Second Symposium on Chemical Evolution and the Origin and Evolution of Life

Edited by
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Proceedings of a symposium sponsored by the National Aeronautics and Space Administration and held at NASA Ames Research Center Moffett Field, California July 23–26, 1985

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Foreword

This report includes the program, session summaries, abstracts, and list of participants from the "Second Symposium on Chemical Evolution and the Origin and Evolution of Life," held July 23-26, 1985 at the NASA Ames Research Center, Moffett Field, CA and organized by Donald L. DeVincenzi.

The purpose of the symposium was for the NASA Exobiology Program principal investigators to present their research progress and to encourage the scientists in different exobiology disciplines to exchange information. More than 165 participants attended, including the principal investigators, staff members of the NASA centers involved in exobiology, graduate students, and other interested guests.

This symposium is held approximately every three years. The first symposium was held August 2-4, 1982 at the NASA Ames Research Center (see NASA Conference Publication 2276). Additional information about the Exobiology Program, such as the annual bibliography of scientific reports and articles sponsored by the program, may be obtained from the NASA Headquarters Program Office.

We would like to thank Vera Buescher for coordinating the 1985 symposium at the NASA Ames Research Center. The scientific session summaries were prepared by the session chairmen.
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Introduction

NASA's Exobiology Program is a multidisciplinary and an interdisciplinary research effort directed towards understanding fundamental questions concerning the origin, evolution, and distribution of life and life-related molecules throughout the universe. The unifying concept underlying all research in exobiology is that the origin and evolution of life is an integral part of the origin and evolution of stars and planets; thus, life is a product of a continuum of physical and chemical processes that started with the origin of the universe itself. In keeping with this theme, the Exobiology Program encompasses four major research areas, each addressing (in a chronological sense) the major epochs associated with the origin and evolution of life on a planet: 1) cosmic evolution; 2) prebiotic evolution; 3) early evolution of life; and 4) evolution of advanced life forms. The program is intriguing because of the fundamental questions it addresses, complex because of the need for research in disciplines as diverse as radioastronomy and molecular biology, and scientifically sound as measured by the continued excellence of its research product.

The classic experiments of Miller and Urey, demonstrating the abiotic synthesis of essential biomolecules, were followed by a marked progression or evolution of research ideas that can be characterized as follows: precise identification of prebiotic simulation products; tests of the generality of conditions under which these syntheses occur; examination of extraterrestrial materials and environments for evidence of similar compounds and processes; adaptation of organisms to simulated extraterrestrial environments; the search for life in lunar samples, on Mars and beyond; and probing the origin of biological structures, metabolic processes, and the genetic code. NASA-sponsored research in these areas has been highlighted by several key discoveries, including the demonstration of the abiotic origin of meteoritic biomolecules, expansion of the range of environmental extremes over which organisms can adapt, characterization of the unusual surface chemistry on Mars, determination of the earliest microbiological phylogenetic relationships, and development of the role of clays in the origin of essential biopolymers.

It can be seen that achieving an understanding of exobiology questions requires a methodical research strategy which traces the history of the biogenic elements from their origins in stellar formation processes, through the chemical evolution of molecules essential for life, and into primitive and ultimately complex living systems. This research strategy involves the synthesis of data collected from solar system exploration.
missions, ground-based and orbiting observatories, and
ground-based and orbiting laboratories.

Solar system exploration spacecraft provide information
concerning the potential for life on and the physical and
chemical characteristics of planets, planetary satellites,
planetesimals and primitive bodies of our solar system—the one
stellar system in which we know life originated. These data
provide insight on how physical and chemical properties of the
biogenic elements and compounds may have influenced the course of
events during the formation of the solar system and the bodies in
it. Direct studies of biogenic elements and compounds in comets,
aroids, planets and their satellites, and dust in interstellar
and interplanetary space, are needed to achieve two major
objectives. The first is to clarify the relationship between
these bodies and the second is to establish the present
distribution of the biogenic elements and compounds in the solar
system as a firm foundation upon which to build a better
understanding of the way in which the dynamics of nebular
evolution and planetary accretion distributed the biogenic
elements and compounds throughout the solar system.

Ground-based and especially orbiting observatories provide a
means to elucidate the processes associated with star formation
and the development of planetary systems, with particular
emphasis on the organic chemical processes associated with these
events. Observational data are used to assess the abundance and
interaction of the biogenic elements into compounds from which
life may derive in stellar systems. Indeed, the fact that
organic compounds in increasing numbers and complexity are being
detected by radioastronomy in the interstellar medium is of
fundamental importance to exobiology. This is because it
demonstrates clearly that the chemical evolution of organic
matter was not restricted to planets, but occurred widely in the
universe as an integral part of cosmic evolution.

Although observatories are important in understanding
exobiology questions, the basis from which understanding emerges
is primarily comprised of insights gained in ground-based and
orbiting laboratories. These are where both theoretical models
and models that simulate interstellar, stellar, and planetary
environments allow exobiologists to formulate hypotheses and
theories regarding the processes that influence the origin,
evolution and distribution of life in the universe. Improvements
in the fidelity of these models are largely derived from sample
analyses of meteorites and cosmic dust, and observational and
explorational data. In turn, information derived from models and
the requirement for "space truth" verification of model
information is often essential in defining the science content
and instrument requirements of various missions.

The next decade offers increasing opportunities for
significant advances in exobiology research. The suite of space missions planned provides a unique opportunity to synthesize observational, space exploration, in situ sample collection data, and simulation experiments in order to investigate the relationship of meteorites, comets, interstellar dust clouds, and cosmic dust collected in orbit in a complementary set of studies. The Exobiology Program is actively planning a series of low Earth orbital investigations involving the Space Shuttle and Space Station and is preparing for the Comet Rendezvous Asteroid Flyby mission (scheduled for launch around 1990) and for the Titan Probe and Mars Network missions (scheduled for launch around 1994), as well as a series of other solar system missions. One of the critical activities planned for the Space Station involves the development of a sophisticated "cosmic dust" collector and source detector that will nondestructively capture particles of cometary, asteroidal, and interstellar origin and provide specific information regarding the source of the particles. On the ground, it is planned for the NASA-sponsored Search for Extraterrestrial Intelligence (SETI) to enter its operational phase to detect evidence of the existence of extraterrestrial civilizations by detecting signals that may be radiating from them.

Although other federal agencies also support specific research tasks relevant to the origin and evolution of life, NASA's Exobiology Program is unique in several respects: 1) an emphasis on the relationship between the origin of life and the properties of the solar system; 2) a scope that ranges from biogenic elements to the search for extraterrestrial life; 3) maintenance of a strong in-house technical core around which an extensive extramural program has been fashioned.

Effective study of questions in exobiology requires space flight resources that are either available now or will be available in the near future. The maximum benefit from these new opportunities will be derived from the talents and creativity of the scientific community as a whole and offers many opportunities for fruitful collaboration on an international scale to continue our exploration of life's relationship with the universe.
Second Symposium on Chemical Evolution and the Origin and Evolution of Life, July 23-26, 1985, NASA Ames Research Center, Moffett Field, California

Program

Speakers are indicated with an asterisk.

Tuesday, July 23, 1985

7:30 AM Visitor Reception Bldg. N-253
Registration, Foyer, Bldg. N-201

8:30 AM Welcome

Jack Boyd*
Associate Director
Ames Research Center

Alan Chambers*
Director of Space Research
Ames Research Center

8:45 AM "Future Directions in Exobiology"

Donald L. DeVincenzi*
(NASA Headquarters, Washington, D.C.)

9:15 AM "Exobiology Flight Experiment Opportunities"

Lynn Griffiths*
(MATSCO, Washington, D.C.)

Session I: Cosmic Evolution of Biogenic Compounds

Chairman: Theodore E. Bunch, NASA Ames Research Center

9:40 AM "Organic Chemistry of Murchison Meteorite: Carbon Isotopic Fractionation"

G.U. Yuen* (Arizona State University, Tempe), N.E. Blair, D.J. Des Marais, J.R. Cronin, and S. Chang
10:00 AM  "Characterization of Biogenic Elements in Interplanetary Dust Particles"
T.E. Bunch*
(NASA Ames Research Center)

10:20 AM  Coffee

10:40 AM  "Boundary Conditions for the Paleoenvironment: Chemical and Physical Processes in Dense Interstellar Clouds"
W.M. Irvine*, F.P. Schloerb, and L.M. Ziurys
(University of Massachusetts, Amherst)

11:00 AM  "Interstellar Isomers"
D. DeFrees* (Molecular Research Institute, Palo Alto, CA), D. McLean, and E. Herbst

11:20 AM  "Photolysis Products of CO, NH_3 and H_2O and Their Significance to Reactions on Interstellar Grains"
J.P. Ferris*
(Rensselaer Polytechnic Institute, Troy, NY)

11:40 AM  "Observational Exobiology"
J. Tarter*
(SETI Institute, University of California, Berkeley and NASA Ames Research Center)

12:00 noon  Lunch

** Session II: Prebiotic Evolution--Planetary **

Chairman: Sherwood Chang, NASA Ames Research Center

1:00 PM  "The Production of Trace Gases by Photochemistry and Lightning in the Early Atmosphere"
1:20 PM  "The Organic Aerosols of Titan"
       B.N. Khare, C. Sagan*, W.R. Thompson,
       E.T. Arakawa, F. Suits, T.A. Callcott,
       M.W. Williams, S. Shrader, H. Ogino,
       T.O. Willingham, and B. Nagy
       (Cornell University, Ithaca, NY)

1:40 PM  "The D to H Ratio on Titan and the Planets:
         Implications for Origin and Evolution of
         Planetary Atmospheres"
         J.P. Pinto* (Harvard University,
         Cambridge, MA), J.I. Lunine, S.-J. Kim,
         and Y.L. Yung

2:00 PM  "Measurements of Physical Properties of Model
         Titan Atmospheres"
         T.W. Scattergood* (SUNY at Stony
         Brook), S. Chang, C.P. McKay, B.J.
         O'Hara, and G.C. Carle

Session III: Solar System Exploration
Chairman: Glenn C. Carle, NASA Ames Research Center

2:20 PM  "Experimental Basis for a Titan Probe Organic
         Analysis"
         C.P. McKay* (NASA Ames Research
         Center), T.W. Scattergood, W.J. Borucki,
         J.F. Kasting, and S.L. Miller

2:40 PM  "A Gas Chromatograph Experiment for a Titan
         Entry Probe"
         G.C. Carle* (NASA Ames Research
         Center), D.R. Kojiro, B.J. O'Hara, J.R.
         Valentin, V.R. Oberbeck, and T.W.
         Scattergood

3:00 PM  Coffee

3:20 PM  "Molecular and Elemental Dust Analyzer (MEDA)
         for the Comet Rendezvous Asteroid Flyby
         Mission"
         B.J. O'Hara* (NASA Ames Research
         Center), G.C. Carle, and B.C. Clark
3:40 PM  "Investigation of Porous Polymer Gas Chromatographic Packings for Atmospheric Analysis of Extraterrestrial Bodies"

G.E. Pollock*  
(NASA Ames Research Center)

4:00 PM  "Miniature Metastable Ionization Detectors for Exobiology Flight Experiments"

F.H. Woeller*  
(NASA Ames Research Center)

4:20 PM  "Multiplex Gas Chromatography: A Novel Analytical Technique for Future Planetary Studies"

J.R. Valentin*  (NASA Ames Research Center), G.C. Carle, and J.B. Phillips

4:40 PM  "Ion Mobility Drift Spectrometry (IMDS) as a Flight Analytical Instrument Technique"

D.R. Kojiro and G.C. Carle*  
(NASA Ames Research Center)

5:00 PM  "New Techniques for the Detection and Capture of Micrometeoroids"

J.H. Wolfe*  (San Jose State University), T.E. Bunch, and G.C. Carle

5:20 PM  Adjourn

Wednesday, July 24, 1985

Session IV: Prebiotic Evolution--Molecular

Chairman: Robert D. MacElroy, NASA Ames Research Center

8:30 AM  "Energy Yields in the Prebiotic Synthesis of Hydrogen Cyanide and Formaldehyde"

R. Stribling and S.L. Miller*  
(University of California, San Diego)

8:50 AM  "Synthesis and Analysis in Studies of Chemical Evolution"

(University of Maryland, College Park)
9:10 AM  "Isotopic Characterisation of Prebiotic Synthesis of Organic Material"
        J.F. Kerridge* (University of California, Los Angeles), S. Chang, R. Shipp, and K. Wedeking

9:30 AM  "Origin of Life and Iron-Rich Clays"
        H.H. Hartman* (Massachusetts Institute of Technology, Cambridge)

9:50 AM  Coffee

10:10 AM "Clay Energetics in Chemical Evolution"
        L.M. Coyne* (San Jose State University)

10:30 AM "Further Work on Sodium Montmorillonite as Catalyst for the Polymerization of Activated Amino Acids"
        F.R. Eirich* (Polytechnic Institute of New York) and M. Paecht-Horowitz

10:50 AM "Adsorption and Condensation of Amino Acids and Nucleotides with Soluble Mineral Salts"
        J. Orenberg* (San Francisco State University) and N. Lahav

11:10 AM "Paleosols and the Chemical Evolution of the Atmosphere"
        H.D. Holland, E.A. Zbinden, and J.P. Pinto* (Harvard University, Cambridge, MA)

11:30 AM "Cooperation of Catalysts and Templates"
        D.H. White* (University of Santa Clara), A. Kanavarioti, C. Nibley, and J.W. Macklin

11:50 AM Lunch
1:00 PM  "Molecular Microenvironments: Solvent Interactions with Nucleic Acid Bases and Ions"
          R.D. MacElroy* (NASA Ames Research Center) and A. Pohorille

1:20 PM  "Intramolecular Interactions in Aminoacyl Nucleotides: Implications Regarding the Origin of Genetic Coding and Protein Synthesis"
          J.C. Lacey, Jr.*, D.W. Mullins, Jr., C.L. Watkins, and L.M. Hall
                   (University of Alabama in Birmingham)

1:40 PM  "Molecular Replication"
          L.E. Orgel*
                   (The Salk Institute for Biological Studies, San Diego, CA)

2:00 PM  "Stereoselective Aminoacylation of RNA"
          D.A. Usher*, M.C. Needels, and T. Brenner
                   (Cornell University, Ithaca, NY)

2:20 PM  "Models of Glycolysis: Glyceraldehyde as a Source of Energy and Monomers for Prebiotic Condensation Reactions"
          A.L. Weber*
                   (The Salk Institute for Biological Studies, San Diego, CA)

2:40 PM  "A Comparative Study of Prebiotic and Present Day Translational Models"
                   (Roswell Park Memorial Institute, Buffalo, NY)

3:00 PM  Coffee

3:20 PM  "Protobiological Information, Bidirectional Recognition, and Reverse Translation"
          S.W. Fox*, T. Nakashima, A. Przybylski, and G. Vaughan
                   (University of Miami, Coral Gables, FL)
3:40 PM  "Photochemical Reactions of Various Model Protocell Systems"
         C.E. Folsome*
         (University of Hawaii, Honolulu)

4:00 PM  "The Principle of Cooperation and Life's Origin and Evolution"
         J. Oro*, G. Armangue, and A. Mar
         (University of Houston)

4:20 PM  "Base Pairing and Base Mis-pairing in Nucleic Acids"
         A.H.-J. Wang* and A. Rich
         (Massachusetts Institute of Technology, Cambridge)

4:40 PM  Adjourn

Banquet

Location: Dinah's Shack, Palo Alto

7:00 PM  Dinner
         Guest Speaker: Stanley L. Miller (University of California, San Diego)
         Topic: "Historical Perspectives on Chemical Evolution"

Thursday, July 25, 1985

Session V: Early Evolution of Life--Geochemical

Chairman: David J. Des Marais, NASA Ames Research Center

8:30 AM  "Carbon Exchange between the Mantle and the Crust, and Its Effect upon the Atmosphere: Today Compared to Archean Time"
         D.J. Des Marais*
         (NASA Ames Research Center)

8:50 AM  "Earth's Early Atmosphere as Seen from Carbon and Nitrogen Isotopic Analysis of Archean Sediments"
         E.K. Gibson, Jr.* (NASA Johnson Space Center), L.P. Carr, I. Gilmour, and C.T. Pillinger
9:10 AM "Use of Laboratory Simulated Pyrolysis in Tracing the History of Sedimentary Organic Matter"

I.R. Kaplan*, E. Tannenbaum, and B.E. Huizinga
(Institute of Geophysics and Planetary Physics, University of California, Los Angeles)

9:30 AM "Isotopic, Petrologic, and Biogeochemical Investigations of Banded Iron-Formations"

J.M. Hayes* (Indiana University, Bloomington), A.J. Kaufman, C. Klein, S.A. Studley, M.E. Baur, and M.R. Walter

9:50 AM "The Lunar Nodal Tide and the Distance to the Moon during the Precambrian Era"

J.C.G. Walker and K.J. Zahnle
(University of Michigan, Ann Arbor)
[This paper was not presented orally.]

10:10 AM Coffee

Session VI: Early Evolution of Life--Biological

Chairman: Lawrence I. Hochstein, NASA Ames Research Center

10:30 AM "Recent Progress in Precambrian Paleobiology"

J.W. Schopf*
(University of California, Los Angeles)

10:50 AM "Higher-order Structure of rRNA"

R.R. Gutell* and C.R. Woese
(University of Illinois, Urbana)

11:10 AM "rRNA Evolution and Procaryotic Phylogeny"

G.E. Fox*
(University of Houston)

11:30 AM "Investigations with Methanobacteria and with Evolution of the Genetic Code"

T.H. Jukes*
(University of California, Berkeley)

11:50 AM Lunch
1:00 PM  "Is the ATPase from Halobacterium \textit{saccharovorum} an Evolutionary Relic?\n
L.I. Hochstein* (NASA Ames Research Center), W. Altekar, and H. Kristjansson

1:20 PM  "Functional and Evolutionary Relationships between Bacteriorhodopsin and Halorhodopsin in the Archaebacterium, \textit{Halobacterium halobium}"

J.K. Lanyi*  
(University of California, Irvine)

1:40 PM  "Thioredoxins in Evolutionarily Primitive Organisms"

B.B. Buchanan*  
(University of California, Berkeley)

2:00 PM  "Biosynthetic Porphyrins and the Origin of Photosynthesis"

D. Mauzerall* (Rockefeller University, New York, NY), A. Ley, and J.A. Mercer-Smith

2:20 PM  "Oxygen and the Evolution of Metabolic Pathways"

L.L. Jahnke*  
(NASA Ames Research Center)

2:40 PM  "Evolution of Thiol Protective Systems in Prokaryotes"

R.C. Fahey* and G.L. Newton  
(University of California, San Diego)

3:00 PM  Coffee

3:20 PM  "Microfossils in the Antarctic Cold Desert - Possible Implications for Mars"

E.I. Friedmann* (Florida State University, Tallahassee) and R. Ocampo-Friedmann
3:40 PM  "Evolutionary Significance of Osmoregulatory Mechanisms in Cyanobacteria"

        J.H. Yopp*, K.A. Pavlicek, and M.H. Sibley
        (Southern Illinois University, Carbondale)

4:00 PM  "Microbial Contributions to the Precambrian Earth"

        L. Margulis, D. Bermudes*, and R. Obar
        (Boston University)

4:20 PM  "Organic $\delta^{13}C$ Values Vary Slightly with Salinity in Microbial Mats at Guerrero Negro, Baja California, Sur, Mexico: Implications for Stromatolite $\delta^{13}C$ Values"

        D.J. Des Marais*, E. Peterson, E. Kwong, and H. Bui
        (NASA Ames Research Center)

4:40 PM  Dinner break

Evening Session

7:30 PM  Discussion Session--Exobiology Flight Experiment Opportunities

        Tom Perry
        (NASA Headquarters, Washington, D.C.)

Friday, July 26, 1985

Session VII: Evolution of Advanced Life

        Chairman: John Billingham, NASA Ames Research Center

8:30 AM  "The Fossil Record of Evolution: Analysis of Extinction"

        D.M. Raup*
        (University of Chicago)

8:50 AM  "The Fossil Record of Evolution: Data on Diversification and Extinction"

        J.J. Sepkoski, Jr.*
        (University of Chicago)
9:10 AM  "Geochemical Anomalies, Bolide Impacts and Biological Extinctions on the Earth"

F. Asaro* (Lawrence Berkeley Laboratory, University of California, Berkeley), L.W. Alvarez, H.V. Michel, and W. Alvarez

9:30 AM  "Climatic Consequences of Very High CO₂ Levels in Earth's Early Atmosphere"

J.F. Kasting* (NASA Ames Research Center)

9:50 AM  Coffee

Session VIII: Search for Extraterrestrial Intelligence

Chairman: Bernard M. Oliver, NASA Ames Research Center

10:10 AM  "A Decade of SETI Observations"

R.S. Dixon* (Ohio State University, Columbus)

10:30 AM  "The Berkeley Serendip Project"

S. Bowyer, D. Werthimer*, J. Tarter, and R. Buhse (University of California, Berkeley)

10:50 AM  "An Infrared Search for Extraterrestrial Laser Signals"

A. Betz* (University of California, Berkeley)

11:10 AM  "Using the IRAS Data to Search in the Asteroid Belt for any Potential Evidence of Galactic Colonization"

M.D. Papagiannis* (Boston University)

11:30 AM  Lunch

1:00 PM  "Overview of the NASA SETI Program"

B.M. Oliver* (NASA Ames Research Center)
<table>
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<th>Time</th>
<th>Title</th>
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| 1:20 PM  | "Stanford Hardware Development Program"  
            A. Peterson, I. Linscott* (Stanford University and NASA Ames Research Center), and J. Burr |
| 1:40 PM  | "Goldstone Field Test Activities: Target Search"  
            J. Tarter* (University of California, Berkeley and NASA Ames Research Center) |
| 2:00 PM  | "Goldstone Field Test Activities: Sky Survey"  
            S. Gulkis and E.T. Olsen* (NASA Jet Propulsion Laboratory) |
| 2:20 PM  | "JPL's Role in the SETI Program"  
            M.J. Klein* (NASA Jet Propulsion Laboratory) |
| 2:40 PM  | Adjourn                                                              |
Scientific Session Summaries
Session I

Cosmic Evolution of Biogenic Compounds

Chairman: Theodore E. Bunch, NASA Ames Research Center

The overall concept of this program is to understand the history of biogenic elements (e.g., C, H, N, O, P, S) and their compounds in the galaxy and the early solar system. The program has three basic goals: 1) trace the physical and chemical pathways taken by the biogenic elements and their compounds from their origins in stars to their incorporation in the pre-planetary bodies; 2) determine the kinds of measurements that can be made on the biogenic elements and compounds in the galaxy and solar system in order to develop theories about the formation of the solar system, prebiotic evolution, and the origin of life; and 3) determine the ways in which the physical and chemical properties of the biogenic elements and compounds may have influenced the course of events during the formation of the solar system and its component bodies.

Meteorite organic chemistry was the topic of the first presentation by Yuen, Blair, Des Marais, Cronin, and Chang. Organic matter in meteorites is basically a product of abiotic processes and may be derived from solar nebula condensates that have been altered by mechanical, thermal, and hydrothermal processes in the meteorite parent body. Although the carbon isotopic composition of individual organic compounds in meteorites is largely unknown, Yuen et al. have determined carbon isotopic ratios for hydrocarbons and monocarboxylic acids in Murchison. For both classes of compounds, the $^{13}\text{C}$ to $^{12}\text{C}$ ratios decreased with increasing carbon number in a parallel manner. This and other isotopic data indicate a kinetically controlled synthesis of heavy homologues from lighter ones.

Bunch discussed analyses of interplanetary dust particles. Microprobe-SEM studies of dust particles indicated two groups: 1) particles similar to carbonaceous chondrites in terms of mineral contents; and 2) unique particles that are enriched in refractory elements, namely Ti and Al. Laser microprobe analyses of particles yielded mass spectra of negative ionic species suggesting the possible presence of poorly crystallized carbon (carbon clusters, CH$^-$), nitrogen-bearing organic matter (CN$^-$, HCN$^-$, CNO$^-$), phosphorus (PO$_2^-$, PO$_3^-$), sulfur, and possibly water (OH$^-$).

Irvine, Schloerb, and Ziurys presented observations bearing on interstellar clouds. Research on the occurrence of organic and other molecules in dense molecular clouds has yielded the identification of four new molecules: CH$_2$C$_2$N, C$_2$O, C$_3$H, and C$_3$H$_2$ (the first interstellar molecular ring to be identified).
Ongoing research also includes modeling chemical processes that are important to the interstellar environment and the dynamics of molecular cloud/new star evolution.

DeFrees, McLean, and Herbst used ab initio molecular orbital theory, reaction rate theories, and molecular cloud models to estimate the relative abundances of interstellar isomers. The existence of the pair, HCN/HNC, has been confirmed; another potential pair, HCO°/HOC°, is near confirmation as HCO° is a known interstellar molecule and the tentative identification of HOC° has been made. Methyl cyanide is also known and the theoretical prediction of methyl isocyanide has prompted the search for its existence in molecular clouds.

Ferris reported results of experiments intended to simulate interstellar grains. Interstellar grains are thought to consist of a silicate core and of inorganic and organic compounds (H₂O, CH₄, CO₂, CO, NH₃) along with possible higher molecular weight organic material. Photolysis of CO, NH₃, and H₂O mixtures have yielded the reaction products lactic acid, glycolic acid, urea, and eight other compounds whose formation mechanism may yield clearer insight into interstellar abiotic organic chemistry.

Tarter summarized the proceedings of two Workshops on Exobiology from Earth Orbit held during the past year that focused on conducting research from some of the proposed spacecraft and observational platforms. Clearly, observation from beyond the Earth's atmosphere prevents optical distortion and precludes absorption of UV and IR radiation. Many answers to questions pertaining to the origin and evolution of biogenic elements and compounds and the detection of terrestrial types of planets can only be obtained from orbiting facilities. A final report on the workshops will contain a list of observational priorities that will ultimately be of great benefit to the exobiology research community.

Session II

Prebiotic Evolution--Planetary

Chairman: Sherwood Chang, NASA Ames Research Center

The epoch of Prebiotic Evolution begins with the formation of planets and ends with the emergence of living systems. Encompassed by this time frame are two kinds of processes: planetary and molecular. Planetary processes occur on global or local scales as a consequence of the development of planets. These processes are responsible for setting the physical and chemical conditions of the planets' various environments, wherein the chemical evolution of organic matter may occur and living
systems may arise. Molecular processes may also occur on macro- or microenvironmental scales, but they comprise the chemical mechanisms by which the structures and functions that are attributable to primitive life forms develop and assemble from the materials of the prebiotic environment. The papers on Prebiotic Evolution were given in Sessions II and IV (summarized below) on the basis of this distinction.

The first paper in the session by Levine, Tennille, Towe, and Khanna tackled the problem of assessing atmospheric sources and rates of production for compounds that could have provided protection to the earliest organisms against potentially lethal solar ultraviolet radiation. Using an atmospheric model in which the dominant species were molecular nitrogen, carbon dioxide, and water, their computations suggested that atmospheric photochemistry could not have produced enough ozone or hydrogen cyanide, nor allowed survival of sufficient volcanogenic sulfur dioxide or hydrogen sulfide to have provided adequate shielding. On the other hand, Levine and co-workers also reported experimental and theoretical results indicating that nitric oxide produced by lightning, then converted to nitric acid and "rained out" of the atmosphere, could have helped attenuate UV radiation in the upper levels of oceans.

A paper by Khare, Sagan, Thompson, Arakawa, Suits, Callcott, Williams, Shrader, Ogino, Willingham, and Nagy reviewed their studies of so-called tholin, a reddish organic solid formed by continuous Tesla coil electric discharges through a simulated Titan atmosphere. These experiments were intended to simulate the irradiation of Titan's upper atmosphere by high energy electrons. The real and imaginary parts of tholin's refractive index were consistent with those deduced for the aerosols in Titan's atmosphere, and similarities in the visible reflection spectra of these materials were described. Molecular analysis of tholins using pyrolysis GC-MS revealed a great variety of hydrocarbons, nitriles, amines, and other nitrogen-bearing species; acid hydrolysis produced amino acids. The work of Khare et al. reflects the viewpoint that the chemistry of Titan's atmosphere constitutes a model for the chemistry of a prebiotic Earth atmosphere dominated by nitrogen, methane, and hydrogen.

The paper by Pinto, Lunine, Kim, and Yung assessed the possible causes for the ratio of deuterated to undeuterated methane in Titan's atmosphere, which is higher by several times than that observed in Jupiter and Saturn. Among the causes investigated were formation of Titan, condensation of methane to form tropospheric clouds, fractionation between atmospheric gas and the putative hydrocarbon ocean or crustal clathrates, and kinetic isotope effects in the photochemical reactions in the atmosphere. Their calculations indicated two processes with sufficiently large effects to account for the fractionation. The first is grain-mediated equilibrium isotopic fractionation.
between molecular hydrogen and methane in the region of the Saturnian nebula from which Titan accreted its methane. The second is the kinetic isotope effect associated with atmospheric photochemical reactions of the acetylenic free radical \((C_2H)\), which destroys undeuterated methane faster than it does deuterated methane. Both processes contributing equally could account for the enrichment.

The final paper of the session by Scattergood, Chang, McKay, O'Hara, and Carle was also related to Titan. This report described simulations of lightning discharges--a hypothetical mechanism for production of aerosols in the lower regions of Titan's atmosphere--and the preliminary analysis of the resulting products. When a simulated atmosphere was subjected to high energy shocks created by a pulsed laser, a reddish-brown waxy solid was produced. Pyrolysis GC analysis of this material produced a variety of simple hydrocarbons, hydrogen cyanide, and acetonitrile. The use of a pulsed laser to produce shocks avoided the possibility of artifacts that might have arisen from the use of metal electrodes and continuous discharges entailed in other lightning simulations. Preliminary evidence of benzene in the laser-shocked gas was noted as possibly relevant to understanding the observations of benzene on Jupiter.

Session III
Solar System Exploration

Chairman: Glenn C. Carle, NASA Ames Research Center

The session on Solar System Exploration was devoted to two major areas: 1) reports of ongoing studies that will define appropriate flight experiments for future planetary opportunities where exobiology science objectives can be addressed; and 2) reports of current research studies into analytical concepts and techniques which will lead to advanced flight instrumentation for exobiology experiments. Experiment definition studies focused on Titan in preparation for the Titan Cassini Probe and on a short period comet, e.g., Kopff, Wild 2, Tempel 2, in preparation for the Comet Rendezvous Asteroid Flyby Mission (CRAF). As in the first Symposium, studies of advanced analytical concepts mainly treated advanced gas chromatographic techniques and components. However, ion mobility drift spectrometry as applied to the special analytical needs of exobiology, e.g., organic molecules, and a novel concept for a micrometeoroid collector and detector were presented for the first time.

McKay, Scattergood, Borucki, Kasting, and Miller reported their work on laboratory and theoretical studies of the atmosphere of Titan with respect to definition of the optimum
flight experiment for a Titan Cassini Probe. Titan is of particular interest as, in many respects, it can be considered as a terrestrial planet. Further, the unique nature of its atmosphere, i.e., 5% CH₄, makes it an analog of some models of the early earth as well as the site of very interesting and pertinent organic chemistry. The authors' simulation studies of lightning-induced chemical processes in model Titan atmosphere gas mixtures produced evidence that existing models may not be adequate to satisfactorily predict bounds on atmospheric constituents for design of a flight experiment. Their work showed that larger amounts of ethane than predicted were present which is in disagreement with the simple shock model. Continuing studies are planned to reconcile theoretical models with experimental results and define flight experimental requirements.

A paper on the development of a flight instrument concept for a Titan entry probe was presented by Carle, Kojiro, O'Hara, Valentin, Oberbeck, and Scattergood. Emphasis was placed on the characterization of the entire atmosphere of Titan which requires the detailed analysis of the various aerosols and hazes as well as the gas phase. Results of preliminary studies on electrostatic, filter, and wire impactor collectors were presented showing that the electrostatic device provided the most promise for efficient collection. Additionally, a concept for a high altitude gas chromatograph sampling system was presented which was demonstrated to be able to obtain representative gas samples in model Titan atmospheres at a simulated altitude of 180 km (1 mbar). Studies are planned to further develop the collection concepts and to apply flight prototype pyrolysis-gas chromatographic systems developed for a cometary dust analyzer to the analysis of model atmosphere gases and aerosol components.

O'Hara, Carle, and Clark presented a paper on a molecular and elemental dust analyzer that is to be proposed for the Cometary Rendezvous Asteroid Flyby mission, which will seek to characterize a comet nucleus in depth. Since comets are presumed to be some of the most primitive bodies in the solar system and may have played an important role in providing the biogenic elements and their compounds to the early Earth, this mission is of particular interest to the exobiology community. The flight instrument concept presented was based on a pyrolysis-gas chromatograph and an X-ray fluorescence spectrometer integrated with a cometary dust collection and distribution system. The instrument proposed would be able to collect and analyze as little as a few micrograms of dust and ice grains ejected from the comet as well as collect and analyze gases in the coma. Molecular analysis would be accomplished with the pyrolysis-gas chromatograph and polar molecules (e.g., H₂O, NH₃, HCOH), light gases (e.g., N₂, CO, Ar, CO₂), and hydrocarbons would be determined to >1 ppm sensitivity in 1 gram of cometary dust. Elemental Analysis would be accomplished with an x-ray fluorescence spectrometer which would determine most elements.
Pollock next presented results on studies of advanced gas chromatographic columns and packing materials. These columns and materials are being developed for future solar system exploration missions where a gas chromatograph may be a candidate instrument, e.g., the Comet Rendezvous Mission, a Titan Entry Probe. Such directed development has been necessary due to the unavailability of efficient, reliable, reproducible, and ultrastable column packing materials, the heart of the chromatographic process, for use in the demanding environment of a flight instrument. Studies leading to an improved miniature light gas column for flight use have been of particular importance due to physical resources limitations aboard future spacecraft. A new porous polymer packing made from divinylbenzene, styrene, and ethyleneglycol dimethacrylate has now been developed. It is fully compatible with the helium ionization detectors to be used in future flight instruments, resulting in a 50% reduction in column size below earlier flight columns, i.e., 8 m vs. 16 m. Similar studies on miniature hydrocarbon-resolving columns have resulted in columns as short as 1 m. Continuing work will include development of improved polar compound-resolving columns as well as studies of improved and ultrastable capillary column coatings.

Woeller then reported studies of the other important element of the gas chromatograph: detectors. Again, past flight and commercially available devices are inappropriate for future missions mainly with respect to sensitivity and size. Woeller's work has focused on new configurations of the helium ionization detector, generically a metastable ionization detector (MID). These MID's are sensitive to $10^{-14}$ moles/sec and when coupled with a special circuit that modulates the applied voltage as a function of signal current have a dynamic range in excess of 7 orders of magnitude. Detectors developed by Woeller are currently being incorporated in a flight instrument for the monitoring of astronaut denitrogenation prior to EVA (Extra Vehicular Activity) and their use is planned for the CRAF mission. Recent work has produced a new MID which is an order of magnitude smaller in active volume than those reported by Woeller earlier. This detector is directly and fully compatible with capillary column applications and produces sensitivities of a few ppb. Woeller also reported on studies of the physical and chemical principles of the MID and pointed out the necessity of maintaining a contaminant-free system. He went on to show that contamination in the gas stream, whether from carrier or column bleed, was an increasingly important consideration as carrier flow and detector volume was reduced.

Valentin, Carle, and Phillips reported on recent advances in the technique of multiplex gas chromatography—a novel mathematical approach where samples are introduced into the chromatographic stream pseudorandomly without regard to elution
of preceding components. The technique provides a large increase in sample throughput thus improving either sensitivity or analysis rate. Additionally, the technique opens up new opportunities for novel sample introduction schemes. Until recently the technique has been rather a laboratory curiosity, because it had never been applied to a practical analytical problem. Valentin reported here of the first practical application of the technique where he analyzes methane in the atmosphere with ambient air serving as both the carrier gas stream and sample. The new technique uses a heated catalytic modulator to selectively oxidize hydrocarbons in the air carrier gas. On command of a computer, the modulator is cooled producing a pulse (or injection) of hydrocarbon containing carrier gas. The remaining chromatographic process is as in the conventional except data are collected by the same computer that controls the modulation pulses. Since as many as 220 visually uninterpretable chromatograms are processed in an hour, this computer also mathematically obtains the final chromatogram. Data presented by Valentin not only demonstrated the utility of the technique for future flight missions to study planetary atmospheres, it revealed some previously unobserved variations in ambient methane concentrations that are currently under study. Future work will also include further studies of catalytic modulators and specialized detectors for application to planetary atmospheres.

Kojiro and Carle reported on ion mobility drift spectrometry, another advanced analytical technique that could be applied to Exobiology's requirements in solar system exploration. An ion mobility drift spectrometer is an ion/molecule reactor coupled with an ion drift spectrometer. Sample molecules enter the reactor where they are ionized forming product ions that are structurally representative of the original sample molecule. The product ions are then extracted from this region into the spectrometer. These ions are separated in an electric field and finally collected providing a signal. The time required for the ions to drift through the field is directly related to their structure and molecular weight. This instrument concept is particularly attractive as a tool for solar system exploration as it is easily interfaced with a gas chromatograph, i.e., it operates at the same pressures as the vent of a gas chromatograph and uses a reasonably high throughput of gas. Kojiro reported on the prospects of fitting such a device to a flight gas chromatograph. He found that the commercial device could be operated with consumables appropriate for a flight instrument and could be used with the miniature columns currently available. He also showed that the device could be used to identify the molecular species important to Exobiology. Plans for future work include miniaturization studies and studies of alternative ion reactions.

Wolfe, Bunch, and Carle presented advanced instrumentation concepts for a micrometeoroid detector and collector that might
be flown on the Space Station. It was stated that in order to understand the origin and distribution of the biogenic elements and their compounds, it will be necessary to study many classes of extraterrestrial objects. Of major importance are the primitive bodies which may shower the earth with fragments in the form of cometary dust. Collection of these particles in a pristine environment as found in space would provide samples for study in Earth-based laboratories. Additionally, detection of these particles and characterization of their paths and energies would aid in verifying their origin. To this end, Wolfe et al. described a particle detector that could effectively "listen" for collisions with a large structure in space using acoustic detectors. The detector structure would, over long periods, be pointed in all directions in space and incoming particle vectors (source), fluence, as well as momentum information, could be accurately determined for the cosmic dust particles. The collection concept advanced was based on electrostatic deceleration of the same particles. Using a computer-controlled, staged decelerator, incoming particles would be detected and, based on their mass and speed, would be sequentially slowed down and brought to rest on a sample-pan. The pan would be removed and replaced occasionally and collected samples would be returned to earth for analysis.

Session IV

Prebiotic Evolution--Molecular

Chairman: Robert D. MacElroy, NASA Ames Research Center

The research areas in Prebiotic Evolution covered in this session included the following: 1) formation of small organic materials under laboratory conditions simulating the primitive Earth; 2) synthesis of organic structures on surfaces, including meteorites, clays and mineral salts; 3) investigation of model systems of catalysis, self-replication and translation; 4) exploration of the environments and molecular structures that may have been important in the generation of prebiotic functions; 5) possibly useful prebiotic energy sources; and 6) evidence for the state of the early biotic environment.

Stribling and Miller reported on an evaluation of the yield of organics (HCN and H₂CO) of spark discharge experiments as a function of energy input. The amount of product resulting from the reactions was determined after increasing time intervals and extrapolated back to zero time. Yields of the order of 0.7 to 6 x 10⁻⁸ moles/cal were observed. The results suggest that products were destroyed during the course of the reaction. The data provide a better evaluation of productivity of various kinds of organic syntheses in the prebiotic environment than has been
available before. The experiments were extended to include other energy input forms, as well as consideration of subsequent reactions of the initial products.

The possible prebiotic formation of organic matter was also reported by Folsome. He had previously reported that organic microstructures formed in spark discharge experiments containing \( \text{N}_2 \), \( \text{CO} \), and \( \text{H}_2 \) could catalyze photoreduction of carbonate to organic carbon. Current studies showed the formation of organic structures after prolonged exposure of \( \text{N}_2 \), carbonate, and water to long wavelength UV, extending his earlier observations. Folsome concluded that such phase-bounded systems can serve effectively to form reduced organics from oxidized carbon in a UV energy flux.

Fox, Nakashima, Przybylski, and Vaughan reported on studies of reverse translation in thermal proteinoids. One object of study was the catalysis of 5'-phosphorimidazolides by thermal polypeptides. It was observed that a deceleration of the reaction is caused by thermal polylysine polymers in the reaction, whereas they accelerate the formation of nucleoside triphosphates. Included in the presentation was a discussion of the appearance of electrical signals apparently generated by proteinoid microspheres, which is interpreted as support for the concept that such entities contain information.

Evidence for prebiotic formation of organics was addressed by Kerridge, Chang, Shipp and Wedeking. The occurrence of organic kerogen-like materials in meteorites has stimulated interest in the synthesis of such materials in laboratory simulations of possible production mechanisms. Methods for analyzing them and comparing them to meteoritic organics have been devised. Decomposition of the material by heat, in the presence and absence of \( \text{O}_2 \), followed by isotopic analysis of the products released as a function of temperature was used as a method of characterization. While carbon fractions of laboratory-produced materials were found to grossly resemble meteoritic materials, the deuterium-hydrogen release patterns were very different. It was suggested that the discrepancies in release patterns may be evidence that meteoritic materials contained several compounds that were formed at different times and from starting materials of differing isotopic compositions.

Another correlation between meteoritic organic syntheses and those that may have occurred on the primitive Earth was suggested by Hartman. Iron-rich clays are found on meteorites, and also are implicated in his hypothesis that they played a significant role in the synthesis of organics on the primitive Earth. Hartman, Sweeney and Kroll have explored the radiolysis of ammonium carbonate in the presence of \( \text{Fe}^{2+} \) and have found that glycine is formed 3-4 times faster than in its absence.
Coyne addressed the role of clays in the origin of terrestrial life. She pointed out that clays have been implicated in the origin of terrestrial life as: a) substrates on which the organic precursors of cellular life were synthesized and assembled and b) as inorganic prototypic life forms that served as templates for cellular life. The capacity to store and transfer chemically significant quantities of electronic energy would have been useful for a and is prerequisite to b. Coyne and her colleagues have predicted and shown experimentally that clays can store and transfer electronic energy. They have also predicted and are investigating the extent to which the energy storage capacity is of sufficient magnitude to impact surface chemistry in or on clays. Previously they investigated the correlation between luminescence, induced by wetting/drying with water and substituted hydrazines, and the degree of interlayer hydration in two series of hydrated kaolins.

Clays as catalysts for polymerization of amino acids were discussed by Eirich and Paecht-Horowitz. They reported the synthesis of a discrete set of condensed poly-amino acids, and have explored stereoselective synthesis on clays in the presence of copper ion. They also reported the production of a predominance of L-alanine peptides when Cu-L-proline was first adsorbed to the clay and when a D,L-alanine adenylate was used as a starting material. They concluded by reporting that studies of preferential adsorption of nucleotides to clay surfaces indicate that preadsorption of adenine (but not adenylic acid) to clay surfaces causes an adsorption of UMP that is proportional to the amount of adenine adsorbed.

Surfaces, not of clays, but of soluble mineral salts, have been studied by Orenberg and Lahav as sites of biopolymer synthesis. They suggest that the process of synthesis is cyclic, as would occur during the wetting/drying cycles of a small pond. A plausible and most primitive mechanism of information transfer operating in a fluctuating environment may include i) adsorption of biomolecules onto mineral surfaces, acting as an adsorbed template; 2) specific adsorption of biomonomers onto the template; 3) condensation of adsorbed monomers; and 4) desorption of the elongated molecule. This mechanism is being tested with a variety of soluble mineral salts, for example, CaSO₄, SrSO₄, FeCl₃, Fe(OH)₃, and ZnSO₄, with several monomeric species (glycine, 5'-AMP, 5'-GMP, and 5'-CMP). The adsorbed templates being tested are poly-A, poly-G, poly-C and poly-U.

Orgel reported further work on the template-directed synthesis of polynucleotides from activated nucleotides. The results reported indicate that 1) good yields and correspondences are obtained provided that the template is rich in C; 2) templates can be as short as 5 monomers long and show efficient activity; 3) synthesis proceeds in the 5'-->3' direction; 4) fidelity is high; and 5) the incorporation reaction is enantiomerically
White, Kanavarioti, Nibley, and Macklin reported on recent progress in the investigation of possible catalysts, protoenzymes and templates in the prebiotic environment. They reported that with a model primitive translation system, consisting of dried clays in the presence of various ribo- and deoxyribo-polynucleotides, an increase in the formation of polypeptides was found with ribo- but not with deoxyribo-polynucleotides. They have also, in collaboration with Orgel, recently initiated investigations into the possible function of small peptides in the polymerization of oligonucleotides.

MacElroy and Pohorille reported recent data on the interaction of water molecules with putative prebiological molecules, such as nucleic acid bases and amino acids. The computer simulation studies were conducted to better understand the role of solvent interactions as an organizing influence on simple prebiotic molecules. One result of the studies demonstrated that the energy of interaction between water molecules in the presence of nucleic acid bases can be quantified, and provides an explanation for the stacking, rather than hydrogen bonded pairing of bases, that is observed in solutions of these solutes. A discussion involving the extrapolation of the results and concepts to include the role of water in determining the structure, and thus the function, of larger molecules (peptides, nucleic acids) was also presented.

The origin of translation mechanisms was the object of a presentation by Lacey, Mullins, Watkins, and Hall. The correlation of physical characteristics of codons and anticodons with amino acid assignments found in the genetic code was discussed. Studies of activated amino acids were reported, specifically including NMR studies of adenylates of amino acids. The data indicate that such adenylates exhibit interactions between the side chains and the adenine ring, and that the strongest interactions occur between L amino acid forms and the ring.

Ponnampuruma, Hobish, Kobayashi, Lu-Lin, and Senaratne focused their presentation on the importance of analysis of materials, such as meteorites that contain abiotic organic materials, and the fact that similar materials can be synthesized abiotically in the laboratory. Further, they called attention to their recent studies of NMR data that demonstrate that definite biased interactions exist between amino acids and their anticodonic nucleotide sequences. Specifically, if those methyl esters of amino acids with homopolymeric nucleotide codes, such as gly, pro, phe and lys, are analyzed by NMR in solution with mononucleotides, their interactions show definite preferences of interaction. The preference increases are maintained and the binding constants are
increased when examined in the presence of dinucleotides.

Usher and Needles reported on the continuation of studies of template-directed synthesis, and specifically on stereoselective aminoacylation of RNA. The 2' hydroxyl groups of RNA can be aminoacylated, starting from an amino acyl-imidazolide, and the process selects the chirality of the amino acid. The chiral selectivity has been found to depend on the presence of an amino protective group, and is influenced by the hydrophobicity of the amino acid side chain. The studies have been conducted using ApA as the model RNA acceptor and involve the use of NMR as a method of examining chiral selectivity.

Energy sources for prebiotic and early biotic forms was the topic of the presentation made by Weber. The hypothesis is that nonenzymatic reactions that generate ATP were possible in the prebiotic environment, and that certain components of the present day glycolytic pathway are likely candidates for consideration. Of particular interest is the oxidation of glyceraldehyde-3'-phosphate to produce a thioester, which in turn can drive the formation of the phosphoanhydride bond of pyro- and polyphosphate. The presentation also suggested that polyglyceric acid can contain information in the form of sequences of D and L glyceric acid residues, that the polymer might act as a catalyst by virtue of the acid base behavior of its hydroxyl groups.

The three dimensional structure of nucleic acids and their role in the generation of the genetic code was the topic of a presentation by Rein, Raghunathan, McDonald, Shibata, and Srinivasan. Folding of polynucleotides was studied using computer graphics methods, and simulations of possible mechanisms of decoding between nucleic acids and protein (translation) were investigated. Possible prebiotic coding schemes were compared to present day translation mechanisms. The central issues that emerged not only involved identification of possible reaction mechanisms in present day systems, but also identified geometrical difficulties associated with some prebiotic translation systems that have been proposed.

Wang and Rich used very high resolution x-ray crystallographic data of nucleic acid structures to illustrate the possible role of structure in the functions that the molecules perform. Of particular interest was the structure of Z-DNA and the consequence that such a structure has on the characteristics of the molecule as a whole. In particular, the types of base-pairing were discussed, raising the issue as to whether base-pairing other than the standard Watson-Crick, which is now most commonly observed in RNA molecules, might have been the structure of importance in the prebiotic evolution of molecules. The conjecture is supported by the relative ease with which crystal lattices of Hoogstein base pairs are generated.
Correlations between atmospheric composition and evolution were discussed in the presentation by Holland, Zbinden and Pinto. Paleosols found in Australian and South African rocks ranging between 1 and 2.9 billion years in age (bya) were examined to determine the oxidation state of the atmosphere. The method is based upon the oxidation state of iron in the rock, which is due to the initial amount of reductant (ferrous iron) in the rock, and the amount of oxidant and CO₂ in the rainfall at the time the paleosol was formed. They conclude that the oxidation state of the atmosphere 2.9 bya was lower than at 2.4 bya.

In addition, presentations were made by staff members of the laboratories of J. Oro and C. Ponnamperuma.

Session V

Early Evolution of Life--Geochemical

Chairman: David J. Des Marais, NASA Ames Research Center

The traditional theme of geochemical research in the Planetary Biology Program has been to examine specifically the morphology of microfossils and the chemistry of organic matter in ancient rocks. Some of the papers in this session addressed this traditional theme. In addition, other papers attempted to define various aspects of the primitive environment in which early life flourished. This broader approach toward studying the history of the biosphere underscores the recognition that numerous interactions between the Earth and the biosphere have exerted a critical influence upon biological evolution.

The presentation by Des Marais noted that, over the great time interval of the Precambrian, interactions between the Earth's mantle and crust very likely influenced the changes in the surface environment. This paper estimated the rate at which carbon is exchanged between the mantle and the crust. Because the upper mantle has cooled by at least 300°C during Earth history, and because the present exchange rate of carbon between mantle and crust is non-negligible (between 1×10^{12} and 8×10^{12} moles C yr⁻¹), the crustal carbon inventory may have been greater on the Archean earth than it is today. This circumstance favored an Archean atmospheric carbon dioxide concentration which was higher, perhaps by a factor of 100 or more, than the present level.

Gibson, Carr, Gilmour, and Pillinger presented results of stepwise combustions of Archean sediments, and sought to identify the origins of the carbon and nitrogen fractions which were evolved at the various temperatures. They proposed that carbon and nitrogen from the sediments' organic matter is released between 300°C and 700°C, and that carbon and nitrogen components
from the ancient atmosphere are released above 900°C. Their presented data suggested that the carbon and nitrogen isotopic compositions of atmospheric carbon dioxide and nitrogen have been remarkably constant over geologic time. Some in the audience questioned the validity of the assumption that the carbon and nitrogen released above 900°C did not include a significant contribution from residual sedimentary organic matter. Future work may clarify this issue.

Kaplan, Tannenbaum, and Huizinga presented results from laboratory experiments in which organic matter was heated in the presence of various geochemically important minerals. This organic matter decomposes at significantly lower rates in calcite and chert matrices than in the presence of clay. Water appears to inhibit the breakdown process. Kaplan and coworkers have also tested montmorillonite and illite clays as well as a variety of kerogen types. Such work allows a more precise interpretation to be made regarding the state of preservation of ancient organic matter.

Hayes, Kaufman, Klein, Studley, Baur, and Walter are conducting a multidisciplinary investigation of banded iron formations which are iron-rich Precambrian sediments whose precipitation is attributed to biological oxidation processes. Prior to the development of a highly oxygenated atmosphere, dissolved iron was an important seawater constituent. Hayes and co-workers have identified stable carbon and nitrogen isotopic heterogeneities in iron formation carbonates. Such patterns are not metamorphic in origin, and they likely reflect biogeochemical processes that occurred shortly after the sediments were deposited. These and other observations are helping to elucidate the processes associated with the deposition and alteration of these significant rock formations.

Although the paper by Walker and Zahnle was not presented at the meeting, its importance merits summary here. The authors proposed that the 23.3-year periodicity observed in Hamersley banded iron formation laminations reflects the climatic influence of the lunar nodal tide. If such is the case, then detailed measurements of iron formation laminae ultimately will help to define the evolution of the Earth-Moon orbital system. Such work promises to eludicate, among other things, the length of Earth days and the distance between the Earth and the Moon during Archean and early Proterozoic time.

Session VI

Early Evolution of Life--Biological

Chairman: Lawrence I. Hochstein, NASA Ames Research Center
This session covered an extremely divergent range of topics. The unifying theme was the notion that contemporary organisms contain within them information which allows for a retrospective look at the evolution of early life.

The session was introduced by Schopf who reviewed several issues associated with the Precambrian environment. Further understanding of this period requires more information concerning: day length, temperature, atmospheric composition, and ultraviolet flux. In addition, Schopf suggested several unsolved problems related to that era: a) why is there no evidence of the primordial soup in sediments; b) was early photosynthesis oxygenic; c) are there markers that relate morphological and biochemical evolution; d) to what extent was lateral gene transfer an important process in the early evolution of life; and e) how did biomass vary over time?

There followed a series of papers dealing with rRNA. Gutell and Woese reported on the possibility of using secondary structures of rRNA as phylogenetic probes. The 16s rRNAs were found to have a common secondary structure within which occurred highly conserved nucleotide regions. Fox described further structural studies with 5s rRNA. The results were consistent with the phylogenies obtained using 16s rRNA sequences. He also found that among the gram negative bacteria, phylogenies obtained from rRNA sequences, DNA hybridization, and cytochrome c sequences are in good agreement. Jukes, addressing the issue as to whether the code was a frozen accident or the result of stochastic processes, concluded it was probably the latter. In addition he reported on codon assignments in mitochondrial DNA and in *Mycoplasma* which violated the dogma of the universal code.

Two papers reported on bioenergetic processes found in the halobacteria. Hochstein, Altekar, and Kristjansson described an ATPase from *Halobacterium saccharovorum*. The subunit composition of this enzyme is clearly unlike that of an F-P, ATPase or other ion-translocating ATPase. Whether this represents a functional or structural precursor of energy-transducing ATPase is not clear. Lanyi discussed the evolutionary relationship between two retinal-containing molecules: bacteriorhodopsin, which functions as a light-dependent proton pump, and halorhodopsin, which acts as a chloride pump. Structural and functional studies revealed that the opsins must be different and that few if any sequence homologies exist.

Buchanan reported on the distribution and properties of several thioredoxins. The thioredoxin system from *Clostridium pasteurianum* behaves like the thioredoxin from photosynthetic organisms in that it was reduced by ferredoxin. Prior to this observation it was thought that ferredoxin acted as the reductant in oxygenic photosynthetic plants and NADPH was the reductant in other organisms. The ferredoxin/thioredoxin system acts to
regulate CO₂ assimilation via the reductive pentose phosphate cycle in organisms that carry out oxygenic photosynthesis. Further evidence for this notion was the occurrence of such regulation in a cyanobacterium (carrying out oxygenic photosynthesis) but not in *Chromatium* (which carries out non-oxygenic photosynthesis). The possibility that this biochemical process left a permanent record (see Schopf's points b and c) suggests the possibility of dating the appearance of anoxygenic and oxygenic photosynthesis. Mauzerall, Ley and Mercer-Smith are studying the origins of photochemical systems and reported on the efficacy of model chemical systems using cobalt complexes and porphyrin precursors as catalysts for the photooxidation of organic molecules.

Fahey and Newton found that the nature of thiol compounds in various organisms appeared to be associated with the oxygen relationship of the organism (i.e., aerobic, facultative, or anaerobic). In an intriguing observation, *Entamoeba histolytica* (which does not possess mitochondria) lacks thiols associated with organisms thought to be likely endosymbiotic candidates. These observations suggest that the nature of intracellular thiols may be useful probes for understanding the role of endosymbiosis in the evolution of life. Yopp, Pavlicek, and Sibley reported on the relationship of osmoregulators to the physiology of a variety of cyanobacteria. The pattern which emerged was that fresh water and marine cyanobacteria used non-reducing carbohydrates whereas the extremely halophilic organisms employed betaine as the osmoregulator. In further studies relating the mode of energy-transduction to the nature of the osmoregulator, organisms which were photoautotrophic accumulated trehalose whereas those which were photoheterotrophic used sucrose.

Jahnke found that the synthesis of sterols and unsaturated fatty acids was enhanced in a methanotroph when grown at low oxygen concentrations. The occurrence of sterol synthesis in a procaryote may permit studying the evolution of oxygen-requiring pathways found in eukaryotic cells in the more primitive procaryotes.

The last set of papers dealt with the properties of organisms found in environments that may serve as either putative Martian environments or Precambrian ones. Friedmann and Friedmann described and provided visual examples of the endolithic communities found in Antarctic rocks. Margulis, Bermudes, and Obar spoke of the organisms found in mat communities. Des Marais, Peterson, Kwong, and Bui reported on carbon isotope fractionation in mats from salt ponds. These studies were carried out to determine if salinity could account for the differences in the carbon isotope ratios in stromatolites and contemporary mats. The results suggested that salinity, per se, would not account for the observed differences.
One of the newer elements of the NASA Planetary Biology Program deals with the evolution of multicellular life over the last billion years. The major thrust of the research is an examination of the way in which extraterrestrial events influenced the evolution of advanced life on Earth. A minor objective is to begin the difficult task of examining important basic questions about the existence of advanced forms of extraterrestrial life. Both questions were discussed extensively in a series of Science Workshops held in 1981 and 1982 at the Ames Research Center and attended by leading scientists from the fields of evolutionary biology, paleontology, astronomy, and the planetary sciences. The Chairman was David Raup from the University of Chicago. A report from this workshop is now available (Milne, D., D. Raup, J. Billingham, K. Niklas, and K. Padian. The Evolution of Complex and Higher Organisms. NASA SP-478. Washington, D.C.: NASA, 1985) and may be obtained from my office at Ames Research Center.

During the July 1985 symposium a number of speakers dealt with different aspects of the evolution of advanced life. Raup discussed the asteroid impact theory of mass extinctions as well as the new hypothesis, proposed by Raup and Sepkoski, that mass extinction may be periodic over the last 260 million years. He discussed the possible astronomical causes that are now being examined. Sepkoski followed with a paper discussing his detailed analysis of the fossil record down to the genera level. He found that periodicity breaks down as one goes back to the Cambrian, that background extinctions decrease markedly with time, that extinction is indiscriminate in the oceanic environment, and that long established taxa are more likely to disappear during mass extinction events than during the normal background intervals.

Asaro, Alvarez, Michel, and Alvarez described the latest Berkeley team results on geochemical anomalies at extinction boundaries. He reported that high iridium concentrations had been found at the Eocene-Oligocene boundary in eight to nine sites around the world, suggesting that this event might also have been caused by an asteroid impact.

Kasting of the Ames Space Science Division discussed the importance of CO\textsubscript{2} in the early atmosphere of the Earth and the current theory that the CO\textsubscript{2} pressure at that time may have been as much as 20 bars. Model\textsuperscript{2} calculations indicate that a runaway greenhouse would not have occurred because of reduced solar luminosity, an increase in planetary albedo because of the CO\textsubscript{2},
and the stabilizing effects of moist convection.

Session VIII

Search for Extraterrestrial Intelligence

Chairman: Bernard M. Oliver, NASA Ames Research Center

This session presented reports on various Extraterrestrial Intelligence (ETI) searches that have been conducted over the past decade, are currently underway, or are proposed for the decade ahead.

The first paper by Dixon described the full-time dedicated sky survey that has been in progress at Ohio State for the past 12 years. The search concentrates on a 500 kHz band centered on the hydrogen line at 21 cm. The scan in right ascension is provided by the Earth's rotation with jumps in declination provided by adjusting the telescope reflector angle periodically. Fifty channels each 10 kHz wide are monitored automatically. The intensity and channel number of signals exceeding threshold are printed out for later study. Two populations of signals have been detected. The first is a small number of signals lasting for over a minute. The second is a large number of signals lasting less than 10 seconds and whose locations appear anticorrelated with the galactic plane. The signals do not recur and their origin is unknown at present.

The second paper, presented by Bowyer, Wertheimer, Tarter, and Buhse described the U.C. Berkeley SERENDIP project, which looks for ETI signals on radio telescopes while they are engaged in radio astronomy. New data processing equipment will extend the sensitivity and frequency coverage of this system. A fast Fourier transform spectrum analyzer provides 65,536 bins 2 Hz in width for a frequency coverage of 131 kHz. After searching for and recording significant peaks in a 100 kHz band the programmable synthesizer jumps to the next 100 kHz band. When the whole IF band has been covered, the scanning repeats. A trial run is planned at the Hat Creek Observatory in late summer.

Betz next described his proposed ETI search in the 10 μm infrared portion of the spectrum. The search postulates powerful CO₂ laser sources. These are to be detected using a laser heterodyne receiver. The IF processing will provide 1000 channels each 1 MHz wide. Using a ground-based IR telescope, several hundred selected stars will be surveyed.

Papagiannis presented his rationale for searching the asteroids of our own solar system for evidence of ETI activity. Such activity might be revealed by excess infrared emission detectable by the IRAS satellite. The IRAS catalogue is expected
to be ready at the end of 1985 and will contain some 10,000 objects. Papagiannis proposes to search this catalogue for objects having anomalous IR spectra, and then to study these objects using radio and optical telescopes.

The remaining five papers were all concerned with the NASA SETI program. Oliver, Chief of the SETI Program Office, presented an overview of the program, which features a two mode search strategy. An all sky survey will cover the frequency range of 1 to 10 GHz using an instantaneous bandwidth of 250 MHz and a resolution of about 30 Hz. Simultaneously, a targeted search will examine the 800 closest solar type stars over the 1 to 3 GHz frequency range, using an instantaneous bandwidth of 10 MHz and a resolution of 1 Hz. In the present R and D phase of the program, signal processing hardware and software is being designed and tested. Algorithms are being developed that for the first time will permit the sensitive detection of not only steady CW (narrowband continuously present signals) but also both CW and pulsed signals that drift in frequency due to doppler effect. A new start is planned for FY 88, with observations beginning in 1990. This program will test the hypothesis that ETI signals can be detected with presently existing radio astronomy or Deep Space Net antennas. If the hypothesis is false, the future of SETI will require much larger, dedicated receiving antennas.

Peterson, Linscott, and Burr reported on the Multichannel Spectrum Analyzer (MCSA) and pattern detector needed for data processing in the targeted search. These devices, currently being refined at Stanford, are highly concurrent processors with computation rates on the order of 10^10 operations per second. A prototype of the MCSA is operational at Goldstone, and has detected Pioneer 10, now outside the solar system. Economical realization of the full scale signal processing equipment requires the use of very large scale integration. This is currently being designed.

Tarter described a number of questions which hopefully can be resolved by the current and planned field tests at Goldstone and possibly at Arecibo. Of particular concern is the RFI (strong man-made interfering signals) environment and how the system can best identify signals as not ETI but RFI. Also of interest are the time statistics of receiver noise particularly in the low probability tails of the distribution. These may well depart significantly from the assumed Gaussian form.

Gulkis and Olsen described some details of the sky survey program including the proposed scanning pattern and the detection algorithms. The RFI surveillance system built by JPL for use at SETI observing sites was also discussed.

Finally Klein spoke about JPL's role in the NASA SETI program. This is primarily in the planning and execution of the sky survey.
but includes the design of feeds and receivers for both the sky survey and the targeted search. A SETI implementation plan for the use of the NASA Deep Space Network facilities for the sky survey is under preparation.
Session I
Cosmic Evolution of Biogenic Compounds
Carbonaceous meteorites remain the only source of isolable organic compounds of extraterrestrial origin, even though radio astronomy has provided evidence for the existence of more than 50 compounds in interstellar space, of which the overwhelming majority are organic. Most investigators now agree that the organic matter in the meteorites are products of abiogenic processes. Most likely, these materials are derived from solar nebula condensates that have been altered to varying degrees by mechanical, thermal, and hydrothermal processes in the meteorite parent body. These processes and the locale in which they occurred are essential to the understanding of the organic chemistry secreted in these specimens. Carbon isotopic fractionation of these organic compounds may reveal information about these processes as they often leave in their products a recognizable isotopic signature.

The carbon isotopic composition of individual organic compounds of meteoritic origin remains unknown, as most reported carbon isotopic ratios are for bulk carbon or solvent extractable fractions. Recently, we managed to determine the carbon isotopic ratios for individual hydrocarbons and monocarboxylic acids isolated from a Murchison sample by a freeze-thaw-ultrasonication technique. The abundances of monocarboxylic acids and saturated hydrocarbons decreased with increasing carbon number and the acids are more abundant than the hydrocarbon with the same carbon number. For both classes of compounds, the $^{13}$C to $^{12}$C ratios decreased with increasing carbon number in a roughly parallel manner, and each carboxylic acid exhibits a higher isotopic number than the hydrocarbon containing the same number of carbon atoms. These trends are consistent with a kinetically controlled synthesis of higher homologues from lower ones.
We assume that comets and cometary particles that we have collected at high altitudes via the U-2 aircraft have been stored in a mostly nonalteration environment for most of their lifetime. If this assumption is correct, then we have a unique opportunity to study near pristine samples, which will allow us insight into the origin of early solar system materials and possibly interstellar matter. Moreover we may be able to understand the evolution of biogenic elements and their compounds from stellar formation through the interstellar medium to their present day configuration.

Those particles that we designate cometary are aggregates of amorphous materials including carbon, iron-magnesium silicates, sulfides, metal and trace amounts of unusual phases. Most aggregates are carbon-rich with major and minor element abundances similar to a fine-grained matrix of carbonaceous chondrites.

Several particles have been analyzed by a laser microprobe. The negative ionic species identified to date include carbon clusters (C₂⁻ thru C₁₃⁻), protonated carbon clusters (C₂H⁻, C₃H⁻ etc.), CN⁻, HCN⁻, CNO⁻, PO₂⁻, PO₃⁻, S⁻, S₂⁻ and OH⁻. These species are similar to those observed in cometary spectra and they support the assumption that organic materials are present. The occurrence of phosphate ions suggests the presence of apatite or whitlockite.

Cometary particle characteristics may indicate that the component grains represent primitive unaltered dust whose overall properties are extremely similar to altered "primitive" dust in carbonaceous chondrites.
It is now well established that stars, and presumably planetary systems, form in dense interstellar clouds of gas and "dust". In individual cases such clouds may contain as much material as millions of Suns, making them the most massive objects in the Galaxy. More than 60 molecular species, the vast majority of them organic, have been identified in the gas phase, and the particulate matter may also be rich in complex organics. These "molecular clouds" thus play a crucial role in the history of the biogenic elements, intermediate between the diffuse interstellar gas which is primarily atomic in composition, and the solar nebula itself, in which the Sun and planets actually formed. The present research includes searches for important new interstellar constituents; observations relevant to differentiating between different models for the chemical processes that are important in the interstellar environment; and coordinated studies of the chemistry, physics, and dynamics of molecular clouds which are the sites or possible future sites of star formation.

Recent research has included the detection and study of four new interstellar molecules: methylcyanoacetylene (CH$_3$C$_3$N), tricarbon monoxide (C$_3$O), propynylidine (C$_3$H), and cyclopropenylidene (C$_3$H$_2$), the latter being the first interstellar hydrocarbon ring; searches which have placed upper limits on the abundance of several other potential constituents of interstellar clouds, including molecular oxygen, CH$_3$NC, HCCN, and CH$_3$CH$_2$C$_2$H; quantitative studies of comparative molecular abundances in different types of interstellar clouds, which have resulted in the first detection in cold, quiescent clouds of SO$_2$, CH$_3$CHO, and CH$_3$OH; investigation of reaction pathways for astrochemistry from a comparison of theory and the observed abundance of related species such as isomers and isotopic variants; studies of possible "tracers" of energetic events related to star formation, including silicon and sulfur containing molecules; and mapping of physical, chemical, and dynamical properties over extended regions of nearby cold molecular clouds.
Interstellar isomers

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The most complex chemical systems known are those characterizing organic life on earth’s surface. They exist at the end of a long evolutionary chain of chemical events which extends from a hot cloud of hydrogen and helium atoms very shortly after the big bang to the earth’s present biosphere. While many of the links in this chain were forged on the planet’s surface, the raw materials came from the solar nebula. Studies of structures in the galaxy which are believed to be analogous to the solar nebula have shown that they have an important organic-molecular component. (Thus, they are called molecular clouds). Furthermore, evidence for the existence of organic molecules in the interstellar precursor to our own solar system lie in the carbonaceous meteorites, phases of which have been shown to have had an interstellar origin. Knowledge of the chemical and physical conditions which prevailed as the earth formed is vital to achieving an understanding of those links in the long chain of chemical events which led to the evolution of life on earth.

Both observational and theoretical studies of molecular clouds are hindered by many difficulties. One way to partially circumvent the difficulties of characterizing the chemistry within these objects is to study the relative abundances of isomers which are synthesized from a common set of precursors. Unfortunately, only one such system has been confirmed, the HCN/HNC pair of isomers. While the basic outlines of its chemistry have been known for some years, there are still many aspects of the chemistry which are unclear. Another potential pair of isomers is HCO+/HOC+; HCO+ is an abundant interstellar molecule and a tentative identification of HOC+ has been made in Sgr B2. This identification is being challenged, however, based on theoretical and laboratory evidence that HOC+ reacts with H2. Another potential pair of interstellar isomers is methyl cyanide (CH3CN, acetonitrile) and methyl isocyanide (CH3NC). The cyanide is well known, however the isocyanide has yet to be observed despite theoretical predictions that appreciable quantities should be present.
Interstellar gas and grains comprise about 10 percent of the mass of the stars in our galaxy. A typical grain consists of a silicate core and a mantle of organics. If the grain is present in a diffuse cloud of interstellar gas the organic mantle consists of relatively non-volatile higher molecular weight compounds. Grains in denser clouds of interstellar dust are believed to be coated with volatile inorganic and organic compounds (H₂O, CH₄, CO₂, CO, NH₃) along with the higher molecular weight organics. Previous studies focussed on modelling the photochemical processes which may occur on grains when the volatile inorganic compounds are converted to the nonvolatile organic compounds.

With the increase in evidence that interstellar grains are the basic building blocks of comets and with the realization that comet collisions with the earth have probably occurred at a much higher frequency than earlier assumed it may be presumed that interstellar dust chemistry played an important role in the early chemistry of the earth.

As a part of the study of the photochemical processes taking place on interstellar grains the photolysis of mixtures of CO, NH₃ and H₂O was performed at 10°K, 77°K and 298°K. The reaction products were determined by GC/MS and HPLC analysis to be lactic acid, glycolic acid, hydroxyaceticamide, urea, biuret, oxamic acid, oxamide, glyceric acid and glyceramide. Ethylene glycol and glycerol were also detected but it is not clear at present whether these are true photoproducts or contaminants. The mechanism of formation of these molecules will be discussed as well as their possible significance to the origins of life.

1. A collaborative study with J. M. Greenberg.


OBSERVATIONAL EXOBIOLGY

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During the past year, two workshops on Exobiology from Earth Orbit have been held at NASA Ames Research Center under the direction of co-chairman John Billingham (NASA Ames) and Bill Irvine (University of Massachusetts). The central concern of these workshops was to examine the possibilities for conducting exobiology research from some of the many spacecraft and platforms that will be placed into Earth orbit in the coming decades. The workshops focussed on three different types of opportunities: collection of pristine samples of interstellar material, in situ experiments, and telescopic observations relating to origin and evolution of the biogenic elements and compounds. This last topic is referred to as observational exobiology, and does indeed offer exciting opportunities for research not possible from ground-based facilities.

The Earth's atmosphere absorbs partially or completely many ultraviolet, infrared and sub-millimeter wavelengths. Atmospheric seeing distorts small images, imposing a limit on the achievable angular resolution at optical and infrared wavelengths that is much poorer than the intrinsic capability of telescope optics. The atomic and molecular species of the atmosphere (particularly O₂ and H₂O) confuse or prevent the spectral studies of similar compounds outside of the terrestrial environment. Telescopes placed in orbit above the atmosphere avoid these problems and enjoy a unique view of the universe. There are many complex questions pertaining to the origin and evolution of the biogenic elements and compounds and the existence of terrestrial types of planets elsewhere that can only be tackled from orbiting facilities. The workshops considered the detailed nature of the spacecraft, platforms and instrumentation most likely to be launched by the United States and Europe in the near future in an attempt to determine what observational programs would be tractable and which areas of interest to exobiology required hardware capabilities beyond those currently envisioned. In addition it was recognized that a vigorous program of laboratory and theoretical support studies was crucial to the ability to correctly interpret and understand the observations pertaining to the complex gas phase or grain surface organic chemistry occurring in non-terrestrial environments.

A second draft of a report on these workshops is in preparation. The final version of that report will contain a prioritized list of observations that would be of value to the exobiology community, with particular emphasis on any areas that are likely to be overlooked by the traditional astronomical users of the orbiting observatories. This should serve as a starting point for encouraging cooperative proposals between the exobiology and astronomical communities for observing time on established facilities and possible modification of future spacecraft, whose instrument complement is not yet fixed.
Session II

Prebiotic Evolution--Planetary
The composition and photochemistry of the early atmosphere were of major importance in chemical evolution and the origin and evolution of life on our planet. The early atmosphere provided the material that, through chemical evolution formed organic molecules of increasing complexity, eventually forming the first living systems. Atmospheric species most probably provided the shielding from biologically lethal solar ultraviolet (UV) radiation so that the newly formed life could thrive and evolve. The shielding of life from UV radiation could have occurred either in the atmosphere or in the early oceans, although it is known that pure ocean water is a very poor UV absorber. Our understanding of the UV shielding of the newly formed life is very uncertain.

Recent atmospheric calculations by several investigators suggest that the prebiological atmosphere was most probably composed of nitrogen (N₂), carbon dioxide (CO₂), and water vapor (H₂O), resulting from volatile outgassing, as opposed to the older view of a strongly reducing early atmosphere composed of methane (CH₄), ammonia (NH₃), and hydrogen (H₂). Photochemical calculations indicate that methane would have been readily destroyed via reaction with the hydroxyl radical (OH) produced from water vapor and that ammonia would have been readily lost via photolysis and rainout. The rapid loss of methane and ammonia, coupled with the absence of a significant source of these gases, suggest that atmospheric methane and ammonia were very short-lived, if they were present at all. An early atmosphere of N₂, CO₂, and H₂O is stable and leads to the chemical production of a number of atmospheric species of biological significance, including oxygen (O₂), ozone (O₃), carbon monoxide (CO), formaldehyde (H₂CO), and hydrogen cyanide (HCN). Using a photochemical model of the early atmosphere, we have investigated the chemical production of these species over a wide range of atmospheric parameters. These calculations indicate that early atmospheric levels of O₃ were significantly below the levels needed to provide UV shielding. We have also investigated the fate of volcanically emitted sulfur species, e.g., sulfur dioxide (SO₂) and hydrogen sulfide (H₂S), in the early atmosphere to assess their UV shielding properties. Our photochemical calculations indicate that these species were of insufficient levels, due in part to their short photochemical lifetimes, to provide UV shielding. However, laboratory experiments conducted in our lightning facility indicate that a mixture of N₂, CO₂, and H₂O exposed to lightning produces significant yields of nitric oxide (NO). Once formed by lightning, NO is chemically converted to water-soluble nitric acid (HNO₃), which readily "rains" out of the atmosphere, providing a significant source of nitrate (NO₃⁻) to the early oceans. As pointed out by Rambler and Margulis, nitrate dissolved in the ocean can act to increase the turbidity of the upper levels of the ocean and may help to attenuate solar UV radiation.
A dark reddish organic solid, called tholin, is synthesized from simulated Titanian atmospheres by irradiation with high energy electrons in a plasma discharge. The visible reflection spectrum of this tholin is found to be similar to that of high altitude aerosols responsible for the albedo and reddish color of Titan. The real (n) and imaginary (k) parts of the complex refractive index of thin films of Titan tholin prepared by continuous D.C. discharge through a 0.9 N₂/0.1 CH₄ gas mixture at 0.2 mb is determined from x-ray to microwave frequencies. Values of n (= 1.65) and k (= 0.004 to 0.08) in the visible are consistent with deductions made by ground-based and spaceborne observations of Titan. Many infrared absorption features are present in k(λ), including the 4.6 μm nitrile band. Molecular analysis of the volatile component of this tholin was performed by sequential and non-sequential pyrolytic gas chromatography/mass spectrometry. More than one hundred organic compounds are released; tentative identifications include saturated and unsaturated aliphatic hydrocarbons, substituted polycyclic aromatics, nitriles, amines, pyroles, pyrazines, pyridines, pyrimidines, and the purine, adenine. In addition, acid hydrolysis produces a racemic mixture of biological and non-biological amino acids. Many of these molecules are implicated in the origin of life on Earth, suggesting Titan as a contemporary laboratory environment for prebiological organic chemistry on a planetary scale.

In Advances in Space Science, 1985, in press.
Measurements of deuterated methane show that Titan’s atmosphere is enriched by at least several times in deuterium compared to the major planets. Potential causative factors for this enrichment are condensation to form tropospheric methane clouds, fractionation occurring over a hypothetical CH$_4$-C$_2$H$_6$ ocean and between the ocean and the clathrate crust beneath, fractionation which occurred during the formation of Titan and fractionation occurring as a result of the evolution of Titan’s atmosphere. The greater part of the observed fractionation is probably derived from the formation of Titan and the subsequent evolution of Titan’s atmosphere driven by photochemistry. The latter process is developed here for the first time. The D/H ratio in a planetary atmosphere is one readily available measure of the origin and evolution of the hydrogen bearing volatiles on the planet. Comparison between D/H ratio in the inner solar system (Earth, Mars and Venus) and the outer solar system (Jupiter, Saturn and Titan) may pose important constraints on current theories.
MEASUREMENTS OF PHYSICAL PROPERTIES OF MODEL TITAN ATMOSPHERES

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One of the major goals of NASA is the study of the nature and evolution of the solar system, in particular, how the chemical and physical evolution of the solar system may have influenced the origin and evolution of life. As part of this effort, the study of the chemical and physical properties of bodies in our solar system is necessary in order to help define the conditions under which evolution must have taken place. Of the objects in the solar system, one of the most interesting is Titan, as ground-based and spacecraft (Voyager) observations of this satellite show it to possess a substantial atmosphere dominated by nitrogen. Present in the atmosphere are also simple hydrocarbons, nitriles and CO and CO2, along with at least three haze layers, one of which gives the satellite its orange-red color. The presence of these materials indicates the occurrence (past or present) of active chemical processes. Thus study of the nature of the materials present in Titan's atmosphere should provide important data points for correlating the relationship between chemical evolution and planetary evolution in our solar system.

One aspect of the study of Titan's atmosphere is the elucidation of the chemical and physical nature of the aerosols. In order to facilitate this, a program to produce laboratory synthesized model materials for Titan's aerosol and to study their chemical and physical properties is now in progress. Various processes, including electric discharge, photolysis by ultraviolet light, and irradiation by energetic particles, will be used to produce the materials. A first set of experiments where a nominal Titan mixture (97% N2, 3% CH4, 0.2% H2) was subjected to pulsed high-temperature shocks yielded a reddish-brown waxy solid. This material was then subjected to pyrolysis/gas chromatography, a technique that has been proposed as a method for analysis of the Titan aerosols. Preliminary results show the material to consist of simple hydrocarbons but little else, at least up to temperatures of 600°C. Since the material was colored (and solid), compounds other than those mentioned above must be present. Work will continue on refining the analytical technique in order to learn more about the nature of candidate Titan aerosols and to provide a method which will enable the analysis of the actual aerosols from a future Titan probe.
Session III

Solar System Exploration
Experimental Basis for a Titan Probe Organic Analysis

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The recent Voyager flyby of Titan produced evidence for at least nine organic compounds in that atmosphere that are heavier than methane. Several models of Titan's atmosphere, as well as laboratory simulations, suggest the presence of organics considerably more complex than those observed. An entry probe for the detailed study of Titan's atmosphere is currently being planned by NASA and the European Space Agency. Clearly, the opportunity to make in situ measurements of the chemical composition of this atmosphere from the exobiological perspective is unique and will provide valuable information leading to a more comprehensive understanding of the relationship between the chemical and physical evolution of the solar system and the appearance of life. However, to ensure that these in situ measurements are definitive with respect to Titan's atmosphere, experiment concepts, and the related instrumentation, must be carefully developed specifically for such a mission. To this end, the possible composition of the environment to be analyzed must be bracketed and model samples must be provided for instrumentation development studies. All conflicting theoretical models of the environment will be examined and all real possibilities will be included.

Laboratory studies to define the optimum flight experiment and sampling strategy for a Titan entry probe are currently being conducted. Titan mixtures (97% N₂, 3% CH₄) are being subjected to a variety of energy sources including high voltage electrons from a DC discharge, high current electric shock, and laser detonation. Gaseous and solid products are produced which are then analyzed. Samples from these experiments are also provided to candidate flight experiments as models for instrument development studies. Preliminary results show that existing theoretical models for chemistry in Titan's atmosphere cannot adequately explain the presence and abundance of all trace gases observed in these experiments. A more comprehensive theoretical model is being developed and will be presented.
A major goal in the study of Exobiology is to understand the relationship between the chemical and physical evolution of the solar system and the appearance of life. Within this context, the elucidation of the structure, particularly of the organics, of the atmosphere of Titan is one of the most important tasks yet to be accomplished towards this goal. Recent observations of Titan by Voyager have provided a more complete picture of its atmosphere. Not only were volatile organics, principally methane, identified and measured, but significantly, a dark-orange to brown haze was observed in the upper atmosphere. This haze or aerosol is thought to be conglomerations of organic molecules which are produced in the upper atmosphere by possibly photochemistry or lightning. Clearly, detailed measurements of this haze, and other aerosol layers, in conjunction with the gaseous molecules in Titan's atmosphere will be important for any future entry probe missions.

Development of a gas chromatographic (GC) technique for analysis of aerosols and volatile organics from a Titan entry probe is now in progress. Preliminary investigations of aerosol collectors have shown that an electrostatic device should be the most efficient for the particle sizes expected in Titan's atmosphere. Such a device particularly lends itself to development of a simple pyrolyzer which can be used to break down any collected organic conglomerate structures into volatile fragments. Those fragments can subsequently be analyzed by GC providing information about the original chemical structure of the aerosol. Studies show that as little as 1-5 µg of model aerosol can be successfully analyzed. High altitude (≤ 200 km) atmospheric gas sampling will also be important on Titan due to the great depth of the atmosphere. Studies show that a GC analysis of model Titan atmospheres at pressures approximating this altitude (2 mbar) can be made with a sensitivity of a few ten's of parts-per-billion for the trace gases of interest.
Comets are some of the most primitive bodies in the solar system and therefore should contain elemental, chemical, and isotopic records of the early history of the solar system. Determining the chemical and elemental composition, with emphasis on the biogenic elements and their compounds, of the grains and dust in the cometary nucleus would aid in placing chemical and physical bounds on the environment in which comets formed as well as providing an inventory of elements and compounds available for planetary accretion of cometary material by the Earth. An opportunity to perform \textit{in situ} analyses of a comet nucleus exists with the Comet Rendezvous Asteroid Flyby (CRAF) mission. An integrated gas chromatograph/X-ray fluorescence instrument (MEDA), being proposed for inclusion onboard the CRAF spacecraft, will measure the molecular and elemental constituents of collected dust grains and ices.

The gas chromatograph (GC), employing helium ionization detectors and three columns designed to separate light gases, i.e., \text{N}_2, \text{CO}, \text{CO}_2, \text{polar gases}, \text{i.e., } \text{H}_2\text{O}, \text{and hydrocarbons, i.e., } \text{C}_4, \text{will measure the volatile compounds of the biogenic elements (C, H, O, N, S) thermally released from collected dust grains. The sensitivity of the GC for compounds of interest is at the picogram level. X-ray fluorescence (XRF) utilizes cryogenically cooled Si(Li) solid state detectors of nominal 150 eV resolution at 5.9 keV. Excitation is by X-rays from Fe-55 radioisotope and alpha particles/X-rays from Cm-244 radioisotope sources. The XRF measures the elemental composition of the collected dust at a detection limit of 100 nanograms per square centimeter for elements such as Si, Fe, O, S, Ca, and C. Based on laboratory work with carbonaceous meteorites, both the GC and XRF can perform meaningful analyses with a few micrograms of collected comet dust.
INVESTIGATION OF POROUS POLYMER GAS CHROMATOGRAPHIC PACKINGS FOR ATMOSPHERIC ANALYSIS OF EXTRATERRESTRIAL BODIES

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For extraterrestrial probes, whether planetary, moon or cometary, atmospheric composition is an important analysis and gas chromatography (GC) is the technique best suited to carry it out. The rationale for such analysis is that the data may provide important information on the origin and evolution of the solar system, chemical evolution and life. Gas chromatographic instrumentation was used quite successfully aboard the Mars and Venus probes, however, for missions of much greater duration, weight, power and volume considerations have caused us to seek ways and means to reduce significantly the size of the instrumentation and increase its sensitivity. Column packings are the functional components of a GC system which cause the separation of multicomponent gas mixtures into individual elutable and measurable peaks for quantitation. The improvement of GC column packings is the subject of this study.

Measurement of the permanent gases in the atmospheres of mission targets is a major objective. A 16 meter long Porapak N column was used on the Venus probe and required a rather high carrier gas flow rate. We have, therefore, surveyed commercial porous polymer types which had some ability to resolve nitrogen, oxygen, argon and carbon monoxide gases. Porapaks N and Q appeared superior to most. Batch to batch variation, however, was quite wide, so we learned how to synthesize porous polymers and investigated some of the factors affecting the separations. A polymer was synthesized which was superior to all commercial products and allowed at least a 50% reduction in length and flow rate of carrier gas. Similar studies were made concerning the separation of hydrocarbons and new porous polymers have been synthesized which represent significant improvements in time of analysis, column length, and carrier gas flow rate. Further work will include column development for polar gases and water and investigation of capillary column usage to reduce further carrier gas requirements.
The exploration of the solar system and an understanding of the origin of life are two of NASA's important goals. An analysis of the planetary atmospheres and volatiles associated with life and the origin of life, will provide information necessary for scientists to attain these goals. Investigating the history and abundances of the biogenic elements and their compounds provides a basis for a detailed understanding of exobiology in the solar system. Gas chromatography has already proven to be a highly successful analytical technique for NASA's flight programs. Gas Chromatographs (GC) have been flown to both Mars and Venus where detailed compositional measurements were made. Although quite small and relatively sensitive when compared to commercially available instruments, these instruments do not appear adequate for the future missions currently being planned. The Metastable Ionization Detector (MID) is three orders of magnitude more sensitive than the thermal conductivity detectors used on previous flight instruments. The miniature MID provides scientists with a much smaller and highly sensitive detector for flight gas chromatographs.

A miniature MID featuring an unconventional triaxial electrode configuration has been developed and used routinely in our laboratories. Although much smaller and lighter than the commercial MID, its performance characteristics parallel those of the traditional design. The detector is compatible with the modulated voltage circuitry, also developed here, and thus can perform over an expanded response range of more than 7 orders of magnitude. A micro volume version of a miniature MID, with an internal volume of less than 8 μl, has recently been designed and is now being tested. The micro volume MID uses carrier gas flow rates of ≈ 2 cc/min thus eliminating the need for makeup gas when capillary columns are used. These prototype detectors represent a three order of magnitude increase in sensitivity and a decrease in weight and volume of two to three orders of magnitude when compared to previous flight GC detectors.
MULTIPLEX GAS CHROMATOGRAPHY: A NOVEL ANALYTICAL TECHNIQUE FOR FUTURE PLANETARY STUDIES

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Determination of molecular species comprised of the biogenic elements in the atmospheres of planets and moons of the solar system is one of the foremost requirements of the exobiologist studying chemical evolution and the origin of life. Flight experiments have been conducted on both Mars and Venus in the past and a wealth of data has been acquired by the gas chromatograph, mass spectrometer, and gas chromatograph/mass spectrometer. Future missions to explore Titan, Saturn, Mars, and Venus will require advanced instrumentation concepts which are highly sensitive, efficient, physically small, and capable of analyzing complex mixtures. Recent advances in gas chromatography suggest that conventional gas chromatography is still one of the most powerful methods available to conduct the desired analyses in future constrained missions, but limitations in the technique still exist which can be alleviated with multiplex gas chromatography.

Multiplex chromatography is a technique where many samples are pseudo-randomly introduced to the chromatograph without regard to elution of preceding components. The resulting data are then reduced using mathematical techniques such as cross-correlation or Fourier Transforms. To demonstrate the utility of this technique for future solar system exploration, chemical modulators have been developed. Several advantages have been realized from this technique in combination with these modulators: improvement in detection limits of several orders of magnitude, improvement in the analysis of complex mixtures by selectively modulating some of the components present in the sample, increase in the number of analyses that can be conducted in a given period of time, and reduction in the amount of expendables needed to run an analysis. In order to apply this technique in a real application, methane in ambient air was monitored continuously over a period of one week. By using ambient air as its own carrier all expendables beyond power were eliminated.
ION MOBILITY DRIFT SPECTROMETRY (IMDS) 
AS A 
FLIGHT ANALYTICAL INSTRUMENT TECHNIQUE 

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A detailed knowledge of the history and abundances of the biogenic 
elements and their compounds throughout the solar system can provide 
the exobiologist with a basis for understanding the conditions necessary 
for chemical evolution and the origin of life. Flight experiments 
conducting in situ analyses have already produced a wealth of 
information on the environments of Venus and Mars. Future missions 
will require instrumentation capable of providing identification and 
quantitation of a multitude of molecular species over a wide range of 
concentrations. In particular, analysis of the complex organics 
expected for a mission to Titan may tax the limits of current analytical 
technology. A flight instrument utilizing IMDS technology can provide 
scientists with a powerful means of obtaining this information.

The Ion Mobility Drift Spectrometer is an ion molecule reactor coupled 
with an ion drift spectrometer. Sample molecules are ionized to form 
product ions in the reactant region. An electric field moves the ions 
through a drift region against the flow of a drift gas where they are 
separated according to their size and structure producing an ion mobility 
spectrum. These spectra provide the IMDS with virtually universal 
sample identification capability. To conform to the rigid limits of 
weight, volume and consumables placed on flight instrumentation, 
several aspects of the IMDS must be studied and redesigned for flight 
use. In addition to miniaturization of the instrument, a reduction in the 
high flow rates used for the drift gas is an obvious necessary 
consideration. The effect of drastically reduced drift flow rates on 
IMDS spectra was investigated by lowering flow rates from 500 ml/min 
to 50 ml/min. Changes in peak shape, drift time and total spectra were 
studied at each flow rate. Although changes did occur, IMDS analysis 
appears acceptable at the lower flow rates. Investigations into 
alternate drift gases and reactive carrier gases are also being pursued.
NEW TECHNIQUES FOR THE DETECTION AND CAPTURE OF MICROMETEOROIDS

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In order to understand the origin and distribution of the biogenic elements and their compounds in the solar system, it will be necessary to study material from many classes of objects. Chemical, elemental, and isotopic measurements of returned samples of comets, asteroids, and possibly extra-solar system dust clouds would provide information on a particularly important class: the primitive objects. Extraterrestrial micron-sized particles in the vicinity of earth are one source of such materials that might otherwise be inaccessible. The Space Station appears to be an eminently suitable platform from which to collect and detect these various particles. The primary challenge, however, is to collect intact, uncontaminated particles which will be encountered at tens of kilometers per seconds.

A concept for a micrometeoroid detector that could be deployed from Space Station has been developed which uses a large area detector plate implanted with acoustic transducers. When an impact event occurs, the resulting signal is subjected to spectral analysis providing positive detection, momentum information, and angle of incidence. The primary advantage of this detector is the large area which increases the probability of measuring events. A concept of a nondestructive micrometeoroid collector for use from Space Station has also been developed. The collector utilizes input port charging of the incoming particle followed by staged high voltage deceleration for nondestructive capture. Low velocity particles (local contamination) would be rejected due to insufficient energy and only uncontaminated micrometeoroids would be collected. Particles so collected would then be returned to Earth for subsequent analysis.
Session IV

Prebiotic Evolution--Molecular
ENERGY YIELDS IN THE PREBIOTIC SYNTHESIS OF HYDROGEN CYANIDE AND FORMALDEHYDE

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Prebiotic experiments are usually reported in terms of carbon yields, i.e., the yield of product based on the total carbon in the system. These experiments usually involve a large input of energy and are designed to maximize the yields of product. However, large inputs of energy result in multiple activation of the reactants and products. A more realistic prebiotic experiment is to remove the products of the activation step so they are not exposed a second time to the energy source. This is equivalent to transporting the products synthesized in the primitive atmosphere to the ocean, and thereby protecting them from destruction by atmospheric energy sources. Experiments of this type, using lower inputs of energy, give energy yields (moles of products/joule) which can be used to estimate the relative importance of the different energy sources on the primitive earth.

Simulated prebiotic atmospheres containing either CH₄, CO or CO₂ with N₂, H₂O and variable amounts of H₂ were subjected to a high frequency Tesla coil. Samples of the aqueous phase were taken at various time intervals from 1 hr to 7 days, and the energy yields were obtained by extrapolation to zero time. The samples were analyzed for HCN with the cyanide electrode and for H₂CO by chromotropic acid. The spark energy was estimated by calorimetry. The temperature rise in an insulated discharge flask was compared with the temperature rise from a resistance heater in the same flask.

The energy yields for HCN production are about 10 n moles/joule with CH₄ (H₂/CH₄ = 1), 5 n moles/joule with CO (H₂/CO = 2), and 0.4 n moles/joule with CO₂ (H₂/CO₂ = 2). In contrast, the reported carbon yields for HCN synthesis with the above mixtures are nearly equal. This demonstrates the importance of using energy yields as a basis of comparison of various energy sources and atmospheric compositions.

The energy yields for H₂CO production are about 2 n moles/joule with CH₄ (H₂/CH₄ = 1), 15 n moles/joule with CO (H₂/CO = 2), and 0.3 n moles/joule with CO₂ (H₂/CO₂ = 3). The reported carbon yields of H₂CO production with these mixtures are also nearly equal.

These results will be compared with calculated production rates of HCN and H₂CO from lightning and a number of photochemical processes on the primitive earth.
SYNTHESIS AND ANALYSIS IN STUDIES OF CHEMICAL EVOLUTION

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Studies of the various processes that may have given rise to life on the earth have demonstrated the appropriateness of an approach that makes use of analysis and synthesis. Analysis of extraterrestrial samples in the form of meteorites has demonstrated the presence of several precursors of biomolecules, most notably a full suite of nucleic acid bases and nucleosides of biological significance. These species were determined after exhaustive extraction of the sample and subsequent analysis using HPLC, GC, MS, and GC-MS. Procedural blanks indicate that these molecules are likely not the result of contamination during the extraction and analysis process. Similar species were found as products of spark discharge experiments in atmospheres thought to mimic primitive earth conditions. These results indicate that the basic chemistry underlying these syntheses is common, and that life may not be unique to the earth.

This lack of "magic" in the formation of important biomolecules takes on even greater significance when we next ask, "What is the nature of the origin of the genetic code?" Studies underway in our laboratory to address this question make use of proton nuclear magnetic resonance spectroscopy as a probe to assess associations between selected amino acids and any of several nucleotides comprising their genetic code and genetic anticode sequences. These studies demonstrate a clear selectivity by the anticode sequences, thus confirming the hydrophobicity studies performed by Lacey et al. These studies further support the contention that life is likely a natural result of the physics and chemistry of the universe.
ISOTOPIC CHARACTERISATION OF PREBIOTIC SYNTHESIS OF ORGANIC MATERIAL

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Many primitive meteorites contain an insoluble organic material, much like terrestrial kerogen, whose mode of origin is currently unknown. When subjected to stepwise decomposition, this material, unlike its terrestrial counterpart, reveals characteristic release patterns for the stable isotopes of carbon, hydrogen and nitrogen as a function of fractional release of each element. The purpose of this study is to try to match those release patterns using organic matter synthesised in the laboratory under controlled conditions. Analogous studies have attempted to reproduce chemical and structural characteristics of the meteoritic material by such syntheses. If successful, such a study would shed light on the origin of kerogen-like organic matter in the early solar system and, by extension, on prebiotic organic synthesis in general.

The range of possible syntheses, starting materials and reaction conditions to be investigated is considerable. Samples analysed to date include: a heavy "oil" produced by Fischer-Tropsch-type catalysis of CO + H₂; a solid residue generated by a plasma discharge in CO + H₂ + N₂; a solid deposited on the electrodes of a Miller-Urey synthesis operating on CH₄ + H₂O + N₂; and a solid residue formed by polymerisation of light hydrocarbons produced by a Miller-Urey discharge acting on CH₄.

Significant structure is observed in the release patterns for the carbon and hydrogen isotopes from the synthetic samples, though there is little evidence for isotopic fractionation during the analysis itself. For neither carbon nor hydrogen do the patterns observed so far resemble those characteristic of meteoritic material; the release patterns for carbon show the same magnitude of isotopic variations as do meteoritic kerogens but differ in detail, whereas for D/H ratios there are vast discrepancies in magnitude as well as in shape of the release profiles. Besides the obvious interpretation of these discrepancies in terms of incomplete sampling of processes, starting materials and/or reaction conditions, it is possible that the meteoritic material represents a mixture of phases produced in different circumstances with intrinsically different isotopic compositions. Evidence bearing on these possibilities will be discussed.
We are exploring the premise that life began with self-replicating iron-rich clays. In association with these clays and u.v. light, polar organic molecules, such as oxalic acid, were synthesized.

The carbonaceous chondrites have both iron-rich clays and organic molecules. It is convenient to classify meteoritic organic matter into 3 categories: insoluble polymer, hydrocarbons and polar organics (soluble in water). Recent work on the $\delta^D$, $\delta^N_{15}$ and $\delta^C_{13}$ has made it clear that these three fractions have been made by three different mechanisms.1,2

A significant fraction of the insoluble polymer has a $\delta^D$ which suggests that it was made in an interstellar medium.3 The hydrocarbons seem to have been made on a parent body by a Fischer-Tropsch mechanism. The polar organics were probably synthesized in a mixture of carbonate $(NH_4)_2CO_3$, Fe$^{++}$ ion and liquid water by radiolysis. In a set of experiments done with Mike Sweeney and M. Kroll we have looked at the radiolysis of $(NH_4)_2CO_3$ in the presence and absence of Fe$^{++}$ ion. The synthesis of glycine in the presence of Fe$^{++}$ ion is 3-4 times that in the absence of ferrous ion. We are exploring the effects of the addition of hydrocarbons to this mixture.

We are also synthesizing iron-rich clays at low temperature and pressure. So far the results are not sufficiently crystalline to look for replication. It should be noted that organic chelating agents such as oxalic acid do increase the crystallinity of the clays but not sufficiently. We are now exploring hydrothermal synthesis of iron-rich clays.

Clays have been implicated in the origin of terrestrial life since the suggestion of Bernal in the 1950's. Originally they were considered as agents which aid in selecting, concentrating and promoting oligomerization of the organic monomeric substituents of cellular life forms. However, more recently, Graham Cairns-Smith has suggested that minerals, with particular emphasis on clays, may have played a yet more fundamental role. He has suggested that clays are prototypic life forms in themselves and that they served as a template which directed the self-assembly of cellular life.

If the "clay-life" theory is to have other than conceptual credibility, clays must be shown by experiment to execute the operations of cellular life, not only individually, but also in a sufficiently concerted manner as to produce some semblance of the functional attributes of living cells. I define the "operations" of life to include processing of energy (conversion, storage and transfer); charge and materials (separation, storage and transport, reaction catalysis and structural stabilization); and information (reception, storage, retrieval). These operations support the functional attributes of life, which include adaptive response to environmental stimuli, self-replication with transfer of information and growth and repair.

My current studies are focussed on the ability of clays to absorb, store and transfer energy under plausible prebiotic conditions and to use this energy to drive chemistry of prebiotic relevance. Conclusions of the work are applicable to the role of clays either as substrates for organic chemistry, or in fueling their own life-mimetic processes.

Several aspects of the energy storage/transfer work are being simultaneously pursued. Investigation of the relationship between thermoluminescence (TL) and electron spin resonance (ESR) in a series of variably Fe/Ca cation exchanged montmorillonites has revealed iron-iron interactions at high iron concentrations. Investigation of the range of the forces which produce the emission of light upon dehydration is being done by measuring the critical moisture content at which light is released from a series of variably hydrated kaolins prepared by Pat Costanzo and Ross Giese. The degree of interlayer hydration markedly affects the profile of light emission on drying. However, it is thought that this change in profile reflects some compositional changes in the structural hydroxyls. If so, some unexpected fundamental insights relating the charge mobility and light release may be gained. The nature of the luminescent trigger is being explored by studying light released on wetting by hydrazine and unsymmetrically substituted dimethylhydrazine (USDMH). Hydrazine complexes with the kaolin surface, intercalates the layers and chemically decomposes. USDMH complexes with the surface, intercalates the layers of some, but not all of the hydrated forms. Formation of the intermediate for the presumed dominant pathway for decomposition should be sterically hindered. Preliminary results indicate the light release to be more directly associated with the intercalation than with the decomposition. Definitive interpretation will require spectroscopic data on the spectral distribution both of the diffuse reflectance and of the light emission, in order to correct for emission/reabsorption effects. The relationship between energy storage and surface reactivity is being investigated using the decomposition of hydrazine as a chemical actinometer. The decomposition of hydrazine is proceeding by at least two mechanistically different pathways on the kaolin surface. The effect of energy storage is being examined.
FURTHER WORK ON SODIUM MONTMORILLONITE AS CATALYST FOR THE POLYMERIZATION OF ACTIVATED AMINO ACIDS

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1) When we catalyzed the polycondensation of amino acid acylates with Na-montmorillonite, the polypeptides were consistently found to exhibit a distribution of discrete molecular weights, for as yet undiscovered reasons. One possible explanation was connected to our stepwise mode of monomer addition. New experiments have eliminated this possibility, so that we are left with the general assumption that this discreteness is the result of a preference of shorter oligomers to add to others of the same length, a feature that could be attributed to some structure of the platelet aggregates of our montmorillonite.

2) We have in the past repeatedly looked for the production of optical stereoisomers, when D,L-amino acids were polymerized on montmorillonite. Recently, we observed that Na-montmorillonite, on which Cu-L-proline was adsorbed prior to the polymerization of D,L-alanine adenylate, produces an excess of about 1.6 : 1 of D-alanine oligomers ($\overline{D}P = 9.5$). The latter consist again of a limited number of fractions (6) of DP's up to 28. Since we used an optically active surface, the essence of the results lies not only in the occurrence of optically active oligomers and polymers, but also in the fact that the latter exhibit the same molecular weight characteristics as the D,L-polymer.

3) We have also started to polymerize all L-isomers of aspartic- and adenyl adenylates. In homo- as well as in co-polymerization (though somewhat less) we encounter severe solubility problems and, thus, so far obtained only lower oligomers, 2-7. These findings are possibly significant for the problem of the selection of L-isomers by early life, and will be further investigated.

4) Preparatory to the work that we contemplate on a parallel synthesis of amino acid and nucleotide oligomers, we continued studies on the co-adsorption of amino acids, nucleotides, and amino acid-nucleotides on montmorillonite. Our findings include adsorption increases of UMP proportional to the preadsorption adenine, but not of adenyl acid, and further that the adsorption of phe, but less so that of lys, is increased when acetyl-adenylate or ATP are absorbed beforehand. ATP is three-fold more adsorbed than AMP, but less than polyadenyl acid or polyuridylic acid. More work is planned to clarify these co-adsorption patterns which will serve as a guide for the planning of parallel amino acid-nucleotide oligomerization experiments.
The directed synthesis of biopolymers in an abiotic environment is presumably a cyclic sequence of steps which may be realized in a fluctuating environment such as a prebiotic pond undergoing wetting-drying cycles. Soluble mineral salts have been proposed as an essential component of this fluctuating environment. The following sequence may be considered as a most primitive mechanism of information transfer in a fluctuating environment: (1) adsorption of a biomolecule onto a soluble mineral salt surface to act as an adsorbed template; (2) specific adsorption of biomonomers onto the adsorbed template; (3) condensation of the adsorbed biomonomers; and (4) desorption of the elongated oligomer. In this investigation, the salts selected for study were CaSO₄·2H₂O (gypsum), SrSO₄, and several other metal sulfates and chlorides. Adsorption of the monomeric species, gly, 5'AMP, 5'GMP, and 5'CMP was investigated. The adsorbed template biopolymers used were Poly-A, Poly-G, Poly-C, and Poly-U. We shall report the results of studies involving these experimental participants, the first two steps of the proposed primitive information transfer mechanism, and condensation of amino acids to form oligomers in a fluctuating environment.
PALEOSOLS AND THE CHEMICAL EVOLUTION OF THE ATMOSPHERE

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The chemistry and mineralogy of soils reflects the chemistry of the atmosphere below which they develop. Today the presence of a cover of land plants can obscure the signature of a highly oxidizing atmosphere. Prior to the advent of higher land plants ca. 400 m.y. ago the obscuring effect of a biologic interface should have been minor. It can be shown that under such conditions the behavior of ferrous iron during weathering depends on the relationship between the ratio of the net concentration of oxidants to the concentration of acids in rainwater, and on the ratio of the oxygen demand to the acid demand for complete weathering of the parent rock. An analysis of the behavior of iron in some 15 paleosols between 1.0 and 2.9 b.y. in age showed some time ago that iron was retained, or largely retained, in paleosols developed on rocks with a low ratio of oxidant demand to acid demand (R value) and was lost from paleosols with a high R value. The results indicate that between 1.1 and 2.9 b.y.b.p. the ratio of the net concentration of oxidants to CO₂ in rainwater was less than ca. 1/600 of the present-day value.

Our work during the past year has sought to extend the data base for paleosols and to define more precisely the relationship between the composition of paleosols and the chemistry of the atmosphere below which they developed. A field excursion to Western Australia last summer netted only a single paleosol (or probable paleosol) from the Peak Hill area. A drill core intersected what seems to be the base of a weathering horizon developed on serpentinite. This horizon is highly oxidized. Although our work on this material is not yet complete, the apparent behavior of the serpentinite during weathering is consistent with prior expectations based on the analysis of other paleosols of similar age. This is also true for the chemistry of the Sturgeon River Falls paleosol in the Upper Peninsula of Michigan, a paleosol that was developed on hydrothermally altered Keewenawan basalts (age 1.1 b.y.) and that has been studied in considerable detail during the past year.

The only paleosol which falls outside the established pattern is a paleosol developed on granite below Dominion Reef sediments (age 2.9 b.y.) in South Africa. Iron has been lost from this paleosol. It is not clear, however, whether iron loss occurred during weathering or at a later time. If the loss of iron occurred during weathering, the oxidation state of the atmosphere was almost certainly lower 2.9 b.y. ago than 2.4 b.y. ago. We expect to collect more material from this paleosol horizon during the summer and hope to be able to settle the matter during the coming year.

Today, O₂ is the dominant oxidant in rainwater. During the past year, calculations carried out by J.F. Kasting have shown that H₂O₂ is probably the dominant oxidant in rainwater falling through an atmosphere containing < 10⁻² to 10⁻³ P.A.L. of molecular oxygen. These calculations have also shown that reductants such as formaldehyde can be important constituents of rainwater falling through low-O₂ atmospheres. Such photochemical products would have reacted with algal mats covering Precambrian soils and with the mineral constituents of the soils themselves. A better understanding of these reactions could be of great importance for relating the observed behavior of iron and related elements to the O₂ content of the Precambrian atmosphere.
COOPERATION OF CATALYSTS AND TEMPLATES

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In order to understand how self-reproducing molecules could have originated on the primitive Earth or extraterrestrial bodies, it would be useful to find laboratory models of simple molecules which are able to carry out processes of catalysis and templating. Furthermore, it may be anticipated that systems in which several components are acting cooperatively to catalyze each other's synthesis will have different behavior with respect to natural selection than those of purely replicating systems. As the major focus of our work, we are trying to devise laboratory models to study the influence of short peptide catalysts on template reactions which produce oligonucleotides or additional peptides. Such catalysts could have been the earliest protoenzymes of selective advantage produced by replicating oligonucleotides. Since this is a complex problem, we are also studying simpler systems which embody only one aspect at a time, such as peptide formation with and without a template, peptide catalysis of nontemplated peptide synthesis, and model reactions for replication of the type pioneered by Orgel.

Three areas of recent progress will be emphasized: (1) In order to develop a model for primitive translation, we studied the reaction of amino acids to form peptides on dried clays with polyribonucleotides added, and found a large yield increase specifically with ribo- but not deoxyribo- polynucleotides. Recent progress with FTIR spectra and direct trapping experiments have demonstrated the presence of acyl ribonucleotide esters between pyroglutamic acid and poly (G). Furthermore, covalent adducts between amino acids and polyribonucleotides could conceivably produce a kind of crude templated peptide formation, and we are directing future efforts toward this goal. (2) We have collaborated with Orgel to find whether short peptides catalyze the template-directed synthesis of oligonucleotides. Although that search was only marginally successful, one offshoot has been a new reaction system developed to provide mechanistic insight into oligonucleotide templating. RNA primers of defined structure have been studied kinetically to ascertain specific rates of each step in the template-directed elongation sequence. (3) Computer modeling has provided new insight into the behavior of small groups of molecules capable of very crude processes of replication, translation, and catalysis. Natural selection would enforce their cooperation to the extent that a 'selfish gene' would actually gain an advantage by slowing down and allowing its partners to catch up rather than racing ahead. Thus mutual catalysis leads to molecular cooperation and the first glimmer of a stable genome, which would not be the case with a purely replicating system.
The possibility of reconstructing plausible sequences of events in prebiotic molecular evolution is limited by the lack of fossil remains. However, with hindsight, one goal of molecular evolution was obvious: the development of molecular systems that became constituents of living systems. By understanding the interactions among molecules that are likely to have been present in the prebiotic environment, and that could have served as components in protobiotic molecular systems, plausible evolutionary sequences can be suggested. When "stable" aggregations of molecules form, a net decrease in free energy is observed in the system. Such changes occur when solvent molecules interact among themselves, as well as when they interact with organic species. A significant decrease in free energy, in systems of solvent and organic molecules, is due to entropy changes in the solvent. Entropy-driven interactions played a major role in the organization of prebiotic systems, and understanding the energetics of them is essential to understanding molecular evolution.

Monte Carlo simulation has been used to explore the interactions and structure of solvent molecules in the vicinity of some simple biomolecules, nucleic acid bases, and around ions. One of the striking results of these computer experiments is that the bases significantly alter the structure of solvents, resulting in a profound change in both enthalpy and entropy. A second observation is that hydrogen bonded bases (Watson-Crick pairs), which form readily in the absence of a solvent (vacuum), or in the presence of apolar solvents (e.g. carbon tetrachloride), were found to be energetically less stable in water than stacked bases. Such data indicate that, in aqueous solution, bases are more stable when stacked above one another, rather than when forming hydrogen bonded pairs. Understanding the behavior of such small systems will allow descriptions of the energetics and dynamics of larger systems.

These data, and data on the formation of ion-solvent complexes, raise fundamental questions about the energetics of the formation of self replicating systems based on nucleic acid interactions. Similarly interesting questions are raised about possible early translation systems and about the role of surfaces. It is clear that a systems view must be adopted when using the energetics and dynamics of molecules to predict molecular behavior, but that such an approach is valid, and is likely to prove fruitful in understanding molecular evolution.
Intramolecular Interactions in Aminoacyl Nucleotides: Implications Regarding the Origin of Genetic Coding and Protein Synthesis

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All contemporary cellular organisms store information as sequences of nucleotides in double stranded DNA. This information is quite useless unless it can be converted into the active molecular species, protein. How this is done in contemporary creatures involves first transcription of one strand to give a complementary strand of mRNA. By a very complex process, the sequence of nucleotides is then translated into a specific sequence of amino acids in a protein. Translation is made possible by a genetic coding system in which a sequence of three nucleotides codes for a specific amino acid. Our problem is to explain how, given four nucleotides for coding and the twenty amino acids for making proteins, the coding system and the process of protein synthesis arose. Our guiding principle has been that the origin and evolution of any chemical system can be understood through elucidation of the properties of the chemical entities which make up the system. There is an underlying logic to the coding system revealed by a correlation of the hydrophobicities of amino acids and their anticodonic nucleotides (i.e. the complement of the codon). This and other work has suggested that the origin of the code might have been a problem of the origin of active sites in which amino acids and their anticodons could be partitioned. Other studies have concentrated on reactions of active acyl compounds relevant to the synthesis of the peptide bond. One compound of great importance in protein synthesis is the aminoacyl adenylate. Its importance lies in the fact that every amino acid going into protein synthesis must first be activated. This is universally accomplished with ATP, resulting in the formation of the energy rich aminoacyl adenylate. Past studies have concentrated on the chemistry of the adenylates, but more recently we have found, through the use of NMR, that we can observe intramolecular interactions even at low concentrations, between amino acid side chains and nucleotide base rings in these adenylates. The use of this type of compound thus allows a novel way of elucidating the manner in which amino acids and nucleotides interact with each other. In aqueous solution, when a hydrophobic amino acid is attached to the most hydrophobic nucleotide, AMP, a hydrophobic interaction takes place between the amino acid side chain and the adenine ring. The studies to be reported concern these hydrophobic interactions.

The adenylates can be easily purified by high pressure liquid chromatography and then lyophilized and dissolved in D2O for the proton magnetic resonance studies. We have made the following observations from these studies:

1. In a series of hydrophobic aminoacyl adenylates (Phe, Leu, Val and Ile), NMR shows that, even at low pH where the adenine ring is protonated, all of these side chains participate in hydrophobic interactions with the "face" of the adenine ring. The importance of this finding is that it shows not only that aromatic side chains may intercalate with adenine residues, but aliphatic side chains as well. The strength of the association varies (Phe > Leu = Ile > Val).

2. If an N-acetyl amino acid is used, it racemizes during synthesis of the adenylate. Again, using HPLC, we have separated the two diastereoisomers and found that in one the Phe ring was associated more strongly with the adenine. We established enzymatically that it is the biologically important L isomer.

3. Using a series of carboxylic acid anhydrides, we found that the longer chains associate more strongly with adenine and, furthermore, that the propionyl chain is the smallest which can associate with the planar "face" of adenine in these compounds. These studies continue to support an active site model for the origin of the code and protein synthesis.
The object of our research program is to understand how polynucleotide replication originated on the primitive earth. We believe this to be a central issue in studies of the origins of life since a process similar to modern DNA and RNA synthesis is likely to have formed the basis for the most primitive system of genetic information transfer.

The major conclusion of our studies so far is that a preformed polynucleotide template under many different experimental conditions will facilitate the synthesis of a new oligonucleotide with a sequence complementary to that of the template. We have, for example, shown that poly(C) facilitates the synthesis of long oligo(G)s and that the short template CCGCC facilitates the synthesis of its complement GGCGG. Very recently we have shown that template-directed synthesis is not limited to the standard oligonucleotide substrates. Nucleic acid-like molecules with a pyrophosphate group replacing the phosphate of the standard nucleic acid backbone are readily synthesized from deoxynucleotide 3'-5'-diphosphates on appropriate templates.

Most of our recent work has used 2-MeImpG and the corresponding derivatives of the other bases as substrates. We have shown that:

1. Synthesis of complementary oligomers is efficient provided the template is rich in C.
2. Oligomers as short as a pentamer are efficient templates.
3. Synthesis proceeds in the 5'→3' direction.
4. The fidelity is high—wrong bases are discriminated from correct bases by at least a factor of 200.
5. The incorporation reaction is enantiomerically specific, but is inhibited by the wrong enantiomer.
Prebiotic chemistry is faced with a major problem: how could a controlled and selective reaction occur, when there is present in the same solution a large number of alternative possible coreactants? This problem is solved in the modern cell by the presence of enzymes, which are not only highly efficient and controllable catalysts, but which also can impose on their substrates a precise structural requirement. However, enzymes are the result of billions of years of evolution, and we cannot invoke them as prebiotic catalysts. One approach to solving this problem in the prebiotic context is to make use of template-directed reactions. These reactions increase the number of structural requirements that must be simultaneously present in a molecule for it to be able to react, and thereby increase the selectivity of the reaction. They also can give a large increase in the rate of a reaction, if the template constrains two potential coreactants to lie close together. A third benefit is that information that is present in the template molecule can be passed on to the product molecules.

If the earliest organisms were based on proteins and nucleic acids, then the investigation of peptide synthesis on an oligonucleotide template is highly relevant to the study of the origin of life. This template-directed synthesis could be remarkably efficient, both in its rate of reaction, and in its ability to discriminate correct from incorrect partners to a reaction. It also could suggest a mechanism for the origin of the genetic code. For the past few years we have been studying a number of possible "working models" for template-directed peptide bond formation. During this work we found that aminoacylation of the "internal" 2'-hydroxyl groups of RNA with the imidazolide of an alpha-amino acid was chirally selective. This is the first example of stereoselection in non-enzymic aminoacylation of RNA, and we have begun investigating in a systematic way the structural requirements for this chiral selection. We have shown that the degree and direction of chiral selectivity depends on the presence or absence of an N-protecting group on the amino acid, and the bulk or hydrophobicity of the side chain, and we are now studying the effect of the leaving group and the structure of the RNA. "Internal" 2'-aminoacyl esters of D,D-3',5'-adenylyl-adenosine (ApA) can be used as models of the transition state for the aminoacylation reaction, and we have studied their proton nuclear magnetic resonance (nmr) spectra to try to understand the basis for the stereoselectivity. The resonance of the alpha-methyl group of D-Ala-D,D-ApA is upfield, and that of L-Ala-D,D-ApA is downfield, with respect to the resonance of the alpha-methyl group of alanine methyl ester. These results suggest that the alpha-methyl group of the D-Ala-D,D-ApA ester is more shielded by the aromatic rings than is the case for the L-Ala ester.
MODELS OF GLYCOLYSIS: GLYCERALDEHYDE AS A SOURCE OF ENERGY AND MONOMERS FOR PREBIOTIC CONDENSATION REACTIONS

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All organisms require energy in a chemical form for maintenance and growth. In contemporary life this chemical energy is obtained by the synthesis of the phosphoanhydride bonds of ATP. Among the biological processes that yield ATP, fermentation is generally considered primitive, because it operates under anaerobic conditions by substrate-level phosphorylation which does not require compartmentation by membranes. Fermentation by the glycolytic pathway, which is found in almost every living cell, is an especially attractive energy source for primitive life. Glycolysis not only produces useful chemical energy (ATP), but intermediates of this pathway are also involved in amino acid synthesis and photosynthetic carbon-fixation. It is our belief that energy and substrates needed for the origin of life were provided by nonenzymatic chemical reactions that resemble the enzyme-mediated reactions of glycolysis. These nonenzymatic reactions would have provided a starting point for the evolutionary development of glycolysis.

Our efforts to model glycolysis have stressed the initial energy-yielding reactions of this pathway. Since these early reactions of glycolysis involve the oxidation of glyceraldehyde-3-phosphate to give initially an 'energy-rich' thioester that is used to drive the synthesis of the phosphoanhydride bonds of ATP, we have studied similar nonenzymatic oxidation and rearrangement reactions of glyceraldehyde that yield 'energy-rich' thioesters, and have examined condensation reactions that use thioesters as an energy source in the synthesis of phosphoanhydrides and polyglyceric acid. We have demonstrated the formation of lactoyl thioester by the rearrangement of glyceraldehyde in the presence of a thiol under anaerobic conditions. In the presence of ammonia this anaerobic reaction also yields alanine, presumably via alanyl thioester. When oxygen is present, this model reaction yields both lactoyl thioester and glyceroyl thioester. We have also shown that thioesters can be used to drive the synthesis of phosphoanhydrides, such as pyrophosphate, tripolyphosphate and phosphorylimidazole. Recently, we have been studying the ability of thioesters to drive phosphorylation reactions via a cyclic phosphorimidazolide intermediate, and the autocondensation of glyceroyl thioester to give polyglyceric acid. The autocondensation of glyceroyl thioester would have allowed the direct use of thioester energy in early polymer synthesis, rather than using its energy to synthesize phosphoanhydrides which are then used to drive polymer synthesis as in contemporary life. We are currently examining the synthesis and properties of polyglyceric acid, since it appears to be a good candidate for the earliest self-replicating and catalytic macromolecule. Presumably, its information content would have been in its sequence of D- and L-glyceric acid residues, and its catalytic ability derived from the acid-base behavior of its hydroxyl groups and bound metal ions.
A COMPARATIVE STUDY OF PREBIOTIC AND PRESENT DAY TRANSLATIONAL MODELS

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It is generally recognized that the understanding of the molecular basis of primitive translation is a fundamental step in developing a theory of the origin of life. However, even in modern molecular biology, the mechanism for the decoding of messenger RNA triplet codons into an amino acid sequence of a protein on the ribosome is understood incompletely. Most of the proposed models for prebiotic translation lack, not only experimental support, but also a careful theoretical scrutiny of their compatibility with well understood stereochemical and energetic principles of nucleic acid structure, molecular recognition principles, and the chemistry of peptide bond formation.

Our studies are concerned with comparative structural modelling and mechanistic simulation of the decoding apparatus ranging from those proposed for prebiotic conditions to the ones involved in modern biology. Any primitive decoding machinery based on nucleic acids and proteins, and most likely the modern day system, has to satisfy certain geometrical constraints. The charged amino acyl and the peptidyl termini of successive adaptors have to be adjacent in space in order to satisfy the stereochemical requirements for amide bond formation. Simultaneously, the same adaptors have to recognize successive codons on the messenger. This translational complex has to be realized by components that obey nucleic acid conformational principles, stabilities, and specificities. This generalized condition greatly restricts the number of acceptable adaptor structures.

Making use of the above criteria, refined models of various previously proposed prebiotic decoding apparatus are examined for consistency using distance geometry and energy based stability analysis on one side, and our newly developed Evans and Sutherland PS 300 system modelling program on the other.

In consideration of the present day translational system, the apparatus is reconstructed by making use of available tRNA crystallographic data, as well as distance constraints extracted from literature on fluorescence energy transfer, cross-linking, and other experiments. Using the above described methodology to integrate these data, we may obtain the possible spatial configurations of the complex. The stereochemical feasibility of the models are examined by computer model building. The presentation will examine the prebiotic models in the context of their potential functional similarity and stereochemical relatedness to present day systems.
Emergence of protobiological information has been suggested by experiments in which heated mixtures of $\alpha$-amino acids order themselves into a self limited array of thermal proteins. The polymers display selective catalytic, hormonal, and other activities. Interactions of varied cationic thermal proteins with polynucleotides indicate selective recognition in both directions. Reverse translation is partly a missing link in the molecular evolution flowsheet. Interest in reverse translation (Fox and Dose, 1972) has been increasing (Root-Bernstein, 1982; Wassermann, 1982; Prusiner, 1982; Melius, 1983; Berger, 1984; Brunori and Talbot, 1985).

Some selectivity has been observed in the catalysis of polymerization of 5'-phosphorimidazolides of various nucleosides (Orgel et al.) in the presence of thermal heteropolypeptides. Added Leuchs homopolypeptides have no measurable effect, except for homopolylysine, which is deceleratory. When thermal heteropolypeptides are added to the reaction, selective effects are observed. The patterns for cytosine and adenine phosphorimidazolides are common as are the patterns of effect of thermal copolyamino acids on uracil and guanine imidazolides. The deceleration by lysine-rich polymers contrasts to the acceleration earlier observed with the same polymers acting on nucleoside triphosphates instead of nucleoside phosphorimidazolides. The self ordering of amino acids serves conceptually as a deterministic evolutionary precursor of the modern coding mechanism.

The possibility for the evolution of information at an early nontemplated protein stage is supported by findings of electrical signals from proteinoid microspheres prepared with no DNA/RNA in their history. The deposition of thermal copolyamino acids on lipid membranes in the Mueller-Rudin apparatus has here been found to produce electrical behavior like that evoked by bacterial EIM polypeptide. A new procedure is to make a film of membrane on the electrode; the results provide maximal repeatability.

The principle of nonrandom biomacromolecular specificity identified by these studies in molecular evolution have been extrapolated to principles of evolution of advanced organisms (Ho and Saunders: Beyond Neo-Darwinism, An Introduction to the New Evolutionary Paradigm, (Academic Press, London, 1984)).

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1/ Information is here operationally defined as capacity for selective interaction of molecule or system.
Photochemical Reactions of Various Model Protocell Systems

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Models abound for the emergence of cellular life on the primitive earth, and for physical environments of that era. That model set which we are studying embodies these assumptions: (1) Pre-genetic cellular forms were phase-bounded systems primarily photosynthetic in nature, and (2) the early earth environment was anoxic (lacking appreciable amounts of free hydrogen).

We had previously shown that model protocells prepared by quenched spark discharge reactions upon N2, CO, H2 gases over water can conduct photochemical reductions of carbonate to organic carbon under anoxic conditions (Nature 291, 482, 1981). However, several serious questions remain as to the plausibility of this particular model system because reducing conditions were used initially to prepare the structures.

We have found that organic structures can also be formed under anoxic conditions (N2, CO3=, H2O) by protracted longwavelength UV radiation. Apparently these structures form initially as organic layers upon CaCO3 crystalloids.

The question remains as to whether the UV photosynthetic ability of such phase bounded structures is a curiosity, or a general property of phase bounded systems which is of direct interest to the emergence of cellular life.

We have addressed the question of the requirement and salient features of a phase boundary for UV photosynthetic abilities by searching for similar general physical properties which might be manifest in a variety of other simple protocell-like structures. Since we have shown that our laboratory protocell models (either those prepared under slightly reducing or under anoxic conditions) can effect the UV photosynthesis of low molecular weight compounds, we are using this reaction as an assay to survey other types of structures for similar UV photosynthetic reactions. Various kinds of structures surveyed are: (1) proteinoids, (2) liposomes, (3) reconstituted cell membrane spheroids, (4) coacervates, (5) model protocells formed under anoxic conditions.

The conclusion which emerges is that phase bounded systems can serve effectively (perhaps by developing appropriate transmembrane potentials, see Tien, J. Phys. Chem., 88, 3172-74, 1984) to reduce oxidized carbon to organic carbon in a world subjected to long-wavelength UV light and supplied with very simple precursors as carbon in the plus-4 (oxidized) state.
In simple terms a living entity is a negentropic system that replicates, mutates and evolves. A number of suggestions have been made recently, such as directed panspermia, atmospheric photosynthesis, genetic overtaking from inorganic processes, etc., as alternative models to the accepted Oparin-Haldane-Urey model of the origin of life on Earth. This has probably occurred because in spite of tremendous advances in the prebiotic synthesis of biochemical compounds, the fundamental problem of the appearance of the first life—a primordial replicating cell-ancestral to all other forms of extant life, has remained elusive. This is indeed a reflection on the different fundamental nature of the problem involved. Regardless of which were the fundamental processes which occurred on the primitive Earth, it had to end up with the fundamental characteristics of an ancestral protocell. The problem of the emergence of the first ancestral cell was one of synergistic macromolecular cooperation, as it has been discussed by authors recently (COSPAR XXV Plenary Meeting). An analogous situation must have occurred at the time of the appearance of the first eucaryotic organism. Procaryotic life appeared probably during the first 600 million years of Earth history when the Earth was sufficiently cool and continually bombarded (in the late accretion period) by comets and minor bodies of the solar system, when the sea had not yet acquired its present form.

The first organisms on Earth depended initially on the available organic matter. At any rate they were living in an anaerobic Earth. When the first energy crisis took place, probable solutions to the problem were: a) the archaeabacterial fixation of $\text{CO}_2$; b) the non-photosynthetic fixation of $\text{CO}_2$ by means of such reducing agents as $\text{H}_2\text{S}$, produced ubiquitously from the Earth's interior (this could also be a model for the satellite of Jupiter, Europa). Later on, with the invention of chlorophyllc photosynthesis other modes of $\text{CO}_2$ fixation and photoconversion processes were introduced. At any rate, about 2,000 million years ago biological evolution had come to a standstill, since the Earth had been populated during 2 billion years of history only by procaryotic unicellular organisms. Another quantum jump was necessary to lead to eucaryotes and eventually to higher organisms. This required another major discovery, which is the use of $\text{H}_2\text{O}$, instead of $\text{H}_2\text{S}$, as a reducing agent by photosynthetic procaryotes. Apparently this was not a minor feat because today we do not yet know the exact mechanisms of this reaction. But at any rate when $\text{O}_2$ became prevalent (10% of PAL) the energy-yielding processes (oxidative phosphorylation) speeded evolution in a tremendous manner. After several unsuccessful trials this oxygenic environment became prevalent 2 x 10$^9$ years ago. This in turn led to the appearance of aerobic free-living bacteria, which together with other procaryotes, gave rise to single-cell eucaryotes by endosymbiotic processes at about 1,400 million years ago. From here the takeoff toward higher organisms could have been expected. In conclusion, synergistic cooperative processes were necessary for the emergence of the first single-celled procaryotes and similar processes became also necessary for the appearance of the first single-celled eucaryote. Therefore there is a need for studies that can elucidate the early cooperative processes among macromolecules which interacted to generate by synergistic cooperation all of the essential attributes of the ancestral cell. Obviously this approach is not the one we have used so successfully in the past going from A to B in the prebiotic synthesis of biochemical compounds.
In recent years we have learned that DNA is conformationally active. It can exist in a number of different stable conformations including both right-handed and left-handed forms. Using single crystal X-ray diffraction analysis we are able to discover not only additional conformations of the nucleic acids but also different types of hydrogen bonded base-base interactions. Although Watson-Crick base pairings are the predominant type of interaction in double helical DNA, they are not the only types. Recently, we have been able to examine mismatching of guanine-thymine base pairs in left-handed Z-DNA at atomic resolution (1Å). A minimum amount of distortion of the sugar phosphate backbone is found in the G'T pairing in which the bases are held together by two hydrogen bonds in the "wobble pairing" interaction. Because of the high resolution of the analysis we can visualize water molecules which fill in to accommodate the other hydrogen bonding positions in the bases which are not used in the base-base interactions.

Studies on other DNA oligomers have revealed that other types of non-Watson-Crick hydrogen bonding interactions can occur. In the structure of a DNA octamer with the sequence d(GGTAAGC) complexed to an antibiotic triostin A, it was found that the two central AT base pairs are held together by Hoogsteen rather than Watson-Crick base pairs. Similarly, the G'C base pairs at the ends are also Hoogsteen rather than Watson-Crick pairing. The cytosines have to be protonated. Hoogsteen base pairs make a modified helix which is distinct from the Watson-Crick double helix. The relative ease with which modifications of hydrogen bonding in the double helix can be found in crystal lattices provides a basis for wondering what contribution they may have played in prebiotic evolution.
Session V

Early Evolution of Life—Geochemical
Paleobiologists now recognize that the earth's biosphere has been profoundly affected by geologic processes. One very important process is the dissipation of heat which has been generated by radioactivity and/or stored within the earth. Heat flow is responsible for crustal movements and therefore it is the principal architect for constructing the environments (e.g. shallow marine, continental, etc.) wherein life developed and flourished. Heat flow has also influenced the movements of volatile elements (e.g. C, N, H, S, rare gases, etc.) both within the earth's crust and between the crust and mantle. The inventory of these elements in the earth's crust is important, not just because some of them constitute the building blocks of organic matter, but also because they influence the biosphere's climate.

The purpose of this work is to evaluate how the decline of heat flow over the course of the earth's history has influenced the carbon inventory in the earth's crust. Such an evaluation must first consider whether the rate at which carbon is presently being exchanged between the mantle and crust is sufficient to play an important role in controlling the crustal inventory. Secondly, this exchange of carbon must be reevaluated in the context of the Precambrian Earth's environment. One very important consideration is that the upper mantle was perhaps 300°C hotter 3 b.y. ago than it is today.

Estimates of the midocean ridge mantle carbon flux can be made by estimating concentration ratios of carbon to helium in hydrothermal fluids and tholeiitic glasses and by multiplying these by the oceanic primordial $^{3}$He flux. The estimated ranges of carbon fluxes for the earth today and 3 b.y. ago are $1x10^{12}$ to $8x10^{12}$ moles yr$^{-1}$ and $3x10^{12}$ to $48x10^{12}$ moles yr$^{-1}$, respectively. These fluxes are comparable in magnitude to the present-day flux estimated for carbonate metamorphism, $6x10^{12}$ moles yr$^{-1}$. A net carbon flux from the mantle of $5x10^{12}$ moles yr$^{-1}$ would require less than 1400 m.y. to generate the present-day crustal carbon inventory. Given present-day geothermal gradients, carbonate sediments can be at least partly subducted into the mantle. Perhaps between 3 and 50 percent of the sedimentary carbon presently transported by the lithospheric plates to subduction zones will eventually be injected into the upper mantle. A hotter upper mantle 3 b.y. ago would have made this injection process less efficient. During the late Archean, the earth's crustal carbon inventory very likely equalled or even exceeded the present crustal inventory. This circumstance, together with the likelihood that the land area at that time was considerably less than it is today, suggests that 3 b.y. ago the atmosphere contained at least two orders of magnitude more CO$_2$ than it does today.
The origin and evolution of the Earth's early atmosphere has long been a topic of great interest but determination of actual compositions over geologic time is a difficult problem. However, recent systematic studies of stromatolite deposits (Precambrian Paleobiology Research Group) has extended our knowledge of Archean ecosystems. It has been shown that many stromatolite deposits have undergone negligible alteration since their time of formation. The discovery of primary fluid inclusions within unaltered 3.5 b.y. old Archean sediments and the observation that the 3.3 b.y. old Barberton cherts have remained closed to argon loss and have not been subjected to thermal metamorphism suggests that an opportunity exists for the direct measurement of the volatile constituents present at their time of formation. Of primary interest to our study was the possibility that the stromatolites and other Archean sediments might retain a vestige of the atmosphere and thus afford an indication of the variations in carbon dioxide and nitrogen isotopic compositions with time.

A suite of essentially unaltered Archean stromatolites and cherts of different ages and geologic sites have been analyzed for their trapped carbon dioxide and nitrogen compositions by the stepped combustion extraction technique utilizing static mass spectrometers for the isotope measurements. Studies of modern-day sediments have shown that both nitrogen and carbon associated with unmetamorphosed organic matter is released in the 300-700°C interval during combustion. Release of carbon from carbonates and graphite is completed prior to 900°C. It has been shown from pyrolysis studies of Archean cherts that modern-day atmospheric argon is lost below 900 to 1000°C and the argon released above this temperature interval represents samples of trapped early atmospheric argon. We have assumed that the carbon dioxide and nitrogen released above 900°C represents gases trapped during the formation of the sediments and may be a remnant of atmospheric gases during Archean times.

Isotopic analysis of nitrogen released at elevated temperatures from samples ranging in age from 1.7 to 3.5 b.y. (Frere, Hamersley, and Barberton Formations) ranged from +6 to +1 %, similar to modern-day atmospheric nitrogen value of 0 %. The nitrogen released from the Archean sediments occurs in at least three forms of different isotopic compositions, ranging from -30 to +18 %. Carbon dioxide released above 900°C for six sediments (Frere, Hamersley, Manjeri, Cheshire, Barberton and Isua Formations) ranged from -7 to -14 %, and the majority of the values were similar to the present day atmospheric value of -8 %. At lower temperatures carbon isotopic compositions ranging from -7 to -56 % were observed. The -56 % value was obtained from the analysis of kerogen extracted from Fortescue Formation. Evidence exists which suggests that many of the samples contain "secondary" carbon and nitrogen of a post-depositional origin in addition to the trapped atmospheric components and indigenous organic material incorporated at the time the sediments were consolidated.
USE OF LABORATORY SIMULATED PYROLYSIS IN TRACING THE HISTORY OF SEDIMENTARY ORGANIC MATTER

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In order to obtain maximum preservation of the organic record, it is desirable for the preserved biological and chemical fossils to alter at a slow rate or not to alter at all. It is generally believed that preservation is mostly a function of shallow burial depth in rocks with low porosity which prevent water circulation. At greater depths, it is generally assumed thermal processes decompose the kerogen. Results from laboratory simulated pyrolyses experiments performed at UCLA show that in addition to depth of burial, preservation of kerogen, and hence any morphologic structure in it, is also dependent on the mineral matrix with which it is associated. In the presence of clay minerals, and especially under dry conditions, extractable lipids released during kerogen decomposition are more rapidly destroyed than in the presence of calcite or chert matrices. The result is production of gas, polar bitumen (resins and asphaltenes) and pyrobitumen (or charred organic matter) and destruction of biomarkers. During such an early reorganization of the kerogen, the biomarker constituents can be destroyed, or unrecognizably altered.

The above process of organic residues maturation appears to be inhibited in the presence of water and is significantly reduced where kerogen is hosted in limestones, dolomites or cherts. These minerals have been characteristically found to be the most reliable in yielding morphological fossils and small quantities of extractable bitumen in Archean and Proterozoic rocks. Shales may contain enrichments of carbon but these usually have low H/C ratios and questionable amounts of extractable bitumen.

To understand the validity of chemical and morphological fossils, in the early geologic record, it will be necessary to understand the process of kerogen in sedimentary rocks.

To test the role of various minerals on the preservation process, kerogen extracted from a variety of rocks has been heated together with montmorillonite, illite and calcite. The kinetics of the process has been monitored and the products quantitatively identified. During the coming year, research will be directed toward continuing the pyrolyses experiments using different types of kerogen under both dry and aqueous conditions.
ISOTOPIC, PETROLOGIC, AND BIOGEOCHEMICAL INVESTIGATIONS
OF BANDED IRON-FORMATIONS

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It is recognized that the first occurrence of BIFs clearly pre-dates biological oxygenation of the atmosphere-hydrosphere system and that their last occurrences extend beyond plausible dates of pervasive biological oxygenation. For this reason, and because enormous quantities of oxidizing power have been sequestered in them, it is widely thought that these massive, but enigmatic, sediments must encode information about the mechanism and timing of the rise of atmospheric O2. By coupling isotopic analyses of iron-formation carbonates with biogeochemical and petrologic investigations, we are studying (i) the mechanism of initial sedimentation of iron; (ii) the role of iron in microbially mediated diagenetic processes in fresh iron-formation sediments; (iii) the logical integration of mechanisms of deposition with observed levels of banding.

We have, thus far, shown that (i) carbonates in BIFs of the Hamersley Group of Western Australia are isotopically inhomogenous; (ii) the nature and pattern of isotopic ordering is not consistent with a metamorphic origin for the overall depletion of 13C observed in the carbonates; (iii) if biological, the origin of the 13C-depleted carbonate could be either respiratory or fermentative; (iv) iron may have been precipitated as Fe3+, then reduced to Fe2+ within the sediment; (v) sedimentary biogeochemical systems may have been at least partially closed to mass transport of carbonate species; and (vi) very-closely correlated variations of carbon- and oxygen-isotopic abundances in the Dales Gorge Members suggest that evaporative processes were important during its deposition.
The origin and early evolution of life on Earth occurred under physical and chemical conditions distinctly different from those of the present day. The broad goal of this research program is to characterize these conditions. One aspect involves the dynamics of the Earth-moon system, the distance of the moon from the Earth, and the length of the day. These have evolved during the course of Earth history as a result of the dissipation of tidal energy. As the moon has receded the amplitude of oceanic tides has decreased while the increasing length of the day should have influenced climate and the circulation of atmosphere and ocean.

We interpret a 23.3 year periodicity preserved in a 2500 million year old banded iron-formation as reflecting the climatic influence of the lunar nodal tide. The corresponding lunar distance would then have been ~ 52 Earth radii. The influence of the lunar nodal tide is also apparent in rocks with an age of 680 million years B.P. Our derived value for lunar distance 2500 million years ago is the only datum on the dynamics of the Earth-moon system during the Precambrian era of Earth history. The implied development of Precambrian tidal friction is in accord with more recent paleontological evidence as well as the long term stability of the lunar orbit.
Session VI

Early Evolution of Life--Biological
RECENT PROGRESS IN PRECAMBRIAN PALEOBIOLOGY

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Ongoing studies at UCLA supported by NASA Grant NGR 05-007-407 include the following:

1. Investigations of stromatolites, microfossils and sedimentary structures in Archean (Warawoona Group, 3.5 Ga) and Early Proterozoic (Fortescue Group, 2.8 Ga) sequences of Western Australia; in Archean (Onverwacht Group, 3.5 Ga) and Early Proterozoic (Transvaal Supergroup, 2.3 Ga) sequences of eastern and central South Africa; in Early Proterozoic (Kona Dolomite, Tyler Fm., Pokegama Quartzite, Biwabik and Gunflint Iron Fms., 2.0 Ga) sequences of North America; and in Middle Proterozoic (Gaoyuzhuang Fm., 1.4 Ga; Wumishan Fm., 1.2 Ga) and Late Proterozoic (Jiudingshan Fm., 0.9 Ga; Wanshan Fm., 0.7 Ga) sequences of northern and south-central China.

2. Laboratory and field studies of modern microbial biocoenoses -- analogues of Precambrian microbial communities -- especially those at Laguna Mormona, Baja California, Mexico.

3. Development of new laboratory techniques for the separation and concentration of minute cellularly preserved fossils for isotopic and organic geochemical analyses.

4. Assembly of a computerized database for assessment of the timing and nature of major events occurring during Precambrian biotic evolution, and of the potential applicability of ancient microbiotas to problems of global biostratigraphy and biogeography.

In addition, during the past year, with support from the UCLA Center for the Study of Evolution and the Origin of Life and the National Geographic Society, a consortium of some three dozen scientists having interest in the interrelated lithospheric-biospheric-atmospheric evolution of the Proterozoic Earth, has been assembled. This multidisciplinary group -- calling itself the P.P.R.G.-P (Precambrian Paleobiology Research Group-Proterozoic) and drawing its membership from Canada, Australia, South Africa, Sweden and the United States -- plans to work together at UCLA in 1987-88 to produce a major monographic work on Proterozoic paleobiology. This new venture will intermesh well with the studies outlined above as part of an ongoing effort to decipher and better define the nature, mode, rate and course of biotic, geologic and environmental evolution during early, Precambrian, Earth history.
A comparative search for phylogenetically covarying basepair replacements within potential helices has been the only reliable method to determine the correct secondary structure of the 3 rRNAs, 5S, 16S, and 23S. The analysis of 16S (and more recently 23S rRNA) from a wide phylogenetic spectrum, that includes various branches of the eubacteria, archaeabacteria, eucaryotes, in addition to the mitochondria and chloroplast, is beginning to reveal the constraints on the secondary structures of these rRNAs. A common secondary structure for all of these 16S-like rRNAs emerged from this analysis, and further, comparisons among these revealed a highly constrained secondary structure core, in addition to the specific regions that are structurally variable. Within the conserved secondary structure core exists many universally conserved nucleotides, with the majority of these clustered into a few regions of the molecule.

Based on the success of this analysis, and the assumption that higher order structure will also be phylogenetically conserved, we have begun a comparative search for positions that show co-variation not involved in secondary structure helices. From a list of potential higher order interactions within 16S rRNA we are presenting two higher-order interactions.

The first of these interactions involves positions 570 and 866. Based on the extent of phylogenetic covariation between these positions while maintaining Watson-Crick pairing, we consider this higher-order interaction proven. The other interaction involves a minimum of six positions between the 1400 and 1500 regions of the 16S rRNA. Although these patterns of covariation are not as striking as the 570/866 interaction, the fact that they all exist in an anti-parallel fashion and that experimental methods previously implicated these two regions of the molecule in tRNA function suggests that these interactions be given serious consideration.
Studies of ribosomal RNA primary structure allow reconstruction of phylogenetic trees for prokaryotic organisms. Such studies reveal a major dichotomy among the bacteria that separates them into eubacteria and archaebacteria. Both groupings are further segmented into several major divisions. The results obtained from 5S rRNA sequences are essentially the same as those obtained with the 16S rRNA data. In the case of Gram negative bacteria the ribosomal RNA sequencing results can also be directly compared with hybridization studies and cytochrome c sequencing studies. There is again excellent agreement among the several methods. It seems likely then that the overall picture of microbial phylogeny that is emerging from the RNA sequence studies is a good approximation of the true history of these organisms.

The RNA data allow us to begin to examine the evolutionary process in a semi-quantitative way. The secondary structures of these RNAs are largely established. As a result it is possible to recognize examples of local structural evolution. Evolutionary pathways accounting for these events can be proposed and their probability can be assessed.
INVESTIGATIONS WITH METHANOBACTERIA AND WITH EVOLUTION OF THE GENETIC CODE

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(1) Evolutionary changes in the genetic code. Mycoplasma capricolum was found by Osawa et al. to use UGA instead of UGG as the code for tryptophan and to contain 75% A + T in its DNA. This change could have been from evolutionary pressure to replace C + G by A + T, resulting in the following steps; first, replacement of UGA stop codons by UAA. This would prevent UGA codons from producing chain termination. The second step would be a mutational change of the anticodon in tryptophan tRNA from CCA (which pairs only with UGG) to UCA (which pairs with both UGA and UGG). The third step would be replacement of UGG tryptophan codons by UGA. None of these changes would be deleterious.

(2) Silent nucleotide substitutions in evolution. Numerous studies have been reported of evolution of proteins as measured by amino acid replacements that are observed when homologous proteins, such as hemoglobins from various vertebrates, are compared. These replacements result from nucleotide substitutions in amino acid codons in the corresponding genes. Simultaneously, silent nucleotide substitutions take place that can be studied when sequences of the genes are compared. These silent evolutionary changes take place mostly in third positions of codons. Two types of nucleotide substitutions are recognized: pyrimidine-pyrimidine and purine-purine interchanges (transitions) and pyrimidine-purine interchanges (transversions). Silent transitions are favored when a corresponding transversion would produce an amino acid replacement. Conversely, silent transversions are favored by probability when transitions and transversions will both be silent. Extensive examples of these situations have been found in protein genes, and it is evident that transversions in silent positions predominate in "family boxes" in most of the examples studied.

(3) Lysis of Methanobacteria (work by John Bush). A streptomycete from cow manure produces an extracellular enzyme capable of lysing the pseudomurein-containing methanogen Methanobacterium formicicum. The lytic activity has been partially purified from culture fluid and appears to be a serine protease. Similar activity has been fractionated from Pronase. Optimal conditions have been developed for lysis of the bacterium by commercial preparations of Proteinase K. The three lytic enzymes have been partially characterized.
IS THE ATPase FROM HALOBACTERIUM SACCHAROVORUM AN EVOLUTIONARY RELIC?

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The ATP Synthase Complex present in the membranes of mitochondria, chloroplasts or bacteria is composed of 2 sectors: F$_0$, an integral membrane protein consisting of 3 subunits mediating proton translocation across the membrane and F$_1$, the catalytic component composed of 5 non-identical subunits. The apparent early origin of the ATP Synthase Complex, as implied by its ubiquitous distribution, seems inconsistent with its structural and functional complexity and raises the question if simpler versions of the ATP Synthase exist. We have searched for such an ATP Synthase in various Archaeabacteria. Here we describe a purified halobacterial ATPase activity which possesses certain properties consistent with those of an ATP Synthase but which has a different subunit structure.

Membranes from H. saccharovorum were treated with detergent so as to extract the ATPase activity. The soluble enzyme was further purified by gel filtration, phenyl sepharose chromatography, and ammonium sulfate-mediated DEAE-chromatography. The final material hydrolyzed 2.9 umols of ATP/min/mg protein which represented a 150-fold purification. The purified enzyme was cold sensitive and was most active and stable in at least 3 M NaCl and at least 3.5 M NaCl respectively. ATPase activity was competitively inhibited by ADP indicating that an E.ADP complex was formed which made unlikely that the hydrolysis of ATP was catalyzed by an alkaline phosphatase or ion-translocating enzymes such as a Na/K ATPases. The purified enzyme was inhibited by DCCD in a manner that resembled the interaction of the inhibitor with the F$_1$ sector. However, only three subunits were detected by sodium dodecylsulfate polyacrylamide gel electrophoresis. Two (the major bands) had molecular weights of 85,000 and 60,000; the third (estimated to represent <10% of the total protein) had a molecular weight of 28,000. Thus, whether this enzyme is a different ATP Synthase or another type of ion-translocating ATPase is not clear. At the present time, studies are underway to determine the function of this ATPase activity.
FUNCTIONAL AND EVOLUTIONARY RELATIONSHIPS BETWEEN BACTE RIORHODOPSIN AND HALORHODOPSIN IN THE ARCHAEBACTERIUM, HALOBACTERIUM HALOBIUM

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The archaebacteria occupy a unique place in phylogenetic trees constructed from analyses of sequences from key informational macromolecules, and their study continues to yield interesting ideas on the early evolution and divergence of biological forms. It is now known that the halobacteria among these species contain various retinal-proteins, resembling eukaryotic rhodopsins, but with different functions. Two of these pigments, located in the cytoplasmic membranes of the bacteria, are bacteriorhodopsin (a light-driven proton pump) and halorhodopsin (a light-driven chloride pump). Comparison of these systems is expected to reveal structure/function relationships in these simple (primitive?) energy transducing membrane components and evolutionary relationships which had produced the structural features which allow the divergent functions.

Both systems consist of a small intrinsic membrane protein (opsin), which binds retinal via a protonated Schiff-base linkage. The retinal undergoes isomerization (trans to 13-cis) upon absorption of light in both cases, which moves the Schiff-base to a new environment in the proteins. From here on, however, the two systems function differently. In bacteriorhodopsin the isomerization is followed by deprotonation of the Schiff-base nitrogen and release of the proton into the extracellular medium. Reisomerization of the retinal occurs only after reprotonation of the Schiff-base from the cytoplasmic side. In halorhodopsin, however, the deprotonation does not take place after the isomerization, thus the spatial displacement of the positively charged nitrogen will cause instead a rearrangement of charges in the protein. It is the redistribution of the charges which presumably cause the movement of chloride ions, known to have bound in the dark to the extracellular side of the protein. Release of the chloride on the cytoplasmic side ultimately accompanies the reisomerization of the retinal. It seems clear that very different primary structures are needed for these proteins to accomplish their different functions. Indeed, analysis of partial amino acid sequences from halorhodopsin shows already that few if any long segments exist which are homologous to bacterio-opsin. Either these proteins diverged a very long time ago to allow for the observed differences, or the evolutionary clock in the halobacteria runs faster than usual.
THIOREDOXINS IN EVOLUTIONARILY PRIMITIVE ORGANISMS

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Thioredoxins are low molecular weight redox proteins, alternating between the S-S (oxidized) and SH (reduced) states, that function in a number of biochemical processes, including DNA synthesis, DNA replication, and enzyme regulation. Until recently, reduced ferredoxin was known to serve as the source of reducing power for the reduction of thioredoxins only in oxygenic photosynthetic cells. In all other organisms, the source of hydrogen (electrons) for thioredoxin reduction was considered to be NADPH. We found in our NASA-supported research that Clostridium pasteurianum, an anaerobic organism normally living in the soil unexposed to light, resembles photosynthetic cells in using ferredoxin for the reduction of thioredoxin. Moreover, the transfer of electrons from reduced ferredoxin to thioredoxin is catalyzed by a flavoprotein enzyme that has not been detected in other organisms. The results reveal the existence of a pathway in which ferredoxin, reduced fermentatively either by molecular hydrogen or by a carbon substrate, provides the reducing power for the reduction of thioredoxin via the flavoprotein enzyme, ferredoxin-thioredoxin reductase.

In related studies, we have found that Chromatium vinosum, an anaerobic photosynthetic purple sulfur bacterium resembles evolutionarily more advanced micro-organisms in having an NADP-thioredoxin system composed of a single thioredoxin which is reduced by NADPH via NADP-thioredoxin reductase. The adoption of the NADP-thioredoxin system by Chromatium seems appropriate in view of evidence that the organism utilizes ATP-driven reverse electron transport, rather than direct photoreduction to reduce electronegative acceptors such as NAD. Accordingly, because of the more oxidizing redox potential, thioredoxin reduction via NADP would be energetically less costly than via ferredoxin and would have the added advantage of lying closer to the main photosynthetic electron transport pathway should there be a need to relate electron transport status to the extent of thioredoxin reduction as is the case in oxygenic photosynthesis. Apropos this point, we have also found that, in contrast to oxygenic photosynthetic organisms, the role of thioredoxin in anoxygenic prokaryotes such as Chromatium seems to lie outside the regulation of photosynthetic CO₂ assimilation.

Our most recent NASA-support research has dealt with the identification of target enzymes of the ferredoxin/thioredoxin system in a cyanobacterium (Nostoc muscorum). The results show that thioredoxin-linked photosynthetic enzymes of cyanobacteria are similar to those of chloroplasts. It thus now seems that the ferredoxin/thioredoxin system functions in regulating CO₂ assimilation via the reductive pentose phosphate cycle in oxygenic but not anoxygenic photosynthetic cells.
BIOSYNTHETIC PORPHYRINS AND THE ORIGIN OF PHOTOSYNTHESIS

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Living matter requires a continuous flux of free energy to remain in its organized state. Thus the evolution of a photosynthetic system may be intimately associated with the successful evolution of living matter. It is probable that photochemistry driven by wavelengths around the maximum of solar energy output is required to support bio-evolution on a terrestrial scale. The present day photosynthetic system is highly optimized for this function. It was hypothesized by Granick that the biosynthetic pathway of photosynthetic pigments recapitulates the evolutionary history of the photosynthetic system. Thus each pigment would have had a photosynthetic function in its time period, to be replaced by the next along the sequence which served a more efficient or more useful function. Since the prebiotic atmosphere was anaerobic, if not reducing, a useful function of primordial photosynthesis would have been to photooxidize reduced substrates such as Fe²⁺, S²⁻ or reduced organic molecules and to emit hydrogen. A major advance occurred with the discovery of a mechanism for the photoformation of oxygen from the omnipresent material water. It is the aim of this research to show that the chemical and photochemical properties of the pigments formed early in the biosynthetic pathway are consistent with these hypotheses.

We have shown that the early biogenic pigments uroporphyrin and coproporphyrin do photooxidize organic compounds and emit hydrogen in the presence of a platinum catalyst. These experiments were carried out in dilute aqueous solution near neutral pH under anaerobic atmosphere, and quantum yields near 10⁻³ were obtained. Thus relevant prebiotic conditions were maintained. Rather than to further optimize conditions, attempts were made to replace the platinum catalyst by a more "prebiotically" suitable catalyst. Trials with an Fe₄S₄(SR)₄ cluster, in analogy to the present hydrogenase and nitrogenase, were not successful. However, experiments using cobalt complexes to catalyze the formation of hydrogen are promising. In analogy with biological photosynthetic systems which group pigments, electron transfer molecules and enzymes in clusters for efficiency, it was found that binding the biogenic porphyrins to the polyvinyl alcohol used to support the platinum catalyst did increase the quantum yield of the reaction. This also made the reaction less dependent on auxiliary electron transfer molecules. It was also found that ultra violet light can serve to photo-oxidize porphyrinogens to porphyrins under anaerobic conditions. Thus the formation of the colorless porphyrinogens (absorbing < 250 nm) by the extraordinarily simple biosynthetic pathway would not be a problem because of the prevalence of UV light in the prebiotic, anoxic atmosphere. We will explore the possible catalytic activity of various cobalt complexes, including derivatives of vitamin B₁₂, as hydrogen forming catalysts under primitive earth conditions. This opens an intriguing connection between the photochemical activity of uroporphyrin, the earliest biogenic porphyrin, and the biosynthetically intimately related vitamin B₁₂.
Life on Earth presumably originated in an essentially anaerobic environment. At some time, perhaps as much as 3.5 billion years ago, the process of oxygenic photosynthesis was "invented" and oxygen gradually accumulated in the atmosphere. While a considerable amount of evidence has been accumulated about the history of oxygen on this planet, little is known about the relative amounts to which primitive cells might have been exposed. One clue may be found in the metabolic pathways of extant microorganisms. Biosynthetic pathways appear to have evolved by sequential steps. The initial enzymatic steps which are found in all organisms are anaerobic, i.e. oxygenases are not involved, while subsequent steps reflect with increasing frequency the use of oxygen as an enzymatic substrate. From the standpoint of evolutionary development, particularly eucaryotic, the emergence of a number of oxygen-requiring processes was crucial. While eucaryotes are principally aerobic organisms, a number are capable of anaerobic growth by fermentation. One such eucaryotic microorganism, Saccharomyces cerevisiae, will grow in the complete absence of oxygen when supplemented with unsaturated fatty acid and sterol. Oxygen-requiring enzymes are involved in the synthesis of both of these compounds. Studies in our laboratory have demonstrated that the oxidative desaturation of palmitic acid and the conversion of squalene to sterols occur in the range of $10^{-3}$ to $10^{-2}$ PAL. Thus, if the oxygen requirements of these enzymatic processes are an indication, eucaryotes might be more primitive than anticipated from the microfossil record. Recent work has focused on the oxygen requirements for sterol and unsaturated fatty acid synthesis in a more primitive procaryotic system.

The synthesis of sterols or monounsaturated fatty acids by an oxidative mechanism is not widespread among procaryotic organisms. A number of bacteria have been shown to use oxygenases for the synthesis of unsaturated fatty acids, including a number of cyanobacteria and bacilli, however, the best example of sterol synthesis in a procaryote is found in a methanotroph, Methylococcus capsulatus. Electron microscopic studies have shown that methanotrophic organisms contain well defined systems of intracytoplasmic membranes which increase when cells are grown at low levels of oxygen. We have attempted to correlate the observed changes in intracytoplasmic membranes in M. capsulatus by studying the quantitative variations in the levels of membrane lipids, principally phospholipid, fatty acid and sterol. Preliminary studies have shown that when cells are grown at lower oxygen levels, phospholipid and sterol synthesis increases, and the fatty acid content changes dramatically. Cells grown at $10^{-2}$ PAL oxygen contain high levels of sterols.
EVOLUTION OF THIOL PROTECTIVE SYSTEMS IN PROKARYOTES

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Biological thiols are essential elements in most aspects of cell function but undergo rapid oxidation to disulfides in the presence of oxygen. The evolution of systems to protect against such oxygen toxicity was essential to the emergence of aerobic life. The protection system used by eukaryotes is based upon glutathione (GSH) and GSH-dependent enzymes but many bacteria lack GSH and apparently use other mechanisms. The objective of this research is to elaborate the thiol protective mechanisms employed by prokaryotes of widely divergent evolutionary origin and to understand why GSH became the central thiol employed in essentially all higher organisms. Thiol-selective fluorescent labeling and HPLC analysis has been used to determine key monothiol components.

The major thiols present in representative species from all major lines of prokaryotic evolutionary descent have been determined. Among the archaeabacteria it has been found that the halobacteria (aerobes) produce γ-glutamylcysteine and thiosulfate in large amounts and produce a disulfide reductase which maintains the γ-Glu-Cys in the reduced state, whereas the methanogens (strict anaerobes) contain sulfide as the major thiol component and have low levels of cysteine and coenzyme M. The eubacteria include the Gram positive bacteria and the radiobacteria whose aerobic and facultative members were found to produce coenzyme A as the major thiol and to contain one or more disulfide reductases which reduce CoA disulfide to its thiol. Anaerobic Gram positive bacteria contained sulfide as the dominant thiol. Several unidentified thiols were detected in specific Gram positive bacteria in substantial amounts and their structures are being elucidated. Representatives of the spirochaetes and the green sulfur bacteria were found to have sulfide as the main thiol component. Glutathione was found to be the dominant thiol only in facultative and aerobic members of the purple photosynthetic and related bacteria, and in the cyanobacteria. The later finding is significant because these two groups are considered to have been the precursors to eukaryotic mitochondria and chloroplasts via the process of endosymbiosis, suggesting that GSH metabolism may have been incorporated into eukaryotes at the same time that mitochondria and chloroplasts were acquired. Our finding that Entamoeba histolytica, a eukaryote lacking both mitochondria and chloroplasts, lacks GSH and GSH-dependent enzymes is consistent with this view. GSH metabolism thus appears to have its origins closely linked to the evolution of oxygenic photosynthesis and oxygen-utilizing metabolism. A key factor in the evolution of GSH as a protective thiol appears to be its slow rate of air oxidation relative to Cys, Cys-Gly, and other thiols with free beta amino groups.
MICROFOSSILS IN THE ANTARCTIC COLD DESERT - POSSIBLE IMPLICATIONS FOR MARS

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In the Ross Desert of Antarctica, the principal life form is the cryptoendolithic microbial community in the surface-near layers of porous sandstone rocks.

Biological, geological and climatic factors interact in a complex and precarious balance, making life possible in an otherwise hostile environment. Once this balance is tipped, fossilization sets in. In the reverse case, new colonization of the rock surface may be initiated. As a result, fossilization is contemporary with modern life and both may be simultaneously present in a mosaic pattern. Also, different stages of fossilization are present. The process of fossilization takes place in a non-aquatic environment.

If primitive life ever appeared on Mars, it is possible that with increasing aridity, life withdrew into an endolithic niche similar to that in the Antarctic desert. Fossilization in a non-aquatic environment may have set in with the result that traces of past life could be preserved. If such was the case, the study of the fossilization process in Antarctica may hold useful information for the analysis of Martian samples for microfossils.
Physiological processes of all life forms on this planet are intrinsically related to their intracellular water potential. The overall goal of this research is the elucidation of the mechanism(s) whereby earth's first oxygenic photoautotrophs (the cyanobacteria) adjust their water potential to that of a changing external water potential (that is, osmoregulate). Osmoregulation is achieved by intracellular adjustment of inorganic and/or organic solutes (osmolytes) involving specific biochemical mechanisms. Structural and biochemical evolution within the cyanobacteria is believed to have been completed (and fixed in present day forms) by the end of the Precambrian eon. Therefore, research using cyanobacteria of all three structural types (unicellular, filamentous and branched), each grown in the photoautotrophic (PA), photoheterotrophic (PH) and chemoheterotrophic (CH) modes of nutrition, should provide insight into the origin and evolution of the photosynthetically-related osmoregulatory mechanisms of eukaryotic organisms. The chloroplasts of these organisms are phylogenetically related to the cyanobacteria.

Studies involving $^{13}$C-NMR and other conventional analytical instrumentation on osmoregulating organisms have provided substantial information on cyanobacterial osmoregulation. Non-reducing carbohydrates are the principal (10-fold greater than amino acids) osmolytes accumulated during light or dark periods in freshwater and marine cyanobacteria, grown in all nutritional modes. Glycinebetaine is the major osmolyte in only the extremely halotolerant species (e.g. Aphanothece halophytica). Unicellular forms (e.g. *Synechocystis* ATCC#27178) accumulate glucosylglycerol, whereas filamentous (e.g. *Calothrix* ATCC#27914) and branched (e.g. *Chlorogloeopsis* ATCC#27181) forms accumulate trehalose in light (sucrose in dark) when grown in PA mode. Under PH nutrition, sucrose is the major osmolyte in both light and dark for all three forms. Glutamate, proline, lysine and arginine accumulate, each depending upon light and nutritional conditions. These osmolytes have roles other than osmotic adjustment. Trehalose prevents membrane dessication and betaine permits enzymatic function in high intracellular potassium ion ($K^+$) by lowering the Km of salt-inhibited enzymes. Halotolerant cyanobacteria, like halobacteria, employ $K^+$ in an osmotic role, but the former possesses enzymes that are inhibited by intracellular salt. Cyanobacteria have, therefore, evolved an alternative mechanism of salt tolerance by synthesizing betaine to allow enzymatic functioning in high intracellular salt.

The betaine effect varies inversely with a particular enzyme's inherent $K^+$ sensitivity. This mechanism of osmoregulation and salt tolerance through betaine synthesis has also been elucidated. Osmotically stressed cyanobacteria accumulate $K^+$ which inhibits the favored synthesis activity of S-Adenosylhomocysteine (SAH) hydrolase. The hydrolytic direction is not inhibited by high $K^+$ and, therefore, SAH is removed. SAH is a potent inhibitor of the methylase enzyme required for betaine synthesis. Betaine then accumulates to a level that permits full activity of the SAH hydrolase in the favored synthetic direction. SAH then accumulates and betaine synthesis ceases.
MICROBIAL CONTRIBUTIONS TO THE PRECAMBRIAN EARTH

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Life has existed on earth for approximately 3.5 billion years. For most of this time, prokaryotic communities including those of microbial mats and stromatolites, some of which preserved as laminated cherts, provided the major biological forces changing the earth. Many changes in atmospheric gas composition (for example the depletion of CO₂) occurred during the Archean and Proterozoic eons as a result of microbial activity. The study of extant microbial communities has been used to help understand the dynamics which contributed to these atmospheric changes.

Our study of microbial mat communities has begun with characterization of the organismic constituents. Continuing microbial characterization has led to the establishment of 3 new prokaryotes: 1) a red Beneckea sp., 2) Arthrobacter simplex strain BC-2, and 3) Spirochaeta bajacaliforniensis.

We have recognized symbiosis in microbial communities as major force in cell evolution. Among the evolutionary enigmas we are investigating is the problem of the origin of the undulipodia (cilia, eukaryotic "flagella"). Undulipodial microtubules are still deployed for major cellular processes such as mitosis and meiosis.

Spirochaeta bajacaliforniensis may yield clues towards the origin of tubulin-microtubules in eukaryotic cells. By immunohistochemistry this spirochete was previously shown to have antitubulin activity. The immuno-active protein was partially purified using standard temperature cycling for brain tubulin. Although two proteins (S1 and S2) co-purify (analogous to alpha- and beta-tubulin) only S1 is antitubulin immuno-reactive. The S1 protein (67K) has now been isolated by gel filtration and chromatofocusing. The partial biochemical characterization of S1 protein that has been achieved includes determination of its isoelectric point (6.3), that polymerization is GTP independent, and peptide mapping. Several prokaryotes have been tested for the presence of the S1-type protein, so far only spirochetes have been found to possess it. We are seeking S1 in cyanobacteria reported to contain microtubules.
ORGANIC $^{13}$C VALUES VARY SLIGHTLY WITH SALINITY
IN MICROBIAL MATS AT GUERRERO NEGRO, BAJA CALIFORNIA SUR, MEXICO:
IMPLICATIONS FOR STROMATOLITE $^{13}$C VALUES

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Stromatolites, layered sedimentary rock structures
produced by communities of microorganisms, constitute the
most abundant early evidence of life on earth. Microbial
mats, which are found most frequently in hypersaline
marine or hot spring environments, serve as useful modern
analogs of stromatolitic communities. Our laboratory is
conducting biogeochemical studies of mats to assist our
interpretations of stromatolites.

Organic carbon preserved in Precambrian stromatolites has
$^{13}$C values typically in the range -19 to -35, whereas
microbial mats growing today in marine hypersaline
environments have $^{13}$C values in the range -6 to -14.
This $^{13}$C shift has been attributed to selective
preservation of isotopically light organics, a decline in
atmospheric CO$_2$ levels, or the restriction of microbial
stromatolitic communities to hypersaline environments in
the Phanerozoic due to grazing pressures in lower salinity
environments. The salinity argument requires that the
organic $^{13}$C of microbial mats increases with salinity,
perhaps ranging from -20 to -35 in less saline waters
(having 0 to 3.3% salt) to -6 to -14 in hypersaline waters
(3.3 to 20% or more).

Microbial mats inhabit those Guerrero Negro salt works
ponds with salinities between 5.0 and 13.0%. Principal
mat-forming cyanobacteria are Microcoleus and Phormidium
(5 to 7% salinities) and Aphanothece (9 to 13%).
Inorganic carbon $^{13}$C values range from about +1 (4% salt)
to -4.4 (6.6%) to -5.6 (13.6%). Carbonate alkalinites in
the ponds range from 2.7x10$^{-3}$ moles/L (4%) to 3.6x10$^{-3}$
moles/L (13%). Microcoleus mats' organic $^{13}$C values vary
from -12.4 to -14.2 with no clear dependence upon
salinity. Aphanothece mats appear to be 1 to 2 permil
enriched, relative to Microcoleus mats.

The data suggest that salinity effects are insufficient by
themselves to cause the $^{13}$C differences observed between
Precambrian stromatolites and modern microbial mats.
Session VII

Evolution of Advanced Life
There is increasing evidence that events in space have had direct effects on earth history and on the history of life on earth. Nowhere is this more evident than in mass extinction. The biosphere has undergone repeated devastation caused by relatively short-lived environmental stress, with species kill rates up to 80% (terminal Cretaceous) and 95% (terminal Permian). For five of the mass extinctions, geochemical or other evidence has been reported suggesting large body impact as the cause of the environmental stress producing the extinctions. Furthermore, it has been argued on statistical grounds that the major extinction events are uniformly periodic in geological time. If it is true that large body impact is a principal cause of mass extinctions and if the periodicity is real, then a cosmic driving mechanism is inescapable. However, much more geological, geochemical, paleobiological, and astrophysical work is needed before this hypothesis can be established.

Paleontological datasets have been developed which detail the ranges in geological time of about 4,000 families and 25,000 genera of fossil marine organisms. These datasets provide a unique opportunity for rigorous analysis of the extinction phenomenon and its distribution in time. Analyses to date have concentrated on the most recent 250 million years of the record (Mesozoic and Cenozoic eras). A stationary periodicity of $26 \times 10^6$ years has been established for extinction events in the family data and these events have been confirmed with the generic data. Furthermore, the generic data, having better time resolution, make it possible to pinpoint the events more exactly. This in turn provides a "map" which can be used as a guide for detailed field and laboratory studies of the events themselves. Geochemical and other analyses of the finer scale details of the events should lead ultimately to a clearer understanding of the nature of the environmental stresses and thence to the nature of the extraterrestrial forces involved. Associated with these studies are analyses of other aspects of earth history which may have signatures indicative of extraterrestrial effects. Included are analyses of the history of reversals of the earth's magnetic field over the last 160 million years. There appears to be a statistically robust, stationary periodicity of $30 \times 10^6$ years in the intensity of reversal activity, a periodicity which may be related to the extinction periodicity.
Synoptic studies of the fossil record of complex life on earth indicate increasingly that extinction, and especially mass extinction, have been extremely important driving forces in life's history. Analysis of a new compilation of geologic ranges for 25,000 genera of marine animals suggests that extinction events have been much more frequent in occurrence and variable in magnitude than previously suspected. At least 30 well-documented and potential mass extinctions can be identified in the dataset. The most recent 10 events, distributed over 260-0 ma, exhibit a stationary periodicity of 26.2 ± 1 ma, implicating a cosmological forcing mechanism. Earlier events, especially in the 575-450 ma interval, are more frequent, possibly indicating either (1) a breakdown of periodicity in the more distant past; (2) an as yet undemonstrated diminution (possibly abruptly) of the period length; or (3) frequent aperiodic terrestrial perturbations of a less stable biota superimposed upon the cosmological periodicity.

Other analyses of the generic dataset indicate three aspects of extinction that may be important in governing what are perceived as "progressive" trends in life's history: (1) The average intensity of background extinction decreases markedly through time from about 50%/7 ma between 500 and 575 ma to less than 10%/7 ma over the last 65 ma. This implies that the rate of change of marine faunas (and their possessed morphologies) has been declining since complex life first diversified. (2) Extinction is indiscriminate with respect to oceanic environments, at least through the Paleozoic Era (245-575 ma). No perceptible large-scale differences that are independent of the intrinsic turnover rates within taxa can be found from nearshore to deep-water habitats. (3) Long-established taxa (especially families), many of which appear archaic in aspect, have a disproportionately higher probability of extinction during events of mass extinction than during normal, background intervals. Therefore, since younger taxa have a higher chance of survival, mass extinctions will speed biotic change even more than expected from simple rebounds following random elimination of faunal elements.
Our group, in collaboration with about 30 geologists and paleontologists, is using geochemical and mineralogical techniques to search for evidence of extraterrestrial impacts associated with mass and lesser biological extinction peaks in the geological record. Such geochemical anomalies, particularly those of Ir, can provide very precise relative dating of rock strata in different parts of the world and determine just how synchronously extinctions of different taxa took place and the extent to which evolution changed more or less gradually or abruptly.

Studies of the Cretaceous-Tertiary boundary serve as a baseline for evaluating geochemical data from the extinction horizons. It was found, for example, that two such sections half way around the world from each other which experienced similar marine (reducing) environments have chemical abundances as similar as two samlings of the same section.

Other studies were generally concentrated on rock strata corresponding to the periodic extinction peaks noted by Raup and Sepkoski. A significant iridium anomaly in late Eocene marine sediments associated with extinctions of radiolaria in low latitudes and attributed to an extraterrestrial source is widely distributed in 8-9 sites around the world. Low intensity multiple Ir anomalies have been found in sediments deposited significantly later at the Eocene-Oligocene boundary, but further testing is necessary to determine their origin. An Ir anomaly at the 150 MY Callovian-Oxfordian boundary observed by others was confirmed in samples from Poland. The origin of the anomaly is not yet determined. No Ir above background was found in samples from the British Yorkshire coast of the 80 MY Pliensbachian-Toarcian boundary. No Ir could be detected in samples of the 230 MY Permian-Triassic boundary from the same quarry that Chinese scientists reported Ir. Negotiations are underway to obtain other samples from China from more propitious regions.

No Ir was detected in samples of the Precambrian-Cambrian boundary from the Siberian platform in Russia where Russian scientists reported an Ir anomaly. Work in progress includes samples from the 92 MY Cenomanian-Turonian boundary, the 340 MY Frasnian-Fammenian boundary, and spherule laden strata in the Precambian. A high capacity Iridium Coincidence Spectrometer which is capable of analyzing 20,000 samples per year is under construction.
CLIMATIC CONSEQUENCES OF VERY HIGH CO₂ LEVELS IN EARTH'S EARLY ATMOSPHERE

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Two factors which would have strongly influenced prebiotic evolution and the origin of life were the composition and climate of the early atmosphere. Current theories of atmospheric evolution favor the idea that the primitive atmosphere consisted primarily of CO₂, H₂O, and N₂, with trace amounts of reduced species such as CO and H₂. CO₂ is particularly important because it is an effective infrared absorber which could have warmed the Earth's surface by contributing to the greenhouse effect. It also provides a source for oxygen atoms which would have influenced early atmospheric chemistry. It is therefore useful to try to understand the factors controlling the CO₂ abundance in the early atmosphere, and to model the climatic and photochemical effects of various plausible CO₂ levels.

Earth has approximately 60 bars of carbon dioxide tied up in carbonate rocks, or roughly 2/3 the amount of CO₂ that Venus has in its atmosphere. Two different lines of evidence, one based on thermodynamics and the other on geochemical cycles, indicate that a substantial fraction of this CO₂ (10-20 bars) may have resided in the atmosphere during the first few hundred million years of the Earth's history. A natural question which arises is whether this much CO₂ would have resulted in a runaway greenhouse, that is, an atmosphere which was too hot to allow the existence of liquid water at the surface. One-dimensional radiative/convective model calculations presented here show that the surface temperature of a hypothetical primitive atmosphere containing 20 bars of CO₂ would have been less than 100 °C; thus, no runaway greenhouse should have occurred. The climatic stability of the early atmosphere is a consequence of three factors: reduced solar luminosity at that time, an increase in planetary albedo caused by Rayleigh scattering by CO₂, and the stabilizing effects of moist convection. The latter two factors are sufficient to prevent a CO₂-induced runaway greenhouse on the present Earth as well, for CO₂ levels up to 100 bars. Further studies are being undertaken to determine whether a runaway greenhouse could have occurred during the latter stages of the accretion process and, if so, whether it would have collapsed once the influx of material slowed down.
Session VIII

Search for Extraterrestrial Intelligence
To the current limits of man's observational and theoretical knowledge, there is no evidence that intelligent life has not arisen elsewhere in the universe. Man's instruments are as yet too feeble to show the absence of life elsewhere, but they do provide the possibility of detecting its presence. There may exist communications signals from other civilizations that could be detected with today's technology. Such signals could be intended for internal consumption (such as our own radio, television, radar, etc.) or for wide dissemination in space (navigation beacons, intercivilization communications, broadcasts seeking emerging civilizations, etc.). The microwave portion of the electromagnetic spectrum has the lowest level of naturally occurring background noise, and is hence the most efficient place to conduct long-range communications. For this reason, the microwave region is a good starting point for a search for extraterrestrial intelligence.

A full-time dedicated search for extraterrestrial radio signals of intelligent origin has been in progress at the Ohio State University Radio Observatory since 1973. The radio telescope has a collecting area of 2200 square meters, which is equivalent to a circular dish 175 feet in diameter. The search concentrates on a 500 kHz bandwidth centered on the 1420 MHz hydrogen line, doppler corrected to the galactic standard of rest. A large portion of the sky visible from Ohio has been searched, with particular emphasis on the galactic center region and the M31 Andromeda galaxy. The survey is largely computer-automated, and all data reduction is done in real time. Two distinct populations of signals have been detected. The first is a relatively small number of signals which persist for over a minute and which are clearly extraterrestrial in origin. The second is a large number of signals which persist less than 10 seconds whose locations are anticorrelated with the galactic plane but show clumps along the galactic axis. None of these signals have been observed to recur, despite repeated observations. The cause of these signals has not yet been determined.
We are developing an automated system designed to perform a real time search for narrow band radio signals in the spectra of sources in a regularly scheduled, non-SETI astronomical observing program. Because we expect this system to run continuously without requiring dedicated observing time, we hope to survey a large portion of the sky at high sensitivity and low cost. This system will compute the power spectrum using a 65,536 channel fast Fourier transform processor with a real time bandwidth of 128 KHz and 2 Hz per channel resolution. After searching for peaks in a 100 KHz portion of the radio telescope's IF band, this system will move to the next 100 KHz portion using a programmable frequency synthesizer; when the whole IF band has been scanned, the process will start again. Unidentified peaks in the power spectra are candidates for further study and their celestial coordinates will be recorded along with the time and power, IF and RF frequency, and bandwidth of the peak.

Most of the hardware has now been developed and we are in the process of finalizing the machine software. We are also in the process of developing software to process the data tapes. We are investigating a number of means for identifying and rejecting power spectra peaks which have a high likelihood of being non-useful. We expect to start a trial run of the instrumentation at the Hat Creek Radio Observatory in Northern California in late summer.
AN INFRARED SEARCH FOR
EXTRATERRESTRIAL LASER SIGNALS

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The focus of NASA's SETI program is on microwave frequencies, where receivers fundamentally have the best sensitivity for the detection of narrowband signals. Such receivers, when coupled to existing radio telescopes, form an optimum system for broad area searches over the sky. For a directed search, however, such as toward 100 selected stars, it can be shown that infrared frequencies are equally as effective for maintaining an interstellar communication link. Although infrared receivers have higher noise levels, the directivity of infrared telescopes is also higher. As a result, the signal-to-noise ratios of radio and infrared links are quite comparable. In addition, the sensitivities of both receiving systems, even at terrestrial levels of technology, are quite close to their respective fundamental limits: background thermal noise for the radio system and quantum noise for the infrared receiver. Consequently, the choice of an optimum communication frequency may well be determined by the power and efficiency levels of available transmitters. In the infrared, CO₂ laser transmitters with >1 MW power can already be built on Earth. For a slightly more advanced civilization, a similar but enormously more powerful laser may be possible by using an entire planetary atmosphere rich in CO₂. Because of these possibilities and our own ignorance of what is really the "optimum" frequency, a search for narrowband infrared signals should be a part of a balanced SETI program.

Detection of narrowband infrared signals is best done with a laser heterodyne receiver similar in function to a microwave spectral line receiver. We have built such a receiver for astrophysical observations at 30 THz (10 microns) and now are adapting the spectrometer for SETI work. The receiver uses a small CO₂ laser as the local oscillator, a HgCdTe diode as the photomixer, and a multichannel intermediate frequency (IF) filterbank. An advanced multichannel IF processor is now being built to detect infrared line radiation in 1000 spectral channels each 1 MHz wide. When completed this processor will be used with a ground-based telescope next year for a survey of several hundred selected stars for narrowband CO₂ laser signals at 30 THz.
USING THE IRAS DATA TO SEARCH IN THE ASTEROID BELT
FOR ANY POTENTIAL EVIDENCE OF GALACTIC COLONIZATION

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The end product of the biological evolution seems to be the appearance of technological civilizations, which are characterized by their superior technology that supersedes their biological capabilities. The Search for Extraterrestrial Intelligence (SETI) has gained in recent years wide scientific recognition (the first IAU Symposium on the Search for Extraterrestrial Life was held with great success in Boston, June 18-21, 1984, and was cosponsored by the IAF/IAA, COSPAR, ISSOL, IUBS, and NASA), and strong momentum in its experimental programs.

The concept of galactic colonization has been debated extensively, with opinions ranging from the impossible to the inevitable, but without a clear resolution. Answers can be obtained only with experimental tests and not with endless debates. One of the alternative scenarios is that the colonization of the Galaxy, including our solar system, occurred a long time ago, but for some reason they have chosen not to reveal their presence to us. A test of this theory would be to search for large space colonies in the asteroid belt, which is an ideal source of raw materials for a space-borne civilization, and where they could have easily remained undetected among the thousands of natural asteroids.

The catalogue of solar system objects obtained from the Infrared Astronomy Satellite (IRAS) observations at 12, 25, 60, and 100 microns, is an ideal source for such a search. The catalogue is expected to be ready at the end of 1985 and will contain more than 10,000 objects. I plan to go carefully through this catalogue, and possibly even through earlier and larger data banks, in search for objects with a peculiar infrared spectrum that might indicate an artificial origin. If any such candidates are found, they will be subjected to further optical and radio tests.

In a comprehensive and universal search for extraterrestrial intelligence, it seems prudent not to forget to check also our own back yard.
OVERVIEW OF THE NASA SETI PROGRAM

Bernard M. Oliver*
NASA Ames Research Center

Scientific discoveries over the past 50 years have completely reversed our opinion as to the prevalence of life in the universe. No longer is the sun's retinue of planets thought to be unique, nor the origin of life on a fertile planet thought to be unlikely. In fact there may be on the order of $10^{10}$ potential life sites in the Galaxy. If life on only 1% of these has evolved intelligence we are not only not alone, we are in a crowd!

The only practical way we know to find other civilizations around other stars is to detect signals they may be radiating either for their own purposes or to attract our attention. The NASA Search for Extraterrestrial Intelligence (SETI) program plan is to scan the microwave window from 1 to 10 GHz with existing radio telescopes and sophisticated signal processing equipment looking for narrow band features that might represent artificial signals.

A microwave spectrometer has been built and is being field tested. A pattern recognition computer to search for drifting CW signals and pulse trains in the output spectra is being designed. Equipment to characterize the radio frequency interference environment has also been built.

The plan is to complete the hardware and software by FY 88. Then, with increased funding, this equipment will be replicated in VLSI form. Observations, both a complete sky survey and a search of nearby solar type stars, will begin in about 1990.

The sensitivity, sky and frequency coverage of this search will far exceed all previous searches but will still be inadequate to detect inadvertent leakage signals from any but the closest stars. We will be testing the hypotheses that very powerful signals exist or that signals are being beamed at us. To detect the kinds of signals we radiate at distances of 100 light years will require a collecting area kilometers in diameter.
Stanford Hardware Development Program

Allen Peterson, Ivan Linscott* and Jim Burr
Radioscience Laboratory, Stanford University

We are developing architectures for high performance, digital signal processing, particularly for high resolution, wide band spectrum analysis. These developments are intended to provide instrumentation for NASA's Search for Extraterrestrial Intelligence (SETI) program. Our approach to real time signal processing is both formal and experimental. We are investigating the efficient organization and optimal scheduling of signal processing algorithms. This work is complemented by efforts in processor architecture design and implementation. Even though we have limited our scope to real time signal processing, our microcoded signal processors are capable of performing more general purpose computations at very high speeds.

We currently are testing a high resolution, multichannel spectrometer that incorporates special purpose microcoded signal processors. We are designing a more general purpose signal processor for the data from the multichannel spectrometer, to function as the processing element in a highly concurrent machine. The processor performance required for the spectrometer is in the range of 1000 to 10,000 million instructions per second (MIPS). We are interested in multiple node processor configurations where each node performs at 100 MIPS. The nodes are microprogrammable and are interconnected through a network with high bandwidth for neighboring nodes, and medium bandwidth for nodes at "larger" distance. We are proceeding with the implementation of both the current multichannel spectrometer and the signal processor as VLSI CMOS chip sets.
Goldstone Field Test Activities: Target Search

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University of California Berkeley Astronomy Department
SETI Institute

In March of this year prototype SETI equipment was installed at DSS13, the 26 meter R&D antenna at NASA's Goldstone complex of satellite tracking dishes. The SETI equipment will remain at this site at least through the end of the summer so that the hardware and software developed for signal detection and recognition can be fully tested in a dynamic observatory environment. The field tests are expected to help us better understand which strategies for observing and which signal recognition algorithms perform best in the presence of strong man-made interfering signals (RFI) and natural astronomical sources.

The SETI prototype consists of a 74000 channel, wirewrap implemented, multi-channel spectrum analyzer (MCSA) mated to a VAX 11/750 computer. The VAX serves as a host for the signal recognition algorithms and directs communications with the antenna control system. A SUN Workstation provides real time data display. A scanning spectrometer, connected to a small rotating dish under independent control of a dedicated mini-computer, provides an RFI site surveillance capability over the frequency range of 1-10 GHz. This equipment has been designed for use in a bi-modal SETI search strategy and is intended to be flexible enough to address the special requirements of both a selected target search mode and a survey of the entire sky.

During a search that looks in the vicinity of nearby solar-type stars, data from one source may be acquired for up to 1000 seconds. This time allows a search for a variety of signal types, in particular, narrowband continuously present signals (CW) at a single frequency (or drifting slowly in frequency) and narrowband pulses that repeat with a regular periodicity somewhere between a few milliseconds and a few hundred seconds. These pulses may also be changing their frequency slowly in time. The field tests give us the opportunity to investigate the effective sensitivity of such a long sidereal observing track in view of the elevation dependent system temperature and RFI contribution. How close to the horizon can we expect to operate at Goldstone, or other sites? In the presence of strong RFI, is it best to remain on source and switch to another band of frequencies, or is it better to remain on frequency and slew to a source in a different part of the sky? Can astronomical sources be easily identified? What are the effects of strong, but transient, RFI on algorithms optimized for recognition of weak pulses or CW signals? Does RFI recognition and rejection become easier if the receiver's local oscillators are not corrected to compensate for the orbital and rotational components of the Earth's motion relative to the target source? How severely will the scintillation caused by the interplanetary and interstellar plasma modulate a distant RFI signal and how well do the algorithms we have developed function in the face of this amplitude modulation? What is the best strategy for obtaining a "reference" spectrum, or fitting a baseline to the channel outputs at a given frequency resolution? What will be the actual percentage of time spent slewing between sources, observing reference sources and making repairs to the overall system? What is the optimum way to schedule the target observations in order to maximize the efficiency of the SETI search and the chances for radio astronomical fallout? How long will it actually take to search the nearest 1000 solar-type over a range of frequencies from 1 to 3 GHz?
The goals are to conduct a research and development program aimed at determining the most effective way to do SETI within the constraints of current technology and estimated budgets. The general search strategy adopted is that which is recommended by the SETI Science Working Group (NASA Technical Paper 2244, Eds. F. Drake, J.H. Wolfe, and C.L. Seeger, October 1983).

The strategy for an all sky survey for SETI has been further developed over the last year. Scan patterns, scan rates, and signal detection algorithms have been developed. Spectral power measurement instrumentation has been tested at the Venus Station of the Goldstone Deep Space Communication Complex. A specially designed radio frequency interference measurement system was built and installed at the Venus Station. A Data Base Management system for storage and retrieval of the RFI data has been partially implemented on a VAX 750 computer at the Jet Propulsion Laboratory.
JPL'S ROLE IN THE SETI PROGRAM

Michael J. Klein*
NASA Jet Propulsion Laboratory

The goal of the JPL SETI Team is to develop the strategies and the instrumentation required to carry out an effective, yet affordable, SETI Microwave Observing Program. The primary responsibility for JPL is the development and implementation of the Sky Survey component of the bimodal search program recommended by the SETI Science Working Group (NASA Technical Paper 2244, 1983). JPL is also responsible for the design and implementation of microwave analog instrumentation (including antenna feed systems, low noise RF amplifiers, antenna monitor and control interfaces, etc.) to cover the microwave window for the Sky Survey and the Target Search observations.

The primary site for the current SETI Field Test activity is the Venus Station of the Goldstone Deep Space Communication Complex. A significant fraction of the JPL work units has been directed toward the support of the Field Tests. A SETI controller was constructed and installed so that pre-programmed and real time SETI monitor and control data can be sent to and from the station controller. This unit will be interfaced with the MCSA. A SETI Hardware Handbook was prepared to describe the various systems that will be used by the project at the Venus Station; the handbook is frequently being expanded and updated. The 65,000 channel FFT Spectrum analyzer in the RFI Surveillance System was modified to permit operation with variable resolutions (300 Hz to less than 1 Hz) and with real-time accumulation, which will enhance the capability of the system for testing Sky Survey search strategies and signal detection algorithms.

Progress was also made in the preparation of a SETI Implementation Plan for the Deep Space Network (DSN), which will be called upon to support the Microwave Observing Program through the use of the DSN antennas and low-noise receiving systems. Modifications will be necessary to meet the radio frequency coverage and the antenna monitor and control functions that are required.
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This symposium was held at the NASA Ames Research Center, Moffet Field, California, July 23-26, 1985. The NASA Exobiology principal investigators reported their recent research findings. Scientific papers were presented in the following areas: cosmic evolution of biogenic compounds, prebiotic evolution (planetary and molecular), early evolution of life (biological and geochemical), evolution of advanced life, solar system exploration, and the Search for Extraterrestrial Intelligence (SETI).