Exobiology Branch (SSX) Overview

The Branch's research focuses on the advancement of the scientific understanding of the origin and distribution of life by conducting research on the cosmic history of biogenic compounds, prebiotic evolution, and the early evolution of life. This is accomplished via laboratory experiments, theoretical studies/computational modeling, and field investigations. Branch personnel are also involved in the development of flight instruments, experiments, and small mission definition with particular emphasis being placed on studies of Mars and the development of instrumentation for martian flight missions. Several Branch scientists are part of a task module that is a component of the Ames membership in the Astrobiology Institute. Branch scientists provide expertise in exobiology, astrobiology, planetary protection, and other areas of planetary science to NASA Headquarters and external review and advisory panels, and some serve as editors and associate editors of scientific journals.

Exobiology studies includes the history, distribution, and chemistry of biogenic elements in the solar system; prebiotic chemical evolution and the origin of life; and the history of Earth's early biosphere as recorded in microorganisms and ancient rocks. The research is conducted both on Earth and in space. The Branch also serves as the center of expertise within the agency for issues of planetary protection. As the agency lead center in exobiology, Branch exobiologists exercise a leadership role in NASA's Exobiology Program through program planning, performance reviews, advisory services to related NASA programs, and external relations.

David F. Blake

Chief, Exobiology Branch (SSX)

TRACE GAS PRODUCTION AND CONSUMPTION IN MICROBIAL MATS

B. Bebout

The Ames Microbial Ecology / Biogeochemistry Research Lab has made contributions to determining the rates and conditions under which various trace gases are emitted and / or consumed by microbial mats and stromatolites. The most promising search strategy for the detection of life on extrasolar planets is the detection of possibly biogenic gases using infrared spectrometry. Space-based interferometers, such as the Terrestrial Planet Finder, should be able to resolve the spectra of several biologically important trace gases in the atmospheres of extrasolar planets, possibly within 10-15 years. Therefore, it is important to provide a conceptual framework for the interpretation of the possible biogenicity of these gases.

Measurements of the production and consumption of reduced gases have been made under current conditions on the Earth, and conditions which are not present now but have existed in Earth's past. To date these measurements indicate that: 1) there is a significant escape of a variety of reduced gases from these communities, 2) there is significant oxidation, but also significant production, of these gases in the surface (oxidized) layers of these communities. Of particular note is the finding of significant rates of production of methane in the aerobic zone of microbial mats, as methanogenesis is thought to be an anaerobic process.

Measurements of trace gas production and consumption have been made in field-incubated microbial mats, in stromatolites, and in samples returned to Ames. Over the past year, the capability to incubate mats under natural conditions has been significantly enhanced with the modification of a greenhouse on the roof of building N239. This greenhouse has been fitted with ultraviolet-radiation-transparent acrylic to accommodate the importance of UV in the ecology of these communities. The capability to incubate mats under natural solar illumination, realistic water flows and temperatures, as well as under atmospheres of variable gas composition, now exists in this greenhouse.

In conjunction with the activities of the Early Microbial Ecosystems Module of the Ames Astrobiology Institute Team, the Biogeochemistry / Microbial Ecology Research Laboratory has participated in a number of field expeditions. Measurements of a number of important biogeochemical processes in microbial mats were made on these trips, including oxygenic photosynthesis, nutrient cycling, and nitrogen fixation.

Technology development continues to center on microsensor technology. In order to be able to better measure light (specifically plane irradiance) within photosynthetic microbial mats, a novel fiber optic microsensor capable of making these measurements even within lithified (i.e., hardened) microbial mats and stromatolites was developed. ❑

SYNTHESIS OF ORGANIC MOLECULES IN THE FRACTURE ZONE OF METEORITE IMPACTS ON EUROPA

J.G. Borucki and B.N. Khare

The objective of this work is to study the synthesis of organic molecules that occurs as a result of meteorite impacts into planets with icy surfaces, such as Europa. Meteorite impacts into icy surfaces cause a large zone of fracturing under the impact crater. Very large voltages are generated during this fracturing and that energy is in effect 'stored' in the ice as electrostatic charges spread over a large area of the ice for substantial periods of time. Over time, the electrostatic charges can accumulate until a critical level ('the break down potential of ice') is reached at which time electrical arcing occurs. In the presence of water-ice, methane, and ammonia, this arcing serves as the energy source for the synthesis of organic molecules. Spark experiments performed on ices that simulate conditions on Europa have produced large organic molecules. Furthermore, these molecules became semi-conducting.

The classic experimental apparatus for spark discharge experiments designed by Miller / Urey / Sagan / Khare consisted of a glass sphere with two electrodes protruding into the cavity of the sphere and connected to an external high-voltage source. The cavity was filled with ammonia, methane, and water vapors and an electrical arc was induced between the electrodes. This simple system generated complex molecules known as tholins. Extending this model to simulated meteorite impacts into ice our experiments have shown that impacts can generate voltages sufficiently high to serve as the energy source for the synthesis of organics in ice.

An ice cylinder (25 centimeters by 61 centimeters long) is formed in a Teflon tube. The thick-walled (2.5 centimeters) Teflon acts to contain the ice from exploding sideways at impact and cushions the ice thus simulating a larger ice field. Four electrodes are embedded in the ice cylinder at 5 centimeters, 20 centimeters, 38 centimeters, and 53 centimeters from the top surface of the ice. Three magnetic coils are wound on the circumference of the tube and a photodiode monitor was placed some 15 centimeters from the top of the ice. A quarter inch diameter solid aluminum sphere served as the simulated 'meteor.'

The Ames Vertical Gun Facility was used to launch the sphere at 5.6 kilometers per second into the ice cylinder cooled to –50 degrees centigrade. Recent test results from this system showed that the voltage created in the ice at the upper most electrode was greater than 300 volts (e.g., the channel saturated). Additionally, several saturated spikes were noted in the oscilloscope trace, indicating that arcing was occuring in the ice during the impact. Large oscillatory magnet signals (10 kilohertz) occurred in the same time frame as the impact, showing that large currents were flowing in the ice, suggesting that the ice became conductive at impact of the projectile.

The second series of experiments had photodiodes monitoring the ice both from the top and from the side some 15 centimeters down from the top through a light pipe. The impact velocity of eighth- to

quarter-inch aluminum spheres was 5 to 6 kilometers per second and the energy of the projectile from 200 to 3000 joules with the ice at a temperature of –170 degrees centigrade. At projectile impact, light emission, high voltage, and a large magnetic field were recorded that lasted some 5 milliseconds, then after a pause of 280 milliseconds a secondary light, voltage, and magnetic field occurred. The voltage and light had four spikes in a 10-millisecond time frame and the emissions correlated with each other indicating that arcing was occurring in the fracture zone under the impact.

The fracture zone under a meteorite impact can be thought of having two regions (like the plates of a capacitor) which will be charged either positive or negative. The charging of the two regions or plates occurs due to the breaking of molecular bonds in the fracture zone and / or crystalline ice that is subjected to piezolectric the effect. Breaking of molecular bonds would produce free electrons and positive and negative ions which would produce the large electrostatic charge imbalances, and would result in the formation of new organic molecules.

Another recent ice experiment was conducted in the laboratory using an ice block with two electrodes imbedded in the ice organic mixture at –200 degrees Centigrade. The results showed that the organics were generated and the ice mixture became semi-conducting. The semi-conducting organics caused the spark to cease and ice mixture became liquid at an outside temperature of –200 degrees Centigrade. The identification of the organics produced is underway.

The result of the above experiments have shown that large (tholin type) organic molecules can be formed in the fracture zones produced by meteorite impacts on the ice surface of Europa. ❑

IMPACTS AND METEORITE ORGANIC COMPOUNDS

G. Cooper, F. Horz, A. Oleary, and S. Chang

The majority meteorites that contain organic compounds are thought to originate in the asteroid belt. Impacts among asteroids and impacts between asteroids and comets with the planets, generate heat and pressure that may have altered or destroyed pre-existing organic matter (depending upon impact velocities). Very little is known about the impact related chemical evolution of organic matter relevant to this stage of the cosmic history of biogenic elements and compounds. At NASA-Ames, research continues in an effort to understand the effects of impacts on organic compounds.

One experimental approach is to subject mixtures of organic compounds, embedded in the matrix of a meteorite, to simulated hypervelocity impacts using a vertical gun. By choice of suitable targets and projectile materials, the compounds are subjected to simulated impacts resulting in various pressures in the range of 100-400 kilobar. Each pressure can then be converted by mathematical equations into the corresponding impact velocity that an actual asteroid or meteorite would have experienced. Most of these velocities are too high to obtain in the laboratory. After the laboratory impacts, the products are analyzed to determine the degree of survival of the organic compounds.

Four classes of organic compounds, known to be indigenous to carbonaceous meteorites, have been studied: organic sulfur, organic phosphorous, polyaromatic hydrocarbons, and amino acids. The

sulfur compounds were sulfonic acids containing one to four carbons. The phosphorous compounds were phosphonic acids, also containing one to four carbons.

Results show that over the range of pressures the general trend is that the survival rates of compounds are inversely proportional to impact pressure (impact velocity). However at lower pressures, 100-200 kilobar (approximately 1-2 kilometers / second), the sulfonic acids containing only one or two carbons, show nearly complete survival. There was a significant drop in survival rates at approximately 300 kilobar for all organic sulfur and phosphorous compounds. Pressures of 300-400 kilobar (4-5 kilometers / second) resulted in survival rates of approximately 20-30% for all one and two carbon compounds, while the three and four-carbon compounds survived at rates of approximately 0-10%. In the case of polyaromatic hydrocarbons and amino acids, a similar trend of decreasing survival rates with increasing pressure was observed. However, these two groups were less stable than the sulfur compounds at lower pressures.

These results indicate that significant amounts of meteoritic organic compounds would have survived impacts within the asteroid belt throughout solar system history. In the context of asteroid impacts on Earth, the results also suggest that the majority of organic compounds would have survived in objects that experienced impact velocities near or below 4-5 kilometers / second. ❑

BIOGEOCHEMISTRY OF EARLY EARTH PHOTOSYNTHETIC ECOSYSTEMS: PRODUCTION OF HYDROGEN AND CARBON MONOXIDE

T.M. Hoehler, B.M. Bebout, and D.J. Des Marais

For the first three-quarters of its history, Earth's biosphere consisted exclusively of microbial life. Most of this period was dominated by photosynthetic microbial mats, highly complex and organized communities of microorganisms that once covered the Earth. For two billion years, these mats were the primary biologic agents of global environmental change (for example, the oxygenation of the atmosphere) and the crucible for evolution of the complex macroscopic life forms we know today. Ames' Early Microbial Ecosystems Research Group studies the biology, chemistry, and geology of closely-related modern microbial mats in order to better understand the important role played by their ancient counterparts.

A key focus is to understand how the chemistry of the mat influences, and is influenced by, the collective activities of the constituent bacteria. The sunlit surface layer of the mat harbors the highest population of active bacteria, is the most productive, and has the most direct interaction with the outside environment. Within this layer, concentrations of two gaseous products of microbial metabolism, hydrogen and carbon monoxide, vary in dramatic fashion during the course of one day (as shown in Figure 22). The light-driven liberation of carbon monoxide has not been previously observed in mat communities. Given the widespread distribution of mats on early Earth, this could have represented a significant but unrecognized contribution to the ancient atmosphere. Hydrogen concentrations in the mat vary by a factor of 10,000 or more during one day-night cycle. This is a much

greater variation than the Earth's surface environment on the whole has experienced during its entire history.

This variation in hydrogen is especially important in the context of the microbiology and chemistry of the mat. Many of the bacteria in the mat utilize hydrogen as an essential means of transferring chemical energy and 'information' to one another. The dramatic daily variations in hydrogen may extensively influence the way in which these organisms interact and function as a collective whole. An important key to global change in the ancient environment, and to half of the evolution of life on Earth, may thus lie in the roller-coaster chemistry of microbial mats. ❑

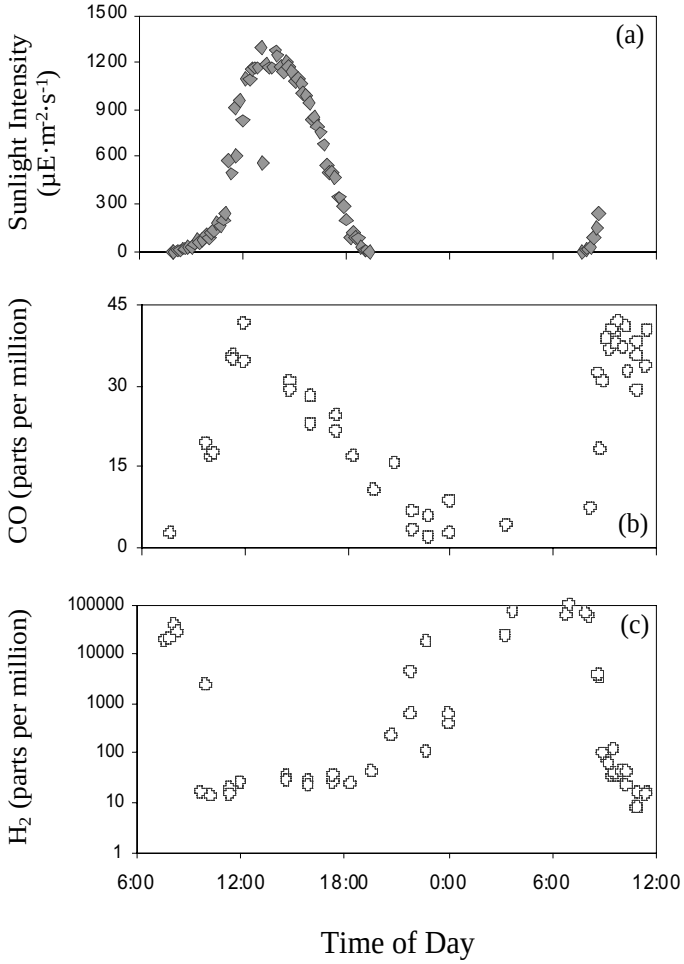

Figure 22: Light intensity (a), carbon monoxide concentration (b), and hydrogen concentration (c) at the surface of a microbial mat from Baja, Mexico during the course of one diel (24-hour day-night cycle). These graphs illustrate the dramatic light-driven chemistry generated by bacteria within the microbial mat. The chemical environment shown here experiences a greatly more substantial shift in conditions over a few hours than the Earth's atmosphere has during it's entire history.

EVOLUTIONARY RELATIONSHIPS OF STROMATOLITE BUILDING CYANOBACTERIA

L. Jahnke, K. Cullings, D. Vogler and H.P. Klein

Stromatolites are one of the most abundant fossils in Precambrian rocks, and as such, provide valuable information about Earth's earliest biosphere. The microfossil record in stromatolites traces Earth's history since the oldest life over 3.5 billion years ago. Modern stromatolite structures are formed by sediment trapping and/or mineral precipitation of microbial mat communities living in shallow water environments. Microbial mats are 'living' stromatolites; modern day analogs that provide an opportunity to study the way ancient microbial communities lived and evolved. Though direct evidence is lacking, fossil stromatolite diversity appears to be under the direct influence of microbial species diversity. Most modern microbial mats are constructed by cyanobacteria, but this may not have been the case for the earliest fossil stromatolites. Oxygenic photosynthesis first evolved in the cyanobacteria, and so understanding the relationship between cyanobacterial and stromatolite morphology is crucial to determining the bio-type of these early stromatolites and the timing of this crucial evolutionary event.

We have focused our efforts on a type of modern 'coniform' stromatolite constructed in the thermal springs of Yellowstone National Park by a fine filamentous cyanobacterium called *Phormidium*. These mats are considered the best analog for the fossil conophytons that are one of the most distinctive groups of Precambrian stromatolites with a fossil record dating back to 3.5 billion years. A variety of stable organic compounds, generally referred to as 'chemical fossils' or 'biomarkers,' have been extracted from these coniform mats, in particular the 2-methylhopanoids. The 2-methylhopanoids are considered a biomarker for the cyanobacteria and detection of its fossil equivalent in 2.7-billion year old sedimentary rocks has established a minimum age for the evolution of oxygenic photosynthesis. Understanding the relationship between the source of this important biomarker, stromatolite morphology and cyanobacterial biodiversity are essential clues in deciphering the identity of the original mat-building community and establishing the antiquity of *Phormidium* conophyton stromatolites.

A variety of morphologically-similar *Phormidium* have been isolated from the Yellowstone coniform mats. They form three distinct groups based on lipid biomarker composition. Two of the *Phormidium* groups synthesize hopanoids, but only one of these, represented by *Phormidium* OSS, synthesizes the cyanobacterial specific 2-methylhopanoids. The third group, represented by *Phormidium* RCO, synthesizes no hopanoids. A variety of molecular tools (denaturing gradient gel electrophoresis, DNA sequencing, and molecular phylogenetics) have been used to characterize the evolutionary relationship among these coniform mat, *Phormidium* isolates. Phylogenetic analysis support the three groups based on lipid biomarker composition (Figure 23). Further, the cyanobacteria isolated thus far form a monophyletic group indicating a single origin. This moderately thermophilic, coniform *Phormidium* clade is as well supported as several other well established cyanobacterial clusters such as the *Microcystis* or salt-tolerant *Euhalothece*. Such close phylogenetic relatedness suggests a common evolutionary path within a close microbial community giving rise to coniform biodiversity. ❑

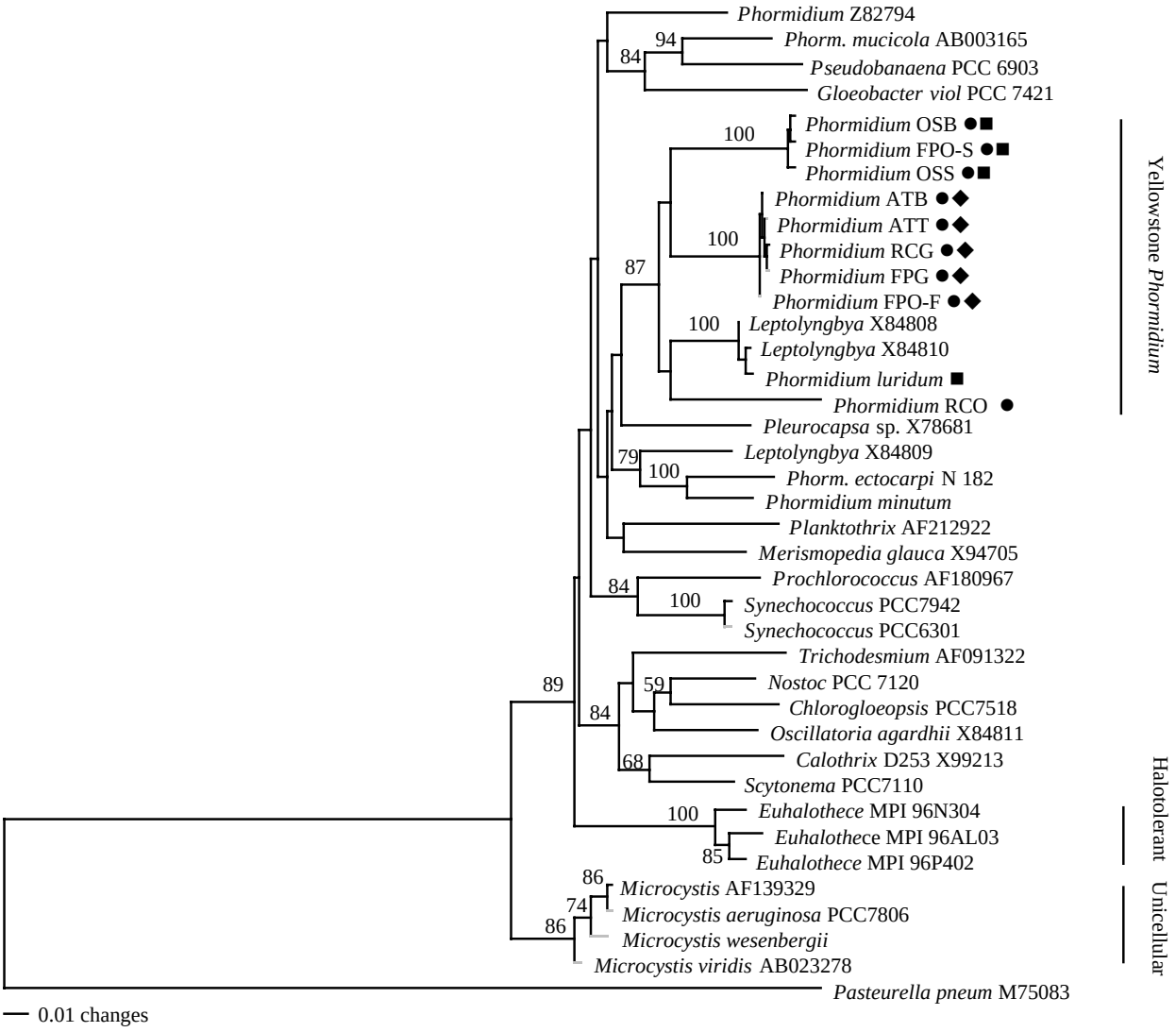

Figure 23: Phylogenetic tree constructed using the DNA sequences for the16S ribosome of Yellowstone* Phormidium *isolates (●) and cyanobacterial species chosen from GenBank to represent major clades showing* Phormidium *group synthesizing 2-methylhopanoids (■) and the group synthesizing only non-methylated hopanoids (◆).

ASTROBIOLOGY LEONID METEOR SHOWER MISSION

Peter Jenniskens, Steven J. Butow , Mark Fonda

The anticipated 1999 Leonid meteor storm provided a unique opportunity to study the nature and composition of meteoroids. Because the timing and intensity of the Leonid showers can be determined to within acceptable parameters to plan observing campaigns, NASA Ames Research Center and the United States Air Force jointly sponsored the Leonid Multi-Instrument Aircraft Campaign ('Leonid MAC'). The airborne campaign produced a wealth of data, images, and spectra that will result in new insights on the nature of cometary debris and the significance of meteors as a seeding mechanism for organics on young planets.

The Leonid meteor storm begins its long journey as cometary ejecta from a periodic comet named 55P / Tempel-Tuttle. Comets are known to contain both simple and complex organics that predate the evolution of the Solar System. The complex organics are thought to remain part of the meteoroids after ejection when the cometary ices have evaporated. Each year our present day Earth passes through an estimated 40,000 tons of such meteoric debris. At the time of the origin of life, about 4 billion years ago, that influx was a hundred fold larger. Earth was void of the basic organic compounds necessary for the origins of life. Many have postulated differing theories ranging from complex, time-dependent geochemistry to singular catastrophic impact events to account for the source of organics. Meteors provide a potential alternative pathway for their introduction.

The 1999 mission had two principle objectives: a) to provide insight into the origins of life on Earth; and b) to assess the impact threat of a meteor storm to satellites orbiting the Earth. It followed a successful NASA sponsored mission in 1998. The NASA and USAF partnership provided 35 scientists from seven different nations two platforms for stereoscopic observations under the best possible observing conditions right under the peak of the shower. The Flying Infrared Signature Technology Aircraft (FISTA) and the Airborne Ranging and Instrument Aircraft (ARIA) were operated by the United States Air Force.

Techniques employed included: state-of-the-art high definition TV technology, near real-time flux measurements using intensified video cameras (the results of which are shown in Figure 24), and spectroscopic measurements of meteors and persistent trains at wavelengths spanning from the near ultraviolet to the mid-IR. Results include the first spectroscopic record of a meteor fireball's afterglow, shown in Figure 25, and the first near- and mid-infrared spectra of meteor trains. The first video record of a meteor storm also shows lightning near the horizon, and may contain clues to whether meteors trigger 'sprites' and 'elves.'

Ames contributed to this mission new and highly successful approaches to meteor and meteor train spectroscopy at visual wavelengths. Inter-plane meteor targeting and spotting software were for the first time deployed to facilitate stereoscopic location and observation of significant meteor events. The mission also demonstrated a virtual mission control concept where aircraft tracking, status and

telemetry were all accessible through an internet browser. An INMARSAT data link from the ARIA aircraft was combined with local area network architecture on both aircraft to create the first airborne 'extranet' connected with NASA Ames Research Center and other ground-based scientists and observatories for near-real time flux reporting. ❑

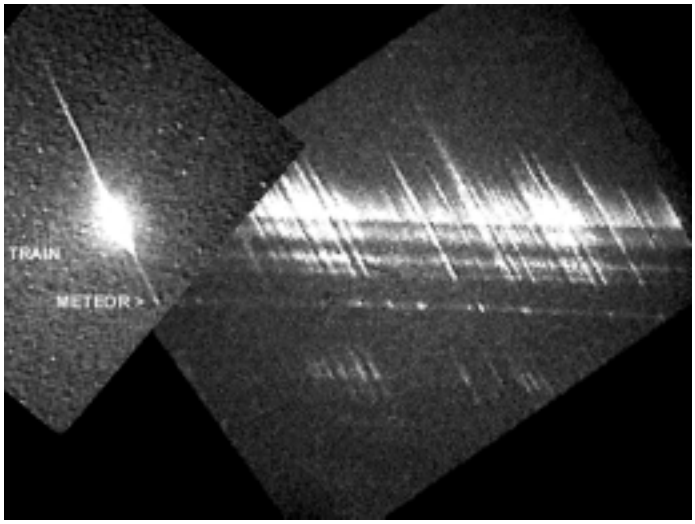

Figure 24: Near real-time flux measurements using intensified video cameras.

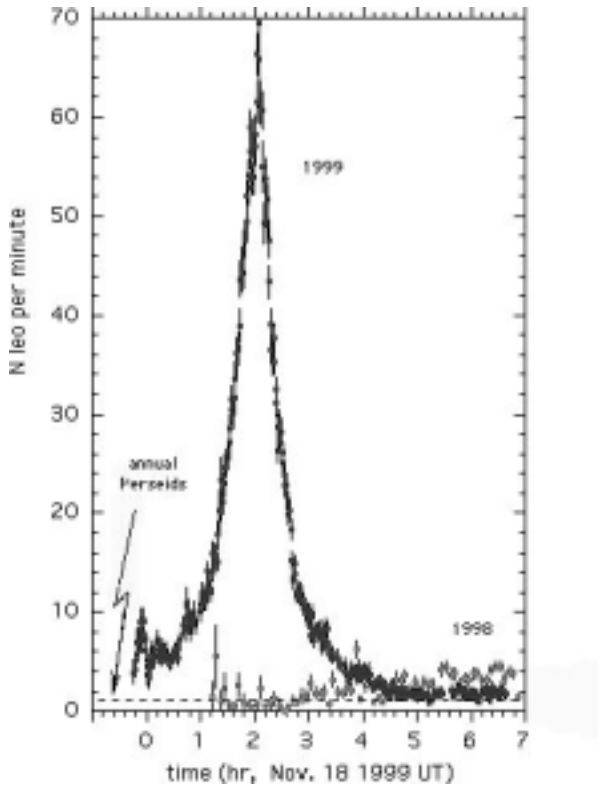

Figure 25: The first spectroscopic record of a meteor fireball's afterglow.

EXPLORING EVOLUTION WITHOUT A GENOME

M.H. New and A. Pohorille

In modern organisms, many essential life functions are performed by proteins, which are synthesized using information encoded in a nucleic acid genome. Darwinian evolution proceeds through small, random changes in the genome. If the proteins produced by an altered genome improve the organism's ability to survive, then that organism is more likely to reproduce and distribute the altered genome to future generations. Thus, the functioning and evolution of living organisms require both proteins and nucleic acids. It is, however, unlikely that both proteins and nucleic acids arose simultaneously on the early Earth, and immediately became inter-connected. How, then, did the earliest living organisms, protocells, perform essential life functions, grow, and evolve?

We propose that initially protocells functioned and evolved without nucleic acids and, instead, small proteins, called peptides, performed cellular functions. Since amino acids, the building blocks of peptides, cannot pair precisely as do nucleic acid bases, the transfer of information between generations via the exact replication of peptides is not possible. Thus a new concept of evolution independent of coded information storage – *non-genomic evolution* – is required.

Central to this concept is the emergence of ligases, proto-enzymes that form the peptide bonds that link amino acids in a peptide. Initially, these ligases were very weak, non-specific catalysts producing peptides of various lengths and sequences. A few of the peptides so generated could have been better catalysts of peptide bond formation than the proto-enzymes that formed them, thereby generating even more peptides, increasing the chances of producing functional ones. Some of these functional peptides were proteases, proto-enzymes that cut peptide bonds. Since proteases cleave unstructured peptides more rapidly than structured ones, and since functional peptides have some degree of ordered structure, proteases would preferentially destroy non-functional peptides. Occasionally, the newly produced peptides would be capable of performing novel functions. If these novel peptides integrated into the protocellular metabolism, they could increase the capabilities of the protocell. Eventually, this process could lead to the emergence (or utilization) of nucleic acids and their coupling with peptides into a genomic system.

To examine the evolutionary potential of a non-genomic system, we have developed a simple, computationally tractable model that is capable of capturing the essential biochemical features of the real system. In the simplest implementation of the model, only two catalyzed reactions were considered: the formation (polymerization) and destruction (hydrolysis) of peptide bonds. Thus, a peptide can play a double role: as a substrate for polymerization or hydrolysis or as a catalyst of these chemical reactions. The properties of the products of these reactions are related to the properties of the reactants. To underscore this relationship, the model is called an Inherited Efficiencies Model.

Computer simulations of the Inherited Efficiencies Model were performed and for many choices of model parameters, the overall catalytic efficiency of a test protocell was observed to increase. Two properties strongly affected the ability of the protocell to evolve: the balance between the probability

that a peptide is an efficient protease and the probability that it is an efficient ligase, and the strength of the preference toward the hydrolysis of unstructured peptides. These results are demonstrated in Figures 26 and 27, both of which show the average catalytic efficiency of ligases in a test protocell as the simulations progress, for two different realizations of the Inherited Efficiencies Model. Figure 26 displays the results of lowering the probability that a peptide is an efficient ligase relative to a reference model (solid line). Although in both models the overall catalytic capabilities of the test protocell increase, when the probability of forming efficient ligases is reduced (dashed line), so is the final catalytic capability of the protocell.

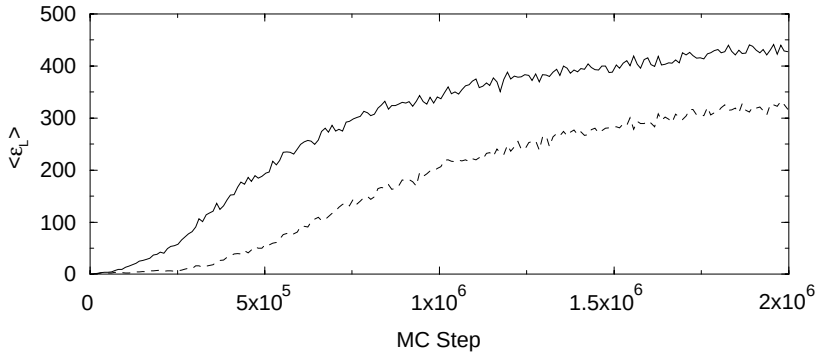

Figure 26: Average catalytic efficiency of the ligases in the test protocell over the course of a simulation. The solid line represents the results of a reference model, in which the probability of forming an efficient ligase was slightly less than the probability of forming an efficient protease; there was a strong preference for the hydrolysis of unstructured peptides. The dashed line displays the results of a simulation in which the probability of forming an efficient ligase has been lowered.

A similar effect can be seen in Figure 27. In this figure, almost all improvement in the catalytic capabilities of the test protocell is eliminated when the preference for the hydrolysis of unstructured peptides is reduced slightly (dashed line) relative to the reference model (solid line). When efficient proteases are easy to form, or when there is little preference for the hydrolysis of unstructured peptides, any long and highly efficient peptides will be destroyed before they can greatly affect the population of peptides within the protocell. Therefore, the rate at which the protocell generates new, and possibly efficient, peptides will be slow.

The results presented here demonstrate the possibility of a novel mechanism of early protocellular evolution. This mechanism does not require the presence of a genome, nor does it rely on any form of sequence complementarity or the exact replication of proteins. It is the preservation of cellular functions and their inter-relationships that must be maintained during this early stage of evolution; not the identity of the actors performing those functions. ❑

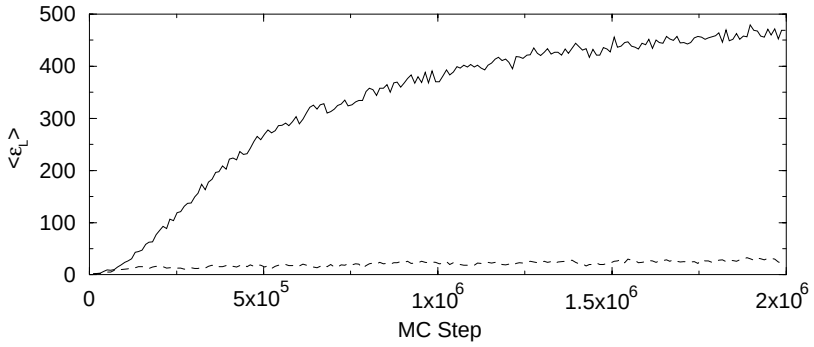

Figure 27: Average catalytic efficiency of the ligases in the test protocell over the course of a simulation. The solid line displays the same reference model as in Figure 26. The dashed line displays the results of a simulation in which the preference for the hydrolysis of unstructured peptides has been reduced slightly.

REDUCED NITROGEN FOR AN ACIDIC EARLY OCEAN

D.P. Summers

This project is concerned with how reduced nitrogen (nitrogen with a low oxidation state) may have been available for the origin of life on the Earth (and potentially on other planets such as Mars). Life today is uses nitrogen in a relatively reduced state. Organisms produce that nitrogen biochemically. However, at the time of the origin of life, those biochemical mechanisms were not yet in place. Therefore, there must have been a non-biological mechanism to produce such nitrogen. Without the availability of reduced nitrogen for the formation of species such as amino and nucleic acids, life could not have started.

One important form of fixed and reduced nitrogen is ammonia. However, current geochemical evidence points to an atmosphere on the early Earth which contained elemental nitrogen (N_2) instead of ammonia. The lighting that would have produced, ultimately, amino acids under a methane / ammonia atmosphere only produced nitrogen monoxide (NO). However, this NO can be converted into nitrite (NO_2^-) and nitrate (NO_3^-) by atmospheric and aqueous processes. Work at Ames has previously shown that one source of ammonia involves the reduction of nitrite to ammonia by the aqueous ferrous iron (iron in the +2 oxidation state; in this case the Fe^{+2} ion), that was common on the early Earth. However, this reaction doesn't form ammonia at acidic pHs (e.g., <7.3). The early Earth is thought to have had a carbon dioxide atmosphere, and since carbon dioxide is acidic, an acidic early ocean is a distinct possibility.

This work has found that a form of ferrous iron, FeS (one form of iron sulfide), will reduce nitrite and nitrate to ammonia under acidic conditions. Turning first to nitrite (NO_2^-), in Figure 28 we see how the concentration of ammonium changes with time when nitrite is added to a suspension of FeS under acidic conditions (pH 6.3). Ammonia is formed at pH 6.3 and at all pHs studied. As the pH becomes more acidic, the yield of ammonia (the amount of nitrite that is converted to ammonia)

increases from 18% to 53%. This is thought to be due to the fact that, under carbon dioxide, less bicarbonate (an ion that is a neutralized form of carbon dioxide) is present in more acidic solutions and that bicarbonate interferes with the reactions. Similarly, it was found that there is a small, but noticeable decrease in the yield of ammonia when chloride and sulfate ions are added. Presumably, these ions tend to block the surface of the FeS particles, preventing the nitrite ion from getting in to react. Phosphate ion has an even bigger effect, cutting the yield by 2/3.

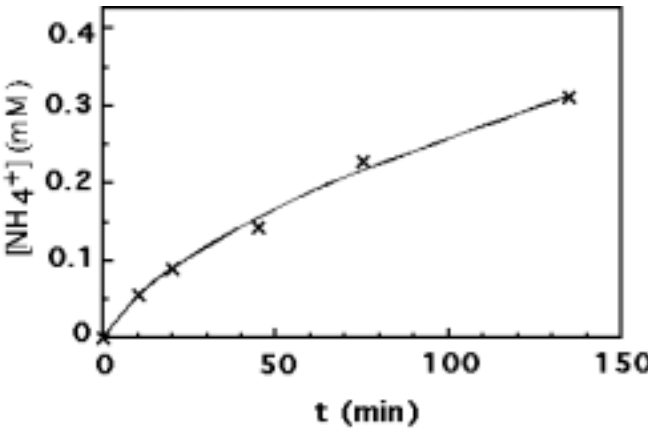

Figure 28: Ammonium concentration-versus-time in the reduction of nitrite by FeS under carbon dioxide at pH 6.3.

FeS also reduces nitrate (NO_2^-) under acidic conditions. Yields from nitrate are much lower, typically 7% in more acid solution (pH <5) and no ammonia is formed at all at neutral pHs. Similarly, the reduction of nitrate is much more sensitive to the presence of added species. No ammonia was produced in the presence of chloride, sulfate, and phosphate ions. It appears as if nitrate is much more sensitive to the presence of blocking ions. Perhaps nitrate is more easily blocked from the surface. The reduction of nitrate was observed with Fe^{+2}, but the reaction was never found to be reproducible (different yields were obtained when the reaction was run under what apparently were the same conditions). The lack of reproducibility of nitrate reduction by Fe^{+2} (which also showed a similar effect) might be related to ease with which the reaction is poisoned.

After reactions, analysis of the surface composition by a scanning electron microscope with a light element detector didn't show the formation of any iron oxide (see Figure 29). However, iron was found dissolved in the solution. Thus, oxidation of the FeS during the reduction of nitrite proceeds by the formation of FeS_2 at the surface and Fe^{+3} in solution.

Clearly, FeS is a good reductant for the conversion of nitrite and nitrate to ammonia. The reaction occurs under acidic conditions which means that such reduction would have been a viable source of ammonia, even it the early ocean were acidic. The reduction of nitrite tolerates the presence of many of the salts that would likely have been present in an early ocean, though some drop in yield is seen. The reduction of nitrate is more sensitive. ❑

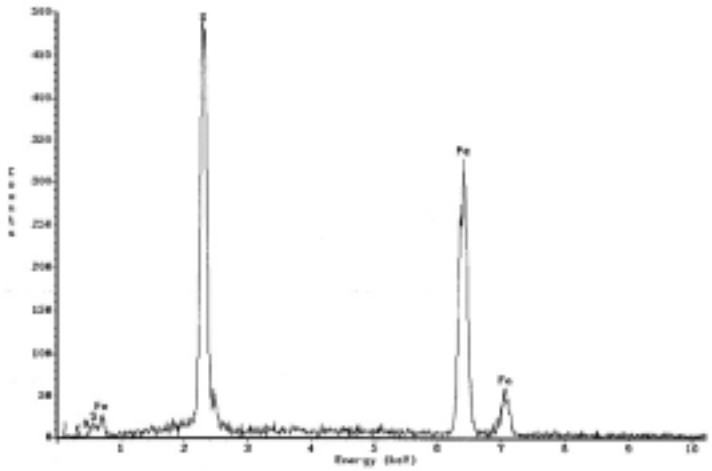

Figure 29: Surface composition of a particle of FeS after reaction with nitrite.

PREBIOTIC PEPTIDE SYNTHESIS

A.L. Weber

Chemical processes occurring on the primitive Earth about four billion years ago yielded molecules that had the ability to make copies of themselves or replicate. These rudimentary replicating molecules eventually developed into contemporary life that uses both protein and DNA molecules for replication. Since the DNA of contemporary life appears to be too complex to have been chemically made on the primitive Earth, the first replicating systems may have been composed solely of small proteins — called peptides. Peptides are good candidates for the first replicating molecules because they are constructed from very simple building blocks – activated amino acid molecules — which could have been made by chemical processes on the primitive Earth.

To understand how peptides that are necessary for the origin of life could have been synthesized on the primitive Earth four billion years ago, a model chemical process was investigated. This model process has the potential to make peptides from very simple chemical ingredients – formaldehyde, ammonia, and hydrogen sulfide. So far, studies of this process have shown that reaction of formaldehyde, glycolaldehyde (a formaldehyde dimer), and ammonia in the presence of a thiol yields amino acids via activated amino acid thioesters capable of forming peptides. In addition to activated amino acids the process also generates important biochemical intermediates (such as pyruvate and glyoxylate), and other products that catalyze their own synthesis (such as amino acids, thiols and imidazoles). The ability of the process to generate catalytic products gives it the potential to be artificially 'evolved' to a higher level of chemical activity made possible by the action of its catalytic products.

A peptide catalyst of the model process, polylysine, was confined to a small semi-permeable container (a small dialysis unit), suspended in a much larger solution of triose sugar substrate. This reaction system functioned as a catalytic flow reactor. It continually pulled new substrate molecules into the dialysis unit to replace those that had been catalytically converted to product (pyruvaldehyde), as the product molecules diffused out of the dialysis unit back into the surrounding substrate solution.

In some respects, this chemical flow reactor resembles fermentation by microorganisms that take in and catalytically convert sugars to products (ethyl alcohol or lactic acid) that eventually diffuse out of the cell back into the surrounding medium. The pathway for peptide synthesis, from formaldehyde to activated amino acids, is an attractive model of an early stage in the origin of life. The model generates products in a single reaction vessel from simple substrates, that catalyze reactions involved in their own synthesis.

In contemporary life metabolic pathways transform organic substrates into useful biomolecules – amino acids, lipids, etc. The energy required to drive metabolism, comes from the transfer of high energy electron pairs in organic substrates to lower energy states, in numerous biochemical end products. Organic substrates are capable of donating the greatest number of high energy electron pairs and have the potential to drive the greatest number of carbon group transformations; the optimal biosynthetic substrate would contain the largest possible number of high energy electron pairs per carbon atom. Viewed this way, the optimal bio-substrate functions like an optimal battery by generating the largest number of high-energy electrons per unit mass of storage material. The biosynthetic ability of a carbon substrate is determined mainly by the number of high-energy electron pairs per carbon atom. Nevertheless, the optimal bio-substrate would also contain any chemical group that strongly facilitates its conversion to a variety of metabolic intermediates of different size and composition. Since the carbonyl group is the only carbon group that strongly facilitates the synthesis of metabolic intermediates of varying size, the optimal bio-substrate would certainly contain one carbonyl group. Based on the foregoing considerations, sugars were found to be the optimal biosynthetic substrate of life. They contain the largest number of high energy electrons per carbon atom, and possess one carbonyl group that facilitates their conversion to a variety of biosynthetic intermediates. This conclusion applies to aqueous life throughout the Universe, because it is based on invariant aqueous carbon chemistry – primarily the universal reduction potentials of carbon groups. ❑