joyce 1989). The lack of chiral centers in these molecules would also eliminate the problem of chiral inhibition of oligomerization discussed above. Pentaerythritol, a five-carbon reduced sugar, can be synthesized by a photochemically catalyzed formose reaction (Shigemasa et al 1977) and has also been postulated as a prebiotic replacement for ribose (Schwartz 1993, Schwartz & de Graaf 1993). These nucleic acid analogs, however, may be too flexible to form stable double-stranded structures (SL Miller, personal communication). Nucleic acid analogs based on hexoses such as glucose, allose, and altrose form more stable double-stranded structures than does DNA (Eschenmoser 1993), but this property is not necessarily advantageous. If nonstandard base-pairing schemes are as stable as the Watson-Crick base pairs that are the basis of the genetic code, a given base sequence may act as template for the replication of both complementary and noncomplementary base sequences. The transfer of genetic information would be seriously disrupted in such a case.

Perhaps the most intriguing nucleic acid analogs currently under study are peptide nucleic acids (PNAs). These are synthetic molecules consisting of the normal nucleic acid bases with a backbone of 2-(aminoethyl)glycine units (Egholm et al 1992a). These molecules form stable double-stranded structures both with each other and with DNA, following normal Watson-Crick base-pairing rules (Egholm et al 1992b). The amino acid component of the backbone is probably a more plausible prebiotic molecule than ribose or other sugars, but the polymerization of bases and amino acids to form PNAs has not been demonstrated in a prebiotic setting. Although the possible role of PNA as the first genetic material has been discussed (Nielsen 1993), the catalytic potential of PNA has yet to be explored. The suitability of PNA as a substitute for RNA in the RNA-world scenario remains unclear.

Future Outlook

Joyce & Orgel (1993) conclude that at this point the original chicken-and-egg problem regarding the evolution of catalytic and informational biomacromolecules appears to have been solved, only to be replaced by another. A self-replicating biomacromolecule as complex as RNA must, it seems, evolve its catalytic self-replicating activity through natural selection; natural selection, on the other hand, requires a self-replicating informational biomacromolecule to serve as the genetic material. Szostak & Ellington (1993), however, point

out that RNA populations with random sequences can contain some individual RNA sequences that are able to bind organic molecules, and so it may not be unreasonable to expect some catalytic self-replicating activity to arise in the absence of Darwinian evolution.

The recent *in vitro* work in RNA evolution discussed above indicates that, given a mechanism for evolution, RNA can acquire a wide range of catalytic specificities and can possibly be as efficient a catalyst as protein (Cech 1993). Given the problems with prebiotic RNA formation discussed above, it seems that the plausibility of an early biochemical system dependent entirely on nucleic acids rests on the demonstration of catalytic activity in a nucleic acid analog more prebiotically plausible than RNA.

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