
SETI Institute
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Planetary Biology, Evolution, and Intelligence

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SETI INSTITUTE NAI PROPOSAL

EXECUTIVE SUMMARY

The Astrobiology Roadmap asks three fundamental questions: (1) How does life begin and evolve; (2) Does life exist elsewhere in the universe? and (3) What is the future of life on Earth and beyond? The SETI Institute will conduct a set of coupled research projects in the co-evolution of life and its planetary environment, beginning with fundamental ancient transitions that ultimately made complex life possible on Earth. We conclude with a project that brings together many of these investigations into an examination of the suitability of planets orbiting M stars for either single-celled or more complex life. Results will help the next generation scientific Search for Extraterrestrial Intelligence (SETI) choose the 10^5 to 10^6 target stars that it will survey for signs of technical civilizations using the new Allen Telescope Array (ATA) being built by the SETI Institute in partnership with the University of California, Berkeley.

SETI is a natural part of the continuum of research that comprises astrobiology. This is recognized explicitly in the Astrobiology Roadmap, which calls for a strategy "for recognizing novel biosignatures" that "ultimately should accommodate a diversity of habitable conditions, biota and technologies in the universe that probably exceeds the diversity observed on Earth." From the life detection point of view, the Roadmap notes that "although technology is probably much more rare than life in the universe, its associated biosignatures perhaps enjoy a much higher 'signal-to-noise' ratio. Accordingly, current methods should be further developed and novel methods should be identified for detecting electromagnetic radiation or other diagnostic artifacts that indicate remote technological civilizations."

Overview of Proposed Research

The research in the Institute's proposal intends to elucidate the co-evolution of life and its planetary environment, typically investigating global-scale processes that have shaped, and been shaped by, both. Throughout, we recognize the importance of pursuing the planetary evolution aspects of this research in the context of comparative planetology: since laboratory experiments are impossible over some of the time and spatial scales relevant to early Earth, we must supplement laboratory data with the insight as we can gain by exploring extraterrestrial environments that may provide partial analogs to the early Earth environment and its processes.

We begin by proposing two new investigations into the oxidation of early Earth's environment. While the biological aspects of this "oxygen transition" have been recently emphasized, both mechanisms to be explored here (peroxy in rocks [Drs. Friedemann Freund and Lynn Rothschild] and aerosol formation in the atmosphere [Dr. Emma Bakes], building on an analogy to processes now occurring in the atmosphere of Saturn's moon Titan) are non-biological. If such mechanisms were to be shown to be quantitatively significant, it would suggest that the oxygen transition on an Earth-like world could take place independently of the invention of any particular metabolic pathways (such as photosynthesis or methanogenesis) that have been proposed as driving this transition. Since Earth's oxygen transition ultimately set the stage for the oxygen-based metabolism evidently essential for metazoa, understanding this transition is crucial to elucidating both Earth's evolution and the evolution of complex (including intelligent) life. Our geological investigations are tightly coupled with microbiological experiments to understand the extent to which the proposed mechanism might have led to the evolutionary invention of oxidant protective strategies and even aerobic metabolism.

One of the major sinks for oxygen on early Earth would have been reduced iron. At the same time iron could have provided shielding against ultraviolet (UV) light that would have been reaching Earth's surface in the absence of the ozone shield generated by atmospheric oxygen. Nanophase ferric oxide minerals in solution could provide a sunscreen against UV while allowing the transmission of visible light, in turn making the evolution of at least some photosynthesic organisms possible. We will test [Drs. Janice Bishop and Lynn Rothschild] this hypothesis through coupled mineralogical and microbiological work in both the lab and the field, and examine its implications not only for Earth but for Mars as well—with an emphasis on implications for upcoming spacecraft observations.

The survival of microorganisms in very high UV environments can also be tested empirically through the exploration of Earth's highest altitude lakes and ponds, in Bolivia and Chile. We propose [Drs. Nathalie Cabrol and Edmond Grin] a series of investigations of these lakes to examine the strategies employed by these microorganisms.

Just as global-scale changes in oxygen (or iron) were critical for the early biosphere, so too would have been global processes involving other key "biogenic" elements such as carbon [Dr. Bakes] or nitrogen [Drs. Rocco Mancinelli, Amos Banin, David Summers, and Bishun Khare]. We propose coupled laboratory and field research to understand the partitioning of nitrogen on early Earth—and on Mars—between different possible reservoirs, and the abiotic to biotic transition in this cycling.

The work described so far examines the evolution of planetary surface habitability. With the recognition that a subsurface ocean likely exists on Jupiter's moon Europa, we know that habitability in possibly entirely subsurface environments must also be explored. We propose spacecraft data analysis and modeling to examine the geology of Europa and its implications for the free energy sources that would be needed to power a europan biosphere [Drs. Cynthia Phillips and Christopher Chyba]. We will then couple these results with terrestrial analog work [Chyba] and direct low-temperature laboratory experiments [Dr. Max Bernstein] to make predictions about the possible abundance and survivability of any oceanic biomarkers that might reach Europa's surface through active geology. These results will have implications for astrobiological exploration of Europa from either an orbiter or a surface lander.

Finally, we suggest research (Drs. Peter Backus, Jill Tarter, and Chyba) to examine the prospects of planets orbiting dwarf M stars being habitable for either microscopic or complex life. The results of this work will directly influence the strategy employed in the next generation SETI search program to begin in 2005.

The SETI Institute

The SETI Institute was founded in 1984 as a nonprofit scientific research institution. From its beginning, its mission has been to explore the origin, nature and prevalence of life in the universe, and to explain this science to the public. The Institute may be best known for its ongoing Search for Extraterrestrial Intelligence (SETI) programs, but the study of virtually all other aspects of astrobiology has been part of our mandate from the beginning.

The Institute employs nearly 120 individuals. Sixty-four of these are employed through the Center for the Study of Life in the Universe, directed by Dr. Frank Drake. Another twenty-six scientists and engineers are employed within the Center for SETI Studies, directed by Dr. Jill Tarter, who is a Co-Investigator on this grant. The remainder are in administration and education. The Institute has a public/private partnership with the University of California Berkeley, with which it is currently building the Allen Telescope Array to conduct the next generation of SETI searches. Funding for the Institute's SETI projects is almost entirely through private funds, whereas research within the Center for the Study of Life in the Universe is nearly entirely funded through peer-reviewed grants. Several of the projects proposed here have so far been funded at the pilot project level through private resources made available by the Institute. This proposal therefore represents a private/public partnership with the opportunity for peer-reviewed funding to leverage previous substantial initial private investments into major research accomplishments.

Strengthening the Community

The SETI Institute's EPO programs have a long and successful history of engaging our scientists and educators with teachers and the general public. The Institute's proposed NAI-EPO program [Ms. Edna DeVore] will comprise four major activities: (1) conduct professional development for high school science teachers implementing *Voyages Through Time (VTT)*, an integrated astrobiology curriculum developed by the SETI Institute, and make VTT a resource available to the entire NAI by inviting other NAI teams to participate in the professional development program; (2) collaborate with the California Academy of Sciences to plan and develop new exhibits and to support and participate in education and outreach programs with CAS throughout the NAI membership period; (3) facilitate education outreach, media opportunities, and public event appearances for Institute NAI scientists; and (4) participate in the NAI EPO network and NASA OSS and Education Activities.

For much of the public, one of the topics of greatest interest in astrobiology is the scientific search for intelligent life. While our research and EPO activities span the range of astrobiology, the SETI Institute is unique in being able to bring forefront scientific research on this issue to the NASA Astrobiology Institute.

Strategic Planning and Management

Professor Christopher Chyba is the Principal Investigator for this proposal. Chyba holds the endowed Carl Sagan Chair for the Study of Life in the Universe at the SETI Institute. Chyba is also an associate professor (research) in the Department of Geological and Environmental Sciences at Stanford University. He teaches undergraduate and graduate courses in astrobiology at Stanford, and is currently the PhD thesis advisor for Mr. Kevin Hand.

Chyba has extensive service as chair or member of numerous NASA and other federal committees, and as a leader and integrator of diverse research projects at the SETI Institute. In 1996 he received a Presidential Early Career Award and in October 2001 was awarded a MacArthur Fellowship for his work in both astrobiology and international security.

Chyba, Mancinelli and DeVore will constitute an ongoing strategic planning and management “troika” for this proposal.

Over the past two years, the Center for the Study of Life in the Universe at the SETI Institute has carried out, using private funding, a strategic planning process that demonstrates its ability to bring together research scientists in interdisciplinary and successful ways. Co-chaired by Chyba and USC geomicrobiologist Ken Nealson, this Strategic Planning Group (SPG) brought together some two dozen scientists and engineers to range across the field of astrobiology and identify new areas of innovative research ripe for pursuit by the SETI Institute.

The projects proposed here will benefit from ongoing NAI-SETI workshops at the Institute that the PI will continue to host. The Co-Investigators for this proposal all have experience in being principal investigators in their own research. No “micromanagement” by the PI of this proposal will be necessary. Rather, the PI’s role will be to ensure communication, cooperation, and synergy among the various research projects.

1. Introduction to Research & Management Plan: Astrobiology and Intelligent Life

The three fundamental questions of astrobiology in the Astrobiology Roadmap are: (1) How does life begin and evolve; (2) Does life exist elsewhere in the universe? and (3) What is the future of life on Earth and beyond? This proposal pursues a unique approach to these questions that has not been previously represented within the NASA Astrobiology Institute (NAI). We propose a set of coupled research projects in the co-evolution of life and its planetary environment, beginning with fundamental ancient transitions that ultimately made complex life possible on Earth., Our proposal concludes with a project that will bring together our knowledge about the stellar and planetary evolution requirements for the origin of life through the evolution of advanced technical intelligence. Results will help the next generation scientific Search for Extraterrestrial Intelligence (SETI) choose the 10^5 to 10^6 target stars that it will survey for signs of technical civilizations using the new Allen Telescope Array (ATA) being built by the SETI Institute in partnership with the University of California, Berkeley.

SETI searches should be pursued in the context of an understanding of the origin and evolution of life, from the simplest single-celled organisms to complex communicating metazoa. Just as studies of the microbial deep biosphere on Earth have informed the search for extraterrestrial life in subsurface environments on Mars or Europa, so can the search for extraterrestrial intelligence be informed by studies of planetary habitability.

SETI is a natural part of the continuum of research that comprises astrobiology. This is recognized explicitly in the Astrobiology Roadmap, which calls for a strategy "for recognizing novel biosignatures" that "ultimately should accommodate a diversity of habitable conditions, biota and technologies in the universe that probably exceeds the diversity observed on Earth." From the life detection point of view, the Roadmap notes that "although technology is probably much more rare than life in the universe, its associated biosignatures perhaps enjoy a much higher 'signal-to-noise' ratio. Accordingly, current methods should be further developed and novel methods should be identified for detecting electromagnetic radiation or other diagnostic artifacts that indicate remote technological civilizations." As will be seen below, this is exactly what the SETI Institute has been doing, and will continue to do in new ways with support from this grant.

Consistent with the Astrobiology Roadmap, funding SETI-related activities is now embraced by NASA. As NASA Associate Administrator Ed Weiler told Congress in 2001, (Subcommittee on Space and Aeronautics 2001), "NASA is no longer prohibited by any congressional language from considering or funding SETI research, so SETI is currently eligible and considered fairly under peer review for NASA opportunities."

1.1 Overview of Proposed Research

The research in this proposal intends to elucidate the co-evolution of life and its planetary environment, typically investigating global-scale processes that have shaped, and been shaped by, both. Throughout, we recognize the importance of pursuing the planetary evolution aspects of this research in the context of comparative planetology: since laboratory experiments are impossible over some of the time and spatial scales relevant to early Earth, we must supplement laboratory data with the insight as we can gain by exploring extraterrestrial environments that may provide partial analogs to the early Earth environment and its processes. (In this overview, we leave out citations to the literature; full citations are provided throughout the text of the proposal.)

We begin by proposing two new investigations into the oxidation of early Earth's environment (Secs. 2 and 3). While the biological aspects of this "oxygen transition" have been recently emphasized, both mechanisms to be explored here (peroxy in rocks and aerosol formation in the atmosphere, building on an analogy to processes now occurring in the atmosphere of Saturn's moon Titan) are non-biological. If such mechanisms were to be shown to be quantitatively significant, it would suggest that the oxygen transition on an Earth-like world could take place independently of the invention of any particular metabolic pathways (such as photosynthesis or methanogenesis) that have been proposed as driving this transition. Since Earth's oxygen transition ultimately set the stage for the oxygen-based metabolism evidently essential for metazoa, understanding this transition is crucial to elucidating both Earth's evolution and the evolution of complex (or even intelligent) life. Our geological investigations in Sec. 2 are tightly coupled with microbiological experiments to understand the extent to which the proposed mechanism might have led to the evolutionary invention of oxidant protective strategies and even aerobic metabolism.

One of the major sinks for oxygen on early Earth would have been reduced iron. At the same time iron could have provided shielding against ultraviolet (UV) light that would have been reaching Earth's surface in the absence of the ozone shield generated by atmospheric oxygen. Nanophase ferric oxide minerals in solution could provide a sunscreen against UV while allowing the transmission of visible light, in turn making the evolution of at least some photosynthesic organisms possible. We will test (Sec. 4) this hypothesis through coupled mineralogical and microbiological work in both the lab and the field, and examine its implications not only for Earth but for Mars as well—with an emphasis on implications for upcoming spacecraft observations. This work could provide insight into a key step in terrestrial biological evolution that also likely played an important role in the oxidation of Earth's surface environment.

The survival of microorganisms in very high UV environments can also be tested empirically through the exploration of Earth's highest altitude lakes and ponds, in Bolivia and Chile. We propose (Sec. 5) a series of investigations of these lakes to examine the strategies employed by these microorganisms. This work will also provide insight into conditions prevailing on lakes that may have existed in early Mars history, and therefore help inform Mars exploration.

Just as global-scale changes in oxygen (or iron) were critical for the early biosphere, so too would have been global processes involving other key "biogenic" elements such as carbon (Sec. 3) or nitrogen (Sec. 6 and 7). We propose coupled laboratory and field research to understand the partitioning of nitrogen on early Earth—and on Mars—between different possible reservoirs, and the abiotic to biotic transition in this cycling.

The work described so far examines interactions among a world's geology, atmosphere, oceans and biology in the evolution of that world's surface habitability. With the recognition that a subsurface ocean likely exists on Jupiter's moon Europa, we now know that habitability in possibly entirely subsurface environments must also be explored. We propose work to examine the geology of Europa and its implications for the free energy sources that would be needed to power a Europan biosphere (Secs. 8 and 9). This work will make use of both spacecraft data and modeling. We will then couple these results with terrestrial analog work (Sec. 9) and direct low-temperature laboratory experiments (Sec. 10) to make predictions about the possible abundance and survivability of any oceanic biomarkers that might reach Europa's surface through active geology. These results will have implications for astrobiological exploration of Europa from either an orbiter or a surface lander.

Finally, the proposal concludes (Sec. 11) with research (to include interdisciplinary workshops) to examine the prospects of planets orbiting dwarf M stars being habitable for either microscopic or complex life. The results of this work will directly influence the strategy to be employed in the next generation search for extraterrestrial intelligence, to begin in 2005.

1.2 The SETI Institute

The SETI Institute was founded in 1984 as a nonprofit scientific research institution. From its beginning, its mission has been to explore the origin, nature and prevalence of life in the universe, and to explain this science to the public. The Institute may be best known for its ongoing Search for Extraterrestrial Intelligence (SETI) programs, but the study of virtually all other aspects of astrobiology has been part of our mandate from the beginning. Indeed, Dr. Chuck Klein, former head of the Viking spacecraft biology team, joined the Institute in 1985 as our first "Life in the Universe" scientist. Since its founding, the SETI Institute has managed more than $136 million in private and government research funds. Our current annual budget is $21 million, of which about $5.4 million is in the form of funding for peer-reviewed grants.

The Institute employs nearly 120 individuals. Sixty-four of these are employed through the Center for the Study of Life in the Universe, directed by Dr. Christopher Chyba, PI on this grant. Another twenty-six scientists and engineers are employed within the Center for SETI Studies, directed by Dr. Jill Tarter, who is a Co-Investigator on this grant. The remainder are in administration and education. The Institute has a public/private partnership with the University of California Berkeley, with which it is currently building the Allen Telescope Array to conduct the next generation of SETI searches. Funding for the Institute's SETI projects is now almost entirely through private funds, whereas research within the Center for the Study of Life in the Universe is nearly entirely funded through peer-reviewed grants. This proposal appropriately brings both research sides of the Institute together, as they naturally both fall within the study of astrobiology. Five of the thirteen projects proposed here have so far been funded at the pilot project level through private resources made available by the Institute, typically through funds from Chyba's Sagan Chair. This proposal therefore represents a true private/public partnership, with the opportunity for peer-reviewed funding to leverage previous substantial initial private investments into major research accomplishments.

The PI and two Co-Is on this proposal request no salary support, but other SETI Institute employees hold "soft-money" positions and therefore request some salary to perform the research proposed. However, SETI Institute overhead (which stands at 20%) is so low compared to other government or academic institutions (often 50% or higher) that our research/cost ratio remains extremely competitive.

1.3 Principal Investigator

Professor Christopher Chyba is the Principal Investigator for this proposal. Chyba holds the endowed Carl Sagan Chair for the Study of Life in the Universe at the SETI Institute. Chyba is also an associate professor (research) in the Department of Geological and Environmental Sciences at Stanford University. He teaches undergraduate and graduate courses on "The Origins of Life in the Solar System" at Stanford, and currently supervises three graduate students and two undergraduates in their research. Chyba serves as the PhD thesis advisor for Mr. Kevin Hand.

Chyba has extensive service on NASA and other federal committees (e.g. chair of the Science Definition Team for NASA's Europa Orbiter Mission, chair NASA's Solar System Exploration Subcommittee, member Executive Committee, NASA's Space Science Advisory Committee, member NASA's exobiology review panel, member National Academy of Science's Committee on International Security and Arms Control) and is a leader and integrator of diverse research projects at the SETI Institute. Chyba's own educational background demonstrates the kind of interdisciplinary science that characterizes astrobiology. His PhD is in astronomy (planetary science), from Cornell University where Carl Sagan was his thesis advisor. His undergraduate degrees are in physics and mathematics, and he also holds a graduate degree (MPhil) in the history and philosophy of science. His earliest peer-reviewed publications were in general relativity, but beginning in 1985 his research shifted to planetary science and, especially, exobiology (as it was then called). His biology training includes the intensive summer courses at MBL Woods Hole in Microbial Diversity (250 laboratory hours, 110 lecture hours) and Molecular Evolution (course run by Mitch Sogin). In 1996 he received a Presidential Early Career Award and in October 2001 was awarded a MacArthur Fellowship for his work in both astrobiology and international security.

1.4 Strategic Planning and Management

Over the past two years, the Center for the Study of Life in the Universe at the SETI Institute has carried out, using private funding, a strategic planning process that showcases its ability to bring together research scientists in interdisciplinary and successful ways. Co-chaired by Chyba and USC geomicrobiologist Ken Nealson, this Strategic Planning Group (SPG) brought together some two dozen scientists and engineers in both full plenary and breakout workshops to range across the field of astrobiology and identify new areas of innovative research ripe for pursuit by the SETI Institute. Members of the group included Barry Blumberg (NAI), Leslie Orgel (Salk), Simon Conway Morris (U. Cambridge), Bill Schopf (UCLA), Lori Marino (Emory), Dan McShea (Duke), Pascale Ehrenfreund (Leiden), Eric Mathur (Diversa Corporation), Jay Melosh (U. Arizona) and many others. The research proposed in section 11 of this proposal is a direct outcome of ideas discussed and pursued at these meetings, then funded at the pilot level by Chyba out of his privately funded Sagan Chair budget.

This SPG paralleled an analogous effort by the Institute to plan its next 20 years of SETI research. In this effort, the Institute brought together 40 scientists and engineers into a SETI Science and Technology Working Group (STWG) that ultimately proposed three major projects. The first of these, the Allen Telescope Array of over three hundred fifty six-meter dishes, is now being built with private funding. The STWG has published its strategic and technical studies in the 550-page book, *SETI 2020: A Roadmap for the Search for Extraterrestrial Intelligence* (Ekers et al. 2002). The projects proposed here will benefit from ongoing NAI-SETI workshops at the Institute that the PI will host, that all Co-Investigators will be expected to attend whenever possible, and that will be open to outside scientists. The Institute already hosts an ongoing colloquium series; these will be continued but focused on reports from proposal Co-Investigators (and associated graduate students) on their ongoing research. Such team group meetings have already been of great value in formulating this proposal, and it will be clear from the tight coupling of many of the sections of this proposal that the Co-Investigators have and will strongly benefit from ongoing collaborations among the leaders of different research tasks. Moreover, as part of Sec. 11 of this proposal, more specialized workshops on planetary habitability around M stars will be held at the Institute. These will necessarily draw on the leading Co-Investigators of several sections of this proposal.

Despite these coordination efforts, it should be emphasized that the Co-Investigators for this proposal all have experience, typically years to decades of experience, in being principal investigators in their own research. No “micromanagement” by the PI of this proposal will be necessary. Rather, the PI’s role will be to ensure communication, cooperation, and synergy among the various research projects. The PI and the Institute have done this quite successfully before, and will ensure that that in this case as well the whole will be greater than the sum of the parts.

1.5 Building the Astrobiology Community

The goal of the proposed Education and Public Outreach (EPO) activities is to share the cutting-edge research and discoveries of astrobiology with educators and the public in order to inspire students to pursue careers in science, technology, engineering and mathematics, and to contribute to general science literacy. The proposed EPO activities will focus on these key audiences: high school science teachers at schools with underserved students in urban, rural and minority communities; science museum visitors--students, teachers, and families; and the general public via the media, lectures, and events. The SETI Institute's EPO programs have a long and successful history of engaging our scientists and educators with these audiences in formal and informal education as well as public outreach.

The Institute's proposed NAI-EPO program will comprise five major activities: (1) conduct professional development for high school science teachers implementing *Voyages Through Time (VTT)*, an integrated astrobiology curriculum developed by the SETI Institute, and make VTT a resource available to the entire NAI by inviting other NAI teams to participate in the professional development program; (2) collaborate with the California Academy of Sciences to plan and develop new exhibits and to support and participate in education and outreach programs with CAS throughout the NAI membership period; (3) facilitate education outreach, media opportunities, and public event appearances for Institute NAI scientists as a part of our ongoing outreach activities; and (4) participate in the NAI EPO network and NASA OSS and Education Activities.

For much of the public, one of the topics of greatest interest in astrobiology is the scientific search for intelligent life—this is a natural first interpretation of the question “Are we alone?”. While our research and EPO activities span the range of astrobiology, the SETI Institute is unique in being able to bring forefront scientific research on these issues to the NASA Astrobiology Institute.

2. Oxygen on Early Earth: A New Geological Hypothesis

Life originated early in Earth’s history. At that time the atmosphere was anoxic, and the conditions were far more reducing than today. Over the period of the next two billion years or more, the Earth system became slowly oxidized (Holland 1984; Kasting 1993; Kasting 2001; Kump et al. 2001; Wiechert 2002). The reasons for this evolution towards an ever more oxidized state remain major topics of investigation. The answer is of major significance to astrobiology for a host of reasons, ranging from the evolution of defensive mechanisms for life to protect itself against assault by oxidants, to the development of a UV-filtering ozone shield, to the availability of a number of electron acceptors for microbial metabolism, as well as the availability of molecular oxygen and its implications for the possibility of metazoa, and ultimately even intelligent life.

There are two important and related questions: (1) How was the oxygen produced that drove Earth's surface environment to a more oxidized state? (2) To what extent and how did early life forms participate in this transition?

On early Earth, the oxygen level of the atmosphere was buffered by ferrous iron (Fe^{2+}), dissolved in, and continuously washed into, the ocean through weathering of the highly reduced, mafic and ultramafic rocks that dominated the early land masses. Over ~10^9 yr the Fe^{2+} oxidized to ferric iron (Fe^{3+}), consuming an estimated ~10^{12} g O_2/yr in the process (Holland 1984). This led to the worldwide precipitation of banded iron formations (BIFs). During this time the O_2 partial pressure in the atmosphere rose slowly. Later, atmospheric O_2 rose to a level that is comparable to its present partial pressure.

Many physical or physico-chemical processes have been evaluated as possible causes for the slow oxidation of the early Earth system. These include photo-dissociation of H_2O in the uppermost atmosphere by solar hard ultraviolet radiation followed by H_2 escape to space (Hunten et al. 1989) or photo-oxidation of Fe^{2+} to Fe^{3+} in a thin surface layer of the ocean (Braterman et al. 1983). However, these reactions and related processes seem inadequate to account for the flux of O_2 needed (Holland 1984). Similarly, O_2 and H_2O_2 production due to ^{40}K decay in Earth's oceans (Draganic et al. 1987, 1991) seems quantitatively insufficient.

Currently, possible biological explanations seem more able to explain Earth's early surface oxidation. One is the hypothesis that microorganisms "invented" oxygenic photosynthesis at a very early stage in their evolution (e.g., (Pierson 1994; Sleep 2001). Based on the discovery of stromatolites in precambrian and even archaean rocks it has been suggested that such microorganisms might have been similar to present-day oxygenic cyanobacteria (Pierson 1994). Like cyanobacteria today, they might have formed stromatolites in shallow coastal waters, i.e., microbial colonies with layer-like textures suggesting phototaxy (e.g. (Copley 2001)). However, phototaxy does not *per se* prove oxygenic photosynthesis. A different hypothesis is that methanogens would have driven an irreversible oxidation of the surface through the production, and subsequent UV photolysis, of methane (CH_4)—leading to hydrogen escape to space (Catling et al. 2001). A sufficient source of CH_4 on early Earth would have led to UV-driven polymerization into an atmospheric haze (Sagan and Chyba 1997, Pavlov et al. 2000, 2001) and subsequent H_2 loss and resulting surface oxidation. This candidate mechanism has a partial analog in the contemporary atmosphere of Saturn's moon Titan, and we explore it in both the Earth and Titan contexts in Sec. 4 of this proposal. Here, we first examine a different, geological hypothesis and its biological implications: the possibility that simple weathering played a key role. If the research to be carried out under this proposal were to show this hypothesis to be correct, this would imply that the oxidation of an Earth-like planet's surface should be expected due to a mechanism that should be quite common, and does not depend on the evolution of a particular metabolic style (methanogenisis). This would suggest that planets with oxygen-rich atmospheres, and therefore the prospect for metazoa and possibly even intelligent life, could be greater than otherwise expected.

2.1 Motivation and Statement of Hypothesis

Previous discussions have had too little to say about the fact that oxygen and its activated species, collectively known as reactive oxygen species (ROS), are highly toxic to life (e.g., (Rothschild and Mancinelli 2001)). Organisms cannot survive unless they possess a biochemical machinery to enzymatically degrade or quench any ROS and to repair damaged cell components, especially DNA (Newcomb and Loeb 1998).

Yet it is hard to believe that the complex biochemical machinery required for oxygenic photosynthesis would have been present in the earliest organisms. This leads us to suspect another source of oxygen on early Earth that provided the necessary evolutionary stimulus, i.e., a "training ground" for microorganisms to "learn" how to respond to ROS. To exert the necessary selective pressure it would have been sufficient if this other source expressed itself primarily in the microenvironment where the organisms lived. Therefore, while the "training" was going on in microenvironments, the rest of the Earth could have remained anoxic. Organisms in the right microenvironments would have been pre-adapted to life on a later, globally oxidized world.

There is another source of oxidative power beyond biology that has not been previously recognized. This source is contained in igneous and high-grade metamorphic rocks. It comprises a small but non-trivial fraction of oxygen anions in minerals of those rocks, which have converted from their usual 2- oxidation state to the higher 1- oxidation state, i.e., from O^{2-} to O^{-}. The O^{-} combines in pairs to form peroxy links, i.e., $O_3Si\text{-}OO\text{-}SiO_3$.

The processes that lead to this unusual change in valency on the O^{2-} are due to the incorporation of small amounts of H_2O in the form of hydroxyl anions, Si-OH, in the minerals of rocks that solidify from magma or recrystallize in an H_2O–laden metamorphic environment. During cooling Si-OH pairs undergo a redox conversion in the course of which the hydroxyl (OH) protons become reduced to H_2 molecules, while two oxygen anions act as electron donors and oxidize from the 2- to the 1- oxidation state. From that moment onward the rocks contain both molecular H_2 and oxidized oxygen anions in the form of peroxy links, $O_3Si\text{-}OO\text{-}SiO_3$ (Freund et al. 2002). The underlying reactions occur in rocks that make up the bulk of the crust and could therefore be of global importance. Techniques for studying these processes have been described in recent papers (Freund 2002, 2003).

To investigate this hypothesis, the main reaction to consider is the hydrolysis of peroxy links:

$$O_3Si\text{-}OO\text{-}SiO_3 + 2H_2O = 2O_3Si\text{-}OH + H_2O_2 \quad (2.1)$$

The hydrogen peroxide (H_2O_2) then decomposes, releasing oxygen via H_2O + O. Eq.(2.1) has potentially far-reaching consequences for the microenvironments in which some early organisms must have lived, *viz.* in the mud and at rock–water interfaces. Such microorganisms would have been exposed to a constant trickle of H_2O_2 liberated as minerals slowly dissolved under the combined action of water and organic acids, which microorganisms typically secrete as part of their metabolism. This scenario leads us to suspect that microenvironments existed in which organisms would have been under the constant challenge to fend off the ROS due to the liberation of H_2O_2 in their immediate surroundings.

Our biological hypothesis is directly connected with the geological hypothesis expressed by Eq.(2.1). We will test the hypothesis that, in spite of anaerobic conditions on early Earth, organisms living in intimate contact with rocks were nevertheless under evolutionary stress to develop the enzymatic defense mechanisms that helped them survive the threat from ROS. Gaining insight into these complex bio-geological relationships will open a new approach to understanding a key step in the evolution of early life, *viz*. the evolution of aerobic metabolism.

Eq.(2.1) has implications not only for the evolution of early life but also for the evolution of the early atmosphere and indeed the Earth system as a whole as it changed from overwhelmingly reduced to ever more oxidized conditions. The reason is that any amount of H_2O_2 liberated during weathering oxidizes reduced components in the environment, foremost ferrous iron, Fe^{2+}, in the early ocean. From the weathering rate of early landmasses and islands, depending on the concentration of peroxy links in average igneous and high-grade metamorphic rocks, we can estimate the flux of H_2O_2, and therefore O_2, into the surface environment.

2.2 Preparatory Work

During preparatory work (Rothschild and Freund 2001) we evaluated several methods to measure the amount of peroxy in rocks, using titration techniques and a new thermal technique (Freund et al. 2000; Rothschild et al. 2002). The latter, which appears to be most promising, is based on the disproportionation of peroxy upon heating, $O_3Si\text{-}OO\text{-}SiO_3 = O_3Si\text{-}O\text{-}SiO_3 + 1/2\ O_2$. We used a Y-doped ZrO_2 oxygen detector to measure the partial pressure of O_2 in a stream of N_2 to which we had added 100 ppm O_2. A typical O_2 evolution curve, obtained by heating a sample of gray granite from Barre, VT, as shown in Fig. 2.1 yielded a peroxy content of at least 500 ppm. Studies of selected single crystals yielded 10-15 times higher peroxy contents.

The preliminary results presented in Fig. 2.1 can be used to estimate the amount of O_2 that could have been liberated on early Earth through weathering. For a global weathering rate of 3 km^3 yr^{-1} (the same as today; Goddéris et al. 1999; Franck and Bounama 2001; Foley et al. 2003) and taking as a conservative value the average peroxy content in igneous rocks such as granite to be 500 ppm, the total amount of O_2 injected into the early Earth's surface environment would have been of the order of $5x10^{12}$ g yr^{-1}. This yearly O_2 flux is about an order of magnitude less than that suggested by Catling et al. (2001) to result from the biological methanogenesis mechanism, but it is about the same as the flux estimated to have been necessary over a period of $\sim 10^9$ years to precipitate the banded iron formations (Holland 1984).

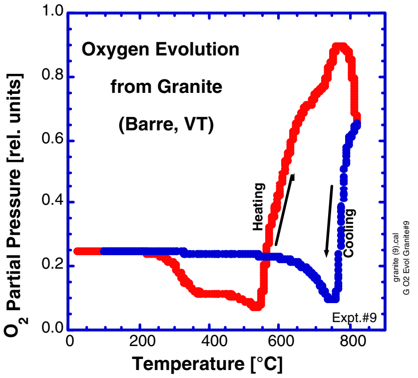


Fig. 2.1: O_2 evolution from crushed granite from the type location Barre, VT, during heating in a stream of N_2 with 100 ppm O_2. Between 250-550°C O_2 is consumed, but above 550°C excess O_2 is released. The amount of O_2 gives an estimate of the average peroxy content in this rock of at least 500 ppm.

Our preparatory work indicates that peroxy in rocks represent a potentially large source of oxygen on a tectonically active planet like Earth with liquid water at the surface and a powerful global weathering cycle. If confirmed by the work that we propose here, the presence of such a large inorganic source of O_2 has far-reaching consequences for our understanding of the evolution of the Earth. It would suggest that any other planet with active tectonics and Earth-like surface conditions is bound to evolve toward an ever more oxidized state—irrespective of the co-evolution of life that is capable of carrying out either methanogenesis or oxygenic photosynthesis.

With respect to the evolution of terrestrial life, the O_2 flux through the weathering of peroxy-bearing rocks provides for relentless environmental pressure forcing certain early microorganisms to adapt to the presence of ROS in their immediate surrounding. If the work proposed here continues to suggest that rocks are indeed an important source of ROS, it will help us understand the evolution of (some) early life from anaerobic to aerobic.

Astrobiologically, this would lead us to predict that life on other Earth-like planets will be under evolutionary pressure to overcome ROS, even under globally anaerobic conditions, and would therefore also be forced to evolve aerobic metabolism.

2.3 Work Plan

The lead Co-Investigators for this section, Drs. Friedemann Freund (SETI Institute) and Lynn Rothschild (NASA Ames) will exploit their complementary backgrounds to test the hypotheses proposed here. Under Dr. Freund, a physicist whose work has led to the discovery of the peroxy content of planetary materials, rock samples will be selected, analyzed for their peroxy content, and prepared for microbiological experiments under conditions that capture the ROS at the mineral surfaces. Dr. Rothschild, an evolutionary microbiologist with expertise in oxidative damage, will determine whether the ROS levels would be sufficient to provoke a selective pressure to evolve detoxification systems.

Physical Studies: The peroxy analysis of minerals and rocks needs to be further refined. Heating, crushing or mechanical deformation of rocks are all methods that take advantage of the inherent weakness of the peroxy bond and its tendency to break apart. These methods can be used to give us information on the concentration of peroxy links in common minerals and rocks susceptible to liberating H_2O_2 during weathering or in contact with acidic secretions from microbes living in intimate contact with mineral surfaces. Selected minerals and rocks will be crushed in inert and O_2-bearing atmospheres. The powders will be heated, varying the heating rate and other parameters. The O_2 evolved will be assessed quantitatively with an O_2-sensitive detector or by GC analysis.

During other crushing experiments we plan to measure the H_2 gas released by GC analysis, as described in Freund et al. (2002). The evolution of H_2 gas will be studied as a function of time and temperature. This is important in the context of the out-diffusion of H_2 over geological time and the accumulation of "excess" peroxy in minerals and rocks. On a prebiotic Earth, much of this H_2 will escape into the atmosphere and subsequently to space. After primitive life became established, this H_2 may have served as an energy source for microorganisms (see Freund et al. 2002).

Following our previously published laboratory practice (e.g. Freund et al. 2002), for controls we will use silicate glass that does not contain measurable amounts of peroxy. We shall replicate every step of the experiments with both rocks and peroxy-free controls. Previously published control experiments indicate that the oxidation state of the atmosphere has little effect on the production of peroxy deep inside the rock mineral matrix (Freund and Wengeler 1982, Freund et al. 1993, 2002).

Our data will allow us to estimate the amount of excess oxygen in minerals and rocks. These values will be used with models for the weathering rate of early Earth to estimate Earth's oxidation rate oxidized over its first 1-2 Gyr. The data will also be used for evaluating such processes on Mars, where igneous rocks may also be peroxy-laden. This aspect of Martian petrology will be of value in understanding the oxidation of Mars and the potential of Mars as a haven for subsurface life.

Biochemical Studies: The mechanism proposed here for the generation of ROS on an anaerobic Earth could provide the impetus for the origin of detoxification mechanisms, and ultimately lead to anaerobic metabolism. However, the only way to test this is to try to recreate this scenario using modern organisms. Therefore, we will use two types of approaches: we will assess damage from oxidants by measuring DNA damage, and we will use fluorescence microscopy to assess the presence of ROS within cells.

To test for oxidative damage in naked DNA, we expose commercially obtained DNA to crushed rocks, digest and de-phosphorylate the DNA, and determine the ratio of the oxidized base 8 hydroxy-2'-deoxyguanosine to the un-oxidized 2-deoxyguanosine, using HPLC with a COULCHEM II electrochemical detector. The HPLC is done in conjunction with the certified Analytical Laboratory at NASA Ames.

The results obtained so far are comparable to those in the literature using both a similar technique as well as immunological techniques (e.g. Mitchell et al. 2002). Briefly, either naked DNA or cells are exposed to the presumptive oxidizing agent. We plan to expand on these findings and to use a wider variety of microorganisms, including anaerobic microorganisms, which are highly susceptible to oxidative damage. We have developed a new experimental method that does not involve rock crushing but does activate ROS.

At the same time as ROS are damaging DNA, repair takes place. Thus, if we want to determine the damage, we need to inhibit the repair mechanisms. The simplest method to achieve this goal with organisms that are meso- or thermophilic is to keep the cells cold during damage. For example, *Cyanidium*, a red alga that in nature is usually found at 40-55°C (e.g. Rothschild 2001)), was exposed to H_2O_2 for one hour both on ice at 0°C and at 20°C. The algae kept on ice showed a >1.5 x higher ratio of 8-hydroxyguanosine to deoxyguanosine. This work will be expanded under this grant, using suitably prepared rock samples as a source of ROS.

If the amount of ROS generated is too little to cause damage to even naked DNA, it is unlikely to have been an impetus for detoxification mechanisms. However, if the levels are so high as to be lethal to even modern aerobic organisms, once again the hypothesis may be flawed

It is possible that ROS are affecting the microbes, but that enzymatic detoxification mechanisms are detoxifying the ROS before they damage the DNA. To test this, we will use a fluorescent stain, 2'7'-dichlorodihydrofluorescein, to determine the presence of ROS within cells. Cells will be stained after exposure to rocks with the suitable controls, stained, and analyzed in Rothschild's lab on a Zeiss Axioskope with a digital camera and image analysis software (all already acquired) that allows the integrated imaging and quantification of intensity of staining, greatly improving prospects for using fluorescent imaging to quantify ROS exposure to individual cells.

We would also like to test whether exposure to the rocks may have a lethal effect. We will use anaerobic and aerobic species, as well as some aerobic species deficient in DNA damage repair. Currently Rothschild has *E. coli*, yeast and *Chlamydomonas* wild-type cells and strains deficient in various types of DNA damage repair. To determine whether the cells are alive, we will use the Live/Dead stain kit from Molecular Probes.

The results of these experiments will tell us: (1) Whether enough ROS are produced to damage DNA; (2) Whether the ROS are entering the cells; (3) Whether there are sufficient ROS to kill modern organisms that do or do not have DNA damage repair mechanisms. In sum, is the "right amount" of ROS produced by the rocks to make a difference to organisms present on early Earth?

2.4 Timeline

Physical studies: Year 1: Set up and test laboratory procedures to measure excess oxygen and lattice-bound hydrogen in minerals and rocks. The procedures will include (i) physical techniques to be applied as a function of temperature, time and grain size of the samples (thermal gas evolution followed by dedicated O_2 and H_2 analysis) and (ii) wet-chemical methods (1-10-phenantroline photometric titration). Year 2 and following: Systematic survey of rocks that are characteristic of the continental crust, both igneous and metamorphic rocks and sedimentary rocks, from different localities worldwide. Survey of individual mineral phases from such rocks. Use laboratory data to model the global O_2 flux on the basis of weathering rates and continental growth rates on the early Earth. Eventually this will permit models for the evolution of any planet with surface or subsurface weathering. Year 3 and following: Systematic study of selected mineral systems that will be crystallized from melt under various water partial pressures, followed by a systematic study of the amount of excess oxygen in such synthetic rocks. At first this study will be conducted at 1 bar pressure, later at elevated pressures up to several kilobar (planned collaboration with Geophysical Laboratory, Carnegie Institution, Washington).

Biological studies: Year 1: Standardization and calibration of the three types of protocols that will be conducted (DNA damage, ROS in cells, and Live/Dead analysis). Continues into year 2 as needed. Years 2-5: Biological tests performed in conjunction with Freund on a time schedule that depends on his measurements of oxygen release.

The work proposed here addresses Goal 4, Objectives 4.1 and 4.2,and Goal 5 of the Astrobiology Roadmap.

3. Titan, Photochemical Haze, and the Oxidation of Early Earth

An important tool of astrobiology is comparative planetology. In particular, since experiments with spatial or temporal scales comparable to those "experiments" in the origin of life that occurred on early Earth cannot be conducted in the laboratory, it is important to explore and contrast conditions on the other worlds of our Solar System with those that may have existed on Earth. In this spirit, we may use Jupiter's moon Europa as an analog to a possible ice-covered early terrestrial ocean (Bada et al. 1994), carbonaceous meteorites as an analog to scenarios for the origin of life at depth (Chyba and McDonald 1995), high-altitude lake environments on Earth as analogs to early Mars or ozone-less Earth (Sec. 5) and the organic chemistry of Saturn's moon Titan as an analog to both organic aerosol production on the early Earth (Sagan and Thompson 1984; Coustenis and Taylor 2000) and hydrogen-loss mechanisms that may help account for the net oxidation of early Earth's surface. The latter two possibilities will be examined in the research proposed in this section, and the relevance and limitations of these Titan-Earth analogs explicitly probed. Slow oxidation of Earth's surface by hydrogen loss due to aerosol formation will supplement the mechanisms considered in Sec. 2 of this proposal, emphasizing that there were evidently a suite of geological, atmospheric, and perhaps biological mechanisms acting on early Earth—and probably on many Earth-like worlds—that would have driven the environment towards more oxidizing conditions, with the implications for metabolism and, ultimately, aerobic life previously discussed in Sec. 2.

3.1 Titan Overview

Models of the accretion of Titan indicate that it formed from an ammonia-methane rich circumplanetary nebula that went on to condense into Saturn and its other satellites (Prinn and Fegley 1981). As a result, Titan is expected to have developed a layered structure containing mixed ices and silicates in the core, with an overlying silicate carapace and a deep ocean of ammonia-water liquid (Sagan and Thompson 1984). Titan's surface, most probably composed of water ice coated in accumulated hydrocarbons and nitriles, is seen by many as a prebiotic chemical laboratory (see

Lunine and McKay 1995). The action of ionizing radiation (Sagan and Thompson 1984), of lightning (Borucki et al. 1984), and of meteorite impacts (Jones and Lewis 1987; Thompson et al. 1992) is likely to have driven an exotic prebiological chemistry, perhaps as far as the amino acid or nucleotide base stage (Fortes 1999). The absence of water provides a serious stumbling block to the formation of biological molecules. However, impact ejecta are expected to contain large quantities of water. Thompson et al. (1992) calculated that around 70% of Titan's organic inventory has been exposed to impact melted water for mean periods of around a century. This may have yielded a range of organic compounds by hydrolysis of tholins (radiation-processed organic solids), although the products would inevitably freeze again, so that potential biological activity on Titan's surface is likely to be trapped in a permanent stasis. On early Titan, hydrothermal reactions between the ocean and the underlying rock layer likely reprocessed a portion of the ocean, plus infalling cometary and chondritic material, into more complex organic compounds (Shock and McKinnon 1993). Significantly, Titan is unique as the only moon in our Solar System that formed or retained a thick atmosphere. This atmosphere contains mainly methane and nitrogen components that have been energetically processed via UV radiation and cosmic ray particles into a complex organic haze in its stratosphere.

3.2 Titan Haze Synthesis and Prebiology

Titan's haze dominates its temperature, atmospheric circulation and climate control. Photochemistry plays a key role in the structure and evolution of the haze. A detailed knowledge of Titan's photochemistry therefore provides a deeper understanding of its global properties. A comprehensive study of organic chemistry and the resulting hydrocarbon haze in a theoretical simulation of Titan's atmosphere provides vital information on similar processes that occurred on early Earth (Sagan and Chyba 1997, Miller et al. 1998, Pavlov et al. 2001a,b). Titan also provides a partial early Earth analog with its reducing atmosphere resembling primitive terrestrial atmospheric chemistry. We have made significant inroads into bridging the longstanding gap in knowledge of Titan's haze photochemistry between simple molecules and complex polymers (Ricca, Bauschlicher and Bakes 2001; Bakes, McKay and Bauschlicher 2002; Lebonnois et al. 2002a,b;2003; Bakes et al 2003). We have also constructed the first ever Titan aerosol charging model to account for photoelectric charging. Bakes et al. (2002a) have shown it is essential to consider this mechanism, highlighting how daytime and nighttime (or Summer and Winter) haze chemistries are quite different. Knowing the charge on macromolecules in the haze forms a solid foundation for a truly representative chemical network. Our charging model has also produced spinoffs resulting in the revision of seminal models of charging (Borucki et al. 1987) and aerosol growth and albedo (Toon et al. 1992) for the Titan haze. In addition, we have included the effects of aerosol charging and macromolecular catalysis of H_2 formation (Bakes et al. 2002b) and inserted this treatment into the Titan photochemical model of Lebonnois et al. (2002a,b). The results of our models are applicable to the hydrocarbon haze postulated to exist in the atmosphere of early Earth (Pavlov et al. 2002a,b) and the hydrogen catalysis is directly relevant, producing H_2 efficiently to fuel methanogenic and anoxygenic photosynthetic bacteria and to provide a physical mechanism by which to efficiently transport unreactive H_2 out of the stratosphere to facilitate the formation of a primitive oxygenated atmosphere.

The applications of this kind of chemistry are therefore wide-ranging and inform: (1) early terrestrial prebiology; (2) impact of icy bodies on planetary or satellite surfaces' (3) distant past or far future scenarios concerning the chemical evolution of Titan's atmosphere and how the physical conditions under which the aerosols formed and reacted with water and ice affect the variety of amino acids synthesized; and (4) evolution of the atmosphere of the early Earth.

3.3 Terrestrial Prebiotic Chemistry

What comparisons can we draw between a prebiotic Earth and present day Titan? If we make the assumption that significant liquid reservoirs are present on Titan, we can draw comparisons between the land-air-sea interactions on both planets (Fortes 1999). On prebiotic Earth, the dominant radiative gas was likely (but not certainly) carbon dioxide (Kasting, 1984), which provided most of the atmospheric opacity. On present-day Titan, nitrogen serves this purpose. Both of these gases are also somewhat soluble in their respective oceans: carbon dioxide in water and nitrogen in methane. Both planets had large liquid seas at the surface, which were intimately related to their atmospheres. Both water on prebiotic earth and methane on present-day Titan are not insignificant species in the atmosphere, having an influence on the chemistry and ultimately the evolution of the planet (Lunine and McKay, 1995). Titan's haze would have a significant interaction with potential liquid reservoirs on the surface. The aromatic structures in the Titan haze can be hydrolysed to form amino acids (Khare et al. 1986). In essence, this prebiological chemistry to some extent parallels early terrestrial chemistry in a reducing or neutral atmosphere. We suspect that the aerosols in early Earth's atmosphere would form via similar chemical mechanisms as those in the Titan haze, incorporating nitrogen into a carbon based aromatic structure. The presence of water on Earth would facilitate hydrolysis of these aerosols to form amino acids and could provide a significant source of building blocks for the origin of terrestrial life. In summary, as a result of defining the quantum chemical mechanisms by which macromolecules and aerosols form on Titan, we can extend this chemistry to parallel that of the early Earth by introducing the crucial step of hydrolysis and subsequent amino acid formation.

3.4 Icy Body Impact Chemistry

The hydrolysis of nitrogenated aromatic macromolecules in both water and an icy matrix could occur by impact-driven, shock-heated chemistry to produce amino acids. Pierazzo & Chyba (1999) have recently shown that the survival of cometary amino acids is plausible for large cometary impacts. Blank (2000?, and private communication) has found that when two icy bodies impact one another, that if one or both bodies contain amino acids, peptides are formed. If an icy body impacted Titan, it would already contain aromatics of the sort that form via atmospheric gas phase chemistry in the Titan haze (reference to comet/meteor composition needed). When impact occured, the formation by shock-heated chemistry of both amino acids and peptides may result, providing a source of prebiological molecules. Since Pierazzo and Chyba (1999) agree that amino acids may plausibly survive large cometary impacts, then the complex organic chemistry which could occur via this kind of impact may be highly relevant to present day Titan as well as the Titan of the past.

3.5 Distant Past and Far Future Scenarios

During the first one ~10^8 yr of Titan's history, there was a warm (300K) aqueous environment with abundant energy sources at Titan's surface (Thompson et al. 1984; McKay et al. 1993; Lunine & McKay 1995). This may be the closest Titan is ever likely to have come to the primitive terrestrial environment in which life is thought to have formed (Fortes 1999). In the absence of evidence to the contrary, we may assume that if there ever was life on Titan, it originated in the same way as it did on Earth, plausibly through a period of abiological chemogeny (Fortes 1999), yielding the building blocks of proteins and DNA (Laczano and Miller 1996; Lifson 1997; Freeland et al. 1999). The main change in Titan's atmosphere over time is most likely to have been due to changes in temperature and the reduction in the amount of methane CH_4 (McKay et al. 1993). This would affect both the rate of formation and the subsequent charge and agglomeration rate of the aerosols. Since we expect aerosols to have formed in this period of Titan's history, we can predict synthesised products via hydrolysis of these aromatics in a potentially warm aqueous environment. The abundance and type of amino acid synthesized may well vary over time due to the changing abundance of CH_4, which alters the aerosol formation rate and the temperature and UV radiation field transmitted to the lower atmosphere. We are well placed to quantify this effect via the modification of the photochemical model of Lebonnois & Toublanc (2000) into a time dependent mode.

Turning to the far future scenario, Khare et al. (1986) point out that while life on Titan is hardly to be expected at its current ambient surface temperature of 95 °C, a few billion years from now, the Sun will enter its red giant phase and for~10^8 yr, the surface temperature of Titan will be above the freezing point of water and chemical evolution with go further towards prebiology. We can take the present day haze composition, containing macromolecules and tholins and model the effects of an emerging liquid environment to see whether the rate of amino acid formation would be significant. The acceleration of prebiology in Titan is an exciting theoretical concept and would further our understanding of precisely how mixing carbon-based aerosols, nitrogenated aromatic hydrocarbons and water may have kick-started terrestrial prebiology.

Moreover, we can make a detailed theoretical analysis (using quantum chemical models and the state of the art Titan photochemical model of Lebonnois & Toublanc 2001) of plausible aerosol hydrolysis chemistry. In addition, the model of Lebonnois & Toublanc may be enhanced by the addition of a time-dependent component that allows us to track the chemical evolution of Titan's atmosphere as its composition changes with time.

In summary, the building blocks of life may change in their compositon and abundance with time, affecting the evolution of prebiology and the eventual emergence of biology. This time-dependent evolution of life at the molecular level may have considerable ramifications concerning the probability of the origins of life on a particular planetary body or satellite. We have all the capabilities right now to investigate this time dependence using a synergy of laboratory experiments and quantum photochemical models of Titan's haze.

3.6 Oxidizing Earth's Surface

Our current research combines the photochemical models of Lebonnois et al. (2002a,b) with the ab initio photoelectric charging model of Bakes et al. (2002a), the hydrogen formation model of Bakes et al. (2002b), the quantum chemical studies of Baushlicher and Ricca (2000) and Ricca et al. (2001) with the laboratory analyses of Khare et al. (2001; 2002). Our results are directly applicable to haze chemistry involving large hydrocarbon molecules. The chemical and thermodynamic processes fuelled by these hydrocarbon molecules is strongly relevant to the reducing or neutral atmosphere of the early Earth (Pavlov et al. 2001a,b). A terrestrial atmospheric organic haze layer is an effective source of gaseous heating via the UV-powered photoelectric effect (Bakes et al. 1994; Bakes et al. 2002a). Bakes et al. (2002a,b) also find that aerosol surface catalysis is an efficient producer of H_2. It is logical that any physical mechanism facilitating the efficient escape of H_2 from the atmosphere of the early Earth would accelerate the oxygenation of the early atmosphere. This is precisely the effect of both aerosol surface catalysis and charged macromolecule catalysis of H_2 formation, be it for Titan's haze or a putative haze on early Earth (Bakes et al. 2002b).

Our models can shed light on the chemical transition from a reducing to an oxygenated atmosphere and they can predict how significant the photoelectric heating from a terrestrial haze would be relative to other sources of heating on the early Earth (Bakes et al. 1994; Bakes et al. 2002a). Our initial studies would concern the charging, growth and albedo of a haze layer in the atmosphere of the early Earth. This will be done for a range of plausible early solar radiation fields to probe how critical the strength of the UV radiation would be in affecting the thermodynamic processes and possible photoelectric heating in the haze. Once a foundation is formed for the charging and heating via haze macromolecules and submicron aerosols, we can make broad predictions about the dominant gas phase and aerosol chemistry. We will estimate the rate of escape of H_2 from the early terrestrial atmosphere via heterogeneous and macromolecular catalysis of H_2 formation. We can gauge its relative importance by comparing our H_2 production and escape rates with those estimated for the transition period between a reducing and an oxygenated early terrestrial atmosphere.

It is straightforward to adapt our existing models (Bakes et al. 2002a,b) to conditions more appropriate to the early Earth in order to study primitive terrestrial haze chemistry, charging and thermodynamics. This will be done by simply altering the altitudinal variation of the UV radiation field, electron and positively charged particle density and gas temperature to match estimates for the early Earth (Canuto et al. 1983; Sagan and Chyba 1997, Heap et al. 2001). Sagan and Chyba (1997) (due to abiotic sources) and Pavlov et al. (2001a,b) (due to biotic sources) predict the presence of a hydrocarbon haze in the early terrestrial atmosphere that may be similar to Titan's haze. We predict that as with the Titan haze (Bakes et al. 2002a,b; Lebonnois et al. 2002a,b), the photoelectric charging of aerosols and the effects of aerosols on H_2 formation will have a significant effect on the haze chemistry and thermodynamics.

3.7 Goals of this Study

Support under this proposal will allow us to adapt the current state-of-the-art photochemical model of Lebonnois and Toublanc by adding: (1) the aerosol charge balance model of Bakes, McKay & Bauschlicher (2002); (2) a time dependent mode involving the Gear Routine to solve stiff differential chemical rate equations; and (3) quantum-chemical calculations involving Titan haze macromolecules on icy surfaces. This would enable us to predict the likelihood of amino acid formation coupled to the chemical composition and time dependent evolution of the haze, from Titan's distant past, through the present epoch, to a far future scenario (time permitting).

Work on the formation of the Titan photochemical haze can be seen as a parallel to aerosol formation in the atmosphere of early Earth. Not only does the formation of the Titan photochemical haze shield the lower layers of the atmosphere from ionizing UV radiation, but synthesized aerosols can also provide the raw materials for the synthesis of the building blocks of life. Furthermore, icy body impacts with Titan may help synthesise peptides, further increasing the complexity of the potential prebiological chemistry. By investigating the formation of amino acids and the chemistry of nitrogenated aromatics such as those formed in the Titan haze in aqueous and icy environments, we can derive broad principles for the general formation of prebiology that we can and will relate to early terrestrial chemistry. Because chemistry runs by the laws of physics, we hope to thereby derive generalized formation mechanisms that can be applied to a diverse array of planetary environments.

3.9 Investigative Timeline

Dr. Emma Bakes is the Co-Investigator primarily responsible for this research, and will devote 25% of her time over the next five years to this effort. Year 1: Implement a quantum chemical investigation of the addition of successive aromatic rings to neutral and charged two-ring molecular structures to confirm a growth trend requiring successively less energy with each additional ring. This chemical pathway will be added to an existing photochemical model of the Titan haze to study its effects on the gas phase chemistry and molecular abundances. A detailed analysis of the photochemical evolution of our large molecules and aerosols with altitude in Titan's atmosphere will be performed. Year 2: Adapt our infrared spectral models to predict the macromolecule emission at relevant altitudes for Titan in order to predict the spectral profile between 2 and 100 μm and to explain data at relevant wavelengths yielded by the Huygens probe. We will also make a user friendly version of our charging routines and our infrared spectral model available for analysis of Cassini/Huygen data. Year 3: Apply the results of the previous two years to the early Earth scenario. Haze chemistry, aerosol growth, agglomeration, corresponding changes in albedo, photoelectric heating (which affects the thermodynamics of a gaseous system) and catalytic H_2 production mechanisms will be investigated for possible thermal and chemical impact on a primitive terrestrial atmosphere and its evolution towards a progressively less reducing environment. Year 4: The implications of the results for the early earth will be analyzed, interpreted and modified to fit the evolutionary timeline of the early terrestrial atmosphere. We will work on modifying the codes to fit a time-dependent Gear routine computational analysis. This will allow us to tweak results over time as well as with respect to atmospheric composition and solar UV field. Year 5: Writing and publication of the results yielded from our previous analysis of the early terrestrial atmosphere, and the incorporation of relevant results from other groups working on the early Earth into our computational models.

The work proposed here will address Goals 2 and 6 of the Astrobiology Roadmap.

4. Iron, the Oxygen Transition, UV Shielding, and Photosynthesis

Iron is geologically abundant, has multiple oxidation states, and is a key metal for life because of its role in many metabolic processes often involving oxygen. Banded iron formations (BIFs), alternating layers of iron-rich and iron-poor minerals, are found on the early Earth and include those dominated by oxides, siderite (iron carbonate), silicates, and sulfides (James 1954; James and Sims 1973; James and Trendall 1982). The bulk of these formed fairly rapidly around 2.5-2.0 Gyr ago, although many formed earlier than 3 Gyr ago (Holland 1984).

One of the unanswered questions about the early Earth is why atmospheric O_2 first rose to higher levels ~2.3 Ga when oxygenic photosynthesis existed much earlier, 2.5 to possibly even 3.8 Ga (Des Marais 2000; Olson 2001; Pace, presentation at the NAI biennial meeting, Feb. 2003). Recent studies have suggested that methane (Catling et al. 2001), sulfur (Kasting et al. 1989) or iron (Konhauser et al. 2000) could have influenced biogeochemical cycles on the early Earth; Secs. 2 and 3 of this proposal consider other possible mechanisms for surface oxidation. Reduced sulfur and/or iron are thought to be the first electron donors available for early organisms and may have been involved in early photosynthesis (Olson 2001). Some or all of these processes may help explain why the oxygenic photosynthesis arose so much earlier than the rise in abundance of atmospheric O_2. The oxygen produced by early photosynthesis (and other mechanisms) may have been used up oxidizing localized deposits of reduced sulfur and/or iron associated with the organisms, thus requiring more time to reach levels sufficient to impact the atmosphere.

Before the buildup of O_2 in the atmosphere, the UV flux to the early Earth was at least as high as it is today, and most likely substantially higher. This is because while the Sun was younger, solar UV radiation from 200 to 320 nm was able to penetrate the ozone-poor early atmosphere. The UV flux from the early Sun (before 3.5 Gyr ago) at these wavelengths would have been only a factor ~2 lower than the solar UV flux today (Chyba and Sagan 1992). Since the peak absorption for DNA is 260 nm, and that of proteins 280 nm, an increase in solar radiation in the 200 to 320 nm range would have been extremely hazardous to early life, especially forms that would have to access solar energy such as photosynthetic organisms (e.g., Rothschild 1999).

We *hypothesize* that evolution of some early photosynthetic organisms is related to the presence of nanophase ferric oxide minerals and BIF deposition during this time period because of the sunscreening capabilities of ferric oxides/oxyhydroxides. *We will test this hypothesis* in the laboratory and in the field by: (1) determining whether these minerals can provide a favorable environment for photosynthetic organisms by supplying the necessary protection at UV wavelengths, while allowing sufficient transmittance at visible wavelengths for photosynthesis; (2) determining which ferric oxides/oxyhydroxides/ oxyhydroxysulfates are active *in situ* where organisms grow; (3) evaluating the performance of imported ferric oxide minerals as a UV radiation shield; and (4) determining the potential for ferric oxides/oxyhydroxides/oxyhydroxysulfates to screen UV where it occurs in nature today.

We will use these data to inform the search for life in other high radiation environments where iron could act as a sunscreen, most importantly on Mars. As described in Sec. 5, we will be able to compare these results for those implicated in the UV strategies employed by microorganisms in high UV environments on contemporary Earth. Perhaps some of the early photosynthetic organisms synthesized their own iron oxide sunscreen, or utilized the iron oxides already present as a sunscreen. Both the solar energy filtration and the oxygen-scavenging ability of these minerals may have been beneficial to these organisms. Our results should provide data for modeling the early reducing and oxidizing chemistry on planets and may help explain whether or not links exist between early phototrophs, BIFs and the oxidizing atmosphere on Earth. Additionally, the project may provide information about the role of such minerals in the protection of modern aquatic organisms from UV radiation or oxidative damage, an area of particular interest to the near-term future of life on planet Earth.

4.1 Significance

This project is inherently interdisciplinary, and involves a novel approach to evaluating the relationship between organisms and their environment. It requires a combination of physics (reflection and absorption of radiation as a function of composition and abundance), geology (mineral identification and formation processes), chemistry (pH, temperature and presence of ions/salts in the environment), and biology (organisms' survival needs).

The fundamental question of this project focuses on how early organisms evolved in a harsh physical environment. This study is expected to lead to a better understanding of how organisms on Earth were able to live in a world bathed in UV radiation, while still accessing the visible radiation (400 to 750 nm) so critical for photosynthesis. Specifically, it will examine the relationship between the formation of nanophase ferric oxide minerals on the early Earth and their impact on the evolution of life at the critical juncture of the transition from anoxygenic to oxygenic photosynthesis. If these iron oxide minerals can provide adequate coverage for primitive photosynthetic organisms, then a link between the survival of these organisms and the formation of nanophase ferric oxides/oxyhydroxides/ oxyhydroxysulfates may exist.

This may also inform future Mars missions. Water on Mars is thought to have played a prominent role in the formation of the hematite deposit in Sinus Meridiani (Christensen et al. 2000, 2001) and in the formation of gullies through seepage and surface runoff (Malin and Edgett 2000), and where evidence of subsurface water ice has been observed recently by the GRS on Mars Odyssey (Boynton et al. 2002; Feldman et al. 2002). Mars Express will soon be orbiting the planet and the Omega spectrometer will be collecting visible-infrared spectra (0.5-5.2 µm) at surface resolutions as low as 300 m across. The CRISM spectrometer (0.4-4 µm at 100-200 m or better spatial resolution) will be flying on the Mars Reconnaissance Orbiter (MRO) scheduled to launch in 2005. These instruments are expected to provide evidence of clays, carbonates, silicates and iron oxides if they are present near the surface. Perhaps some of the smaller, pixel-sized, hematite deposits identified by TES on Mars also contain other minerals that are commonly associated with BIFs. Understanding the visible/infrared spectral character of natural and synthetic ferric oxide-bearing systems capable of screening UV radiation for phototrophs will be important as we evaluate the new spectral data returned from Mars Express and the MRO.

The work proposed here addresses Goal 4, Objectives 4.1 and 4.2,and Goals 2, 5 and 6 of the Astrobiology Roadmap.

4.2 Extending Current State of Knowledge

In addition to its sunscreening capability, iron is an integral component in the evolution of life. Although iron is the fourth most abundant element on the Earth's crust, it is frequently a limiting factor in biological systems (Falkowski et al. 1998) because the bioavailability of iron depends on its redox state and solubility (Martin 1992). The iron balance between organisms and their environment can be viewed as a web, where multiple processes and systems are interlinked and interdependent. The traditionally accepted geologically controlled anoxic-oxic transition (e.g. Des Marais 1992) may be sufficient to explain the processes shaping the evolution of early Earth. However, if the possibility exists that biologically mediated processes also played a role in the rise of oxygen, it could be that a combination of geological and biological processes is crucial in the evolution of habitable worlds.

Photosynthesis was a critical evolutionary breakthrough; however, photosynthetic organisms faced a dilemma. On the one hand, they needed access to solar radiation for energy; on the other, the UV rays were extremely damaging. Despite our current atmosphere, which attenuates most radiation below 300 nm, ultra violet radiation (UVR) causes DNA damage to life. Without the ozone layer, UVR would have posed a substantial burden to early life. Photosynthesizers were forced to protect themselves either through UV damage repair or by finding a shield from harmful UVR that still transmits photosynthetic radiation (~400-900 nm). Of primary importance is a filter at ~250-290 nm, where DNA and protein absorptions occur (e.g., Rothschild 1999). Many kinds of materials could have blocked UVR on the early Earth including iron (Olson and Pierson 1986; Pierson et al. 1987), ferric oxide minerals (our suggestion), sulfur vapor in the atmosphere (Kasting et al. 1989), a photochemical haze (Sagan and Chyba 1997, Miller et al. 1998; see also Sec. 3), and a combination of inorganic and prebiotic organic compounds in the oceans (Cleaves and Miller 1998; Cockell 2000). Sagan and Pollack (1974) suggested that a depth of ~1 cm below the surface on Mars would be a possible photosynthetic niche, allowing visible light to penetrate while reducing the UVR to acceptable levels.

Ferric oxides are unique among the range of possibilities in that they transmit light through much of the visible region, it is universally accepted that they were available in early environments on the Earth, and they are synthesized by many organisms. Thus, *we suggest here that ferric oxides may be critical in the early evolution of a life-supporting planet as a sunscreen that allows the evolution of photosynthesis prior to the accumulation of sufficient stratospheric ozone.* We propose several experiments to test our hypothesis that the evolution of some early photosynthetic organisms is related to the presence of nanophase ferric oxide minerals and BIF deposition. Specific objectives of these experiments include determining the influence of selected nanophase iron oxide minerals on living photosynthetic organisms through controlled UV absorption experiments in the lab, and identifying the nanophase iron oxide minerals forming in natural environments such as Iron Springs near Nymph Creek, Yellowstone National Park, where we believe the iron oxide minerals are assisting the organisms.

BIFs have been associated on Earth with a major transformation in the redox environment of the oceans and atmosphere, the kinds of organisms present, and the surface mineralogy (e.g. Holland 1984; Beukes and Klein 1992; Des Marais 1997; Holland 1999; Catling and Moore 2000). Ehrenreich and Widdel (1994) recently summarized three likely mechanisms of BIF deposition. These include (1) chemical oxidation of dissolved Fe(II) by oxygenic phototrophs (e.g. cyanobacteria) in oxygenated ocean water, (2) abiotic UV light-driven aqueous oxidation of Fe(II) giving off H_2, and (3) biological oxidation of Fe(II) by anoxygenic photosynthetic organisms. Localized, ancient iron formations are associated with hydrothermal activity in many locations documented by Gross (1983), as well as small, current sites in Yellowstone (Pierson et al. 1999) and Iceland (Bishop and Murad 2002). Such sites on the early Earth may have provided a convenient habitat for early photosynthesizers. Holland (1984) supports volcanism as a source of many smaller BIFs, especially those associated with volcanic features, but argues that volcanic processes are unlikely to be responsible for many of the large BIFs because of the enormous volume of iron-rich material and relatively short formation time for the bulk of the iron formations.

Perhaps the ferric oxide/oxyhydroxide minerals that formed the smaller BIFs enabled the then new photosynthesis mechanism to become more widespread. It is likely that oxygenic photosynthesis occurred at least 600 Myr prior to the time of high atmospheric O_2 levels (Des Marais et al. 1992). The negative influence of solar radiation may have initially hindered the evolution of photosynthesis, until appropriate ferric oxide sunscreening niches were found. If our hypothesis is correct, then the presence of nanophase iron oxides could have significantly enhanced survival rates of photosynthetic organisms, thereby linking iron oxides to an increase in atmospheric O_2 levels.

The Thermal Emission Spectrometer (TES) on board the Mars Global Surveyor (MGS) mission has provided spectral data that enabled Christensen et al. (2000, 2001) to identify a large deposit of crystalline, gray hematite on Mars in Sinus Meridiani. They evaluate possible formation mechanisms for this deposit and suggest formation via precipitation of Fe-rich hydrothermal fluids as the most likely process. Controversial evidence for large bodies of water on Mars in the past (Baker et al. 1991; Head et al. 1999), plus recent evidence for surface water on Mars (Malin and Edgett 2000) support the possibility that BIFs might have formed on Mars, as well as Earth. Additional smaller regions have been identified on Mars where crystalline, gray hematite is present at 20% or more abundance levels (Christensen et al. 2001). If these aqueous iron oxide deposits on Mars are associated with BIFs and/or redox changes in the atmosphere on Mars, it would be interesting to consider the possibility of photosynthesis as well. The idea that Mars has experienced more recent hydrological processes than previously thought was inspired by Malin and Edgett (2000).

Burns (1993) first suggested the possibility of abiotic BIFs on Mars in the form of dessicated iron oxide/silica deposits. Schaefer (1996) discussed the potential formation of BIFs on Mars through several abiotic mechanisms including oxidation of ferrous iron by free oxygen, photooxidation of ferrous iron, oxidation of ferrous iron by H_2O_2 and anoxic precipitation of ferrous iron by changes in pH. More recently, Calvin (1998) suggested that BIFs on Mars may have precipitated ferrous clays and other dark ferrous minerals and provided a model to explain the dark regions on Mars through a BIF-like mechanism.

Iron has been linked to the evolution of photosynthesis and the origin of BIFs (Cloud 1973; Pierson and Parenteau 2000). Cloud (1973) asserts that ferrous iron in solution served as a sponge for the biologically generated oxygen that was formed as a waste product of photosynthesis and which would have been toxic to life if it accumulated. According to Cloud's model, the formation of ferric oxides kept O_2 levels sufficiently moderate for photosynthesizers to live and grow. Recent studies have shown that some forms of iron stimulate photosynthesis (Pierson 1994; Pierson et al. 1999; Pierson and Parenteau 2000) and earlier studies showed that iron could be important in protecting the organisms from UV radiation (Olson and Pierson 1986; Pierson and Olson 1989). Related studies (Emerson and Revsbech 1994a,b; Pierson et al. 1999; Pierson and Parenteau 2000) have shown that organisms are intimately clustered with amorphous or nanophase iron oxides on the scale of a few µm. Ferric oxide-bearing minerals that are produced via biologically mediated processes are typically nanophase in scale (~1-10^2 nm in size). This small size would have facilitated the formation of niches for microorganisms because of the high surface area. If nanophase ferric oxides did provide a protective niche for photosynthetic organisms, this could have allowed for a much more rapid evolution of these organisms than otherwise possible and would have implications for the anoxic-oxic transition on Earth.

In a pre-Viking assessment of the possibility of life on Mars, Sagan and Lederberg (1976) argue that liquid water is the most stringent limiting factor. They suggested that the low oxygen partial pressure would be a negligible impediment to life and that the UV flux could have been countered by living below the surface or by developing a UV-absorbing exoskeleton or shield (that might also be able to conserve water). Such speculation has been largely forgotten since the lack of strong evidence for life by the Viking biology experiments (e.g. Klein 1978). Weiss et al. (2000) recently voiced the availability of liquid water, rather than energy or other factors, as the most important limiting factor for organisms on Mars. With the recent geomorphologic evidence supporting frozen aquifers and some liquid water on Mars (Malin and Edgett 2000; Christensen 2003), it may be timely to re-evaluate the possibility of life on Mars, and the possible niches that may be available now (or in the past) for life on Mars-like planets. In a recent summary of a variety of chemical energy sources for bacteria, Nealson (1997) described ecosystems on Earth that may have been possible on Mars (or other planets) at one time in the past. These include Antarctic endoliths or dry valley lakes, hydrothermal regions, and deep subsurface ecosystems. If our hypothesis that nanophase ferric oxides could protect photosynthetic organisms is correct, then Mars-like planets with abundant ferric oxides and some liquid water may be able to support life.

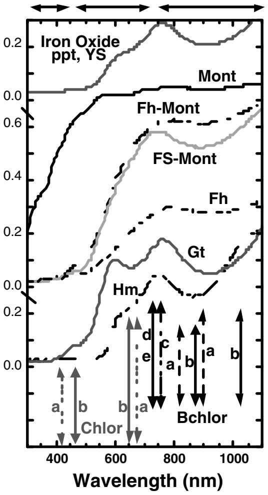


Fig. 4.1 Optical properties of a Yellowstone precipitate, clays and iron oxides in relation to chlorophyll absorptions. Spectra are shown for montmorillonite (mont), ferrihydrite-montmorillonite aggregates (Fh-mont), ferrihydrite-schwertmannite-montmorillonite aggregates (FS-mont), ferrihydrite (Fh), goethite (Gt), and hematite (Hm). Approximate pigment absorption energies are indicated for chlorophyll a and b, and bacteriochlorophyll a, b, c, d, e.

The optical properties of iron oxide minerals vary substantially depending on the mineral structure (e.g., Bishop et al. 1995; Bishop and Murad 1996). The nanophase minerals ferrihydrite and schwertmannite exhibit UV-visible spectral properties that allow transmittance at chlorophyll absorption energies, while blocking the damaging UV rays. These minerals are also frequently formed in the presence of the *Thiobacillus ferrooxidans* (for schwertmannite, pH 2-3.5) and *Gallionella ferruginea* (for ferrihydrite, pH ~7-8), although inorganic formation mechanisms also exist (e.g., Murad et al. 1994; Bigham et al. 1996; Cornell and Schwertmann 1996). Other minerals, such as hematite and goethite, may also serve as effective sunscreens; however, these typically form in larger crystalline grains and are not as frequently associated with soils and microorganisms. Ferrihydrite is the third most prevalent biogenically produced mineral on Earth (Lowenstam 1981).

At Yellowstone National Park iron oxide precipitates, or sinters, are frequently found in the water or on the shores at hydrothermal sites in conjunction with photosynthetic organisms. Extended visible region reflectance spectra are shown in Fig. 4.1 for an orange precipitate collected from the banks of Nymph Creek, where UV radiation studies have been performed (Rothschild et al., work in progress). As shown through the low reflectance (high absorbance) at short wavelengths in Fig.

4.1, radiation is blocked by the precipitate at wavelengths shorter than ~500 nm, but allowed to penetrate at longer wavelengths. For comparison, the extended visible region reflectance spectra of selected iron oxide/oxyhydroxide/ oxyhydroxysulfate minerals are shown as well (from Bishop et al. 1995; Bishop and Murad 1996). Hematite and goethite are crystalline minerals, while ferrihydrite (ferric oxyhydroxide) and schwertmannite (ferric oxyhydroxysulfate) are nanophase minerals and exhibit broader spectral bands. Schwertmannite contains sulfate, whereas the others contain only Fe, O, OH and/or H_2O. The absorption bands for chlorophyll *a* and *b* (Salisbury and Ross, 1992) and the chlorophyll found in green and purple bacteria (Stanier et al. 1986) are indicated in Fig. 4.1 for comparison. A recent study of organisms at Yellowstone by Wilson et al. (2000) has shown that Fe(II)-Fe(III) cycling is linked to H_2O_2 concentration and both may be important environmental factors in pigmentary grains.

Preliminary spectral measurements of suspensions of nanophase ferrihydrite-clay-aggregates (Fh) and ferrihydrite-schwertmannite-clay-aggregates (Fh/Sw) have been performed and the spectral absorbance of variable concentrations of these pigmenting agents are shown in Fig. 4.2. This shows that these suspensions should mask some of the harmful UV rays while allowing some visible light to pass through for photosynthesis. Growth experiments with organisms are required in order to determine if sufficient light at critical energies penetrates through the organism growth.

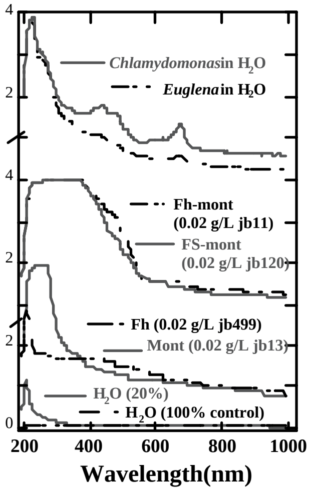


Fig. 4.2 UV-VIS absorption spectra of nanophase iron oxide suspensions with variable concentrations.

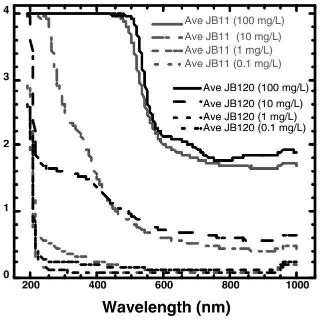


Fig. 4.3 Absorbance of Euglena and Chlamydonomonas in suspensions. The spectral absorbance due to chlorophyll in these organisms is clearly observed near 450 and 670 nm.

Preliminary tests of the toxicity of the Fe performed on active cultures of two photosynthetic protests, *Chlamydomonas* and *Euglena*, showed that this is not a problem. Test measurements were also performed to ensure that the chlorophyll spectral features can be observed and tested for organisms grown in iron oxide suspensions. Shown in Fig. 4.3 are absorbance spectra of several suspensions of *Chlamydomonas* and *Euglena* in media plus H_2O and the nanophase iron oxides/clay aggregates from Fig. 4.1. These spectra show that the chlorophyll pigments can be clearly seen above the spectra of the iron oxides suspensions.

4.3 Approach and Methodology

This project sounds fairly intuitive, leading to the suspicion that this work must have been done before. However, extensive review of the literature has shown that others have been primarily concerned with the abundance of iron (Pierson and Olson 1989; Pierson 1994; Wilson et al. 2000) and morphology of iron oxide-organic clusters (e.g. Emerson and Revsbech 1994a,b; Pierson et al. 1999; Pierson and Parentau 2000). Previous investigations (Olson and Pierson 1986; Pierson et al. 1987; Pierson and Olson 1989; Pierson 1994) have evaluated the transmittance of light through microbial mats and organic sediments in order to determine that some of these natural materials were effective in blocking the damaging UV rays with as little as 1 mm depth and that the spectral properties of the mats are an important aspect of the organisms' environment. However, little consideration has been given so far to the mineral structure of the iron oxides, or the impact of these minerals on the spectral environment of the organism. This study is thus critical in its ability to link studies of early evolution on the Earth with the search for life elsewhere.

Our proposed projects include UV transmission experiments in the lab and in the field. Some of the lab experiments will require synthesis and characterization of fresh iron oxide/oxyhydroxide minerals. The field experiments will require collection of the *in situ* iron oxide/oxyhydroxide minerals for characterization.

4.4 Outline of Proposed Tasks

Task 1: Determine whether these minerals can provide a favorable environment for photosynthetic organisms. We will test the iron oxide/oxyhydroxide minerals ferrihydrite and schwertmannite (in a clay matrix) and freshly prepared iron oxide/oxyhydroxide minerals as UV radiation shields for photosynthetic organisms. This will involve whole organisms and DNA dosimeters and take place in the lab and in a special environment on the roof of the lab building. Task 2: Determine which ferric oxides/ oxyhydroxides/ oxyhydroxysulfates are active *in situ* where organisms grow. We will run UV transmission experiments in naturally occurring bodies of water high in iron. First among these is in Nymph Creek and adjacent iron springs, Yellowstone National Park. Other likely sites include Rio Tinto (Spain), Iron Mountain (California), and Landmannalaugar (Iceland). We will test the already present iron oxide/oxyhydroxide minerals as UV radiation shield for *Cyanidium* and other photosynthetic organisms, collect samples of the iron oxide surface layers for characterization, and compare growth rates using fresh iron oxide/oxyhydroxide minerals and *in situ* iron oxides. Task 3: Analyze spectral, chemical and biological properties of iron oxides, organisms and their environments. Compare spectral character in UV, visible and near-IR regions of synthetic iron oxides and iron-bearing components of mats. Evaluate differences in spectral and chemical factors with respect to the organisms used.

4.5 Detailed Descriptions of Proposed Tasks

Task 1**.** Growth experiments will be performed using representatives of an ancient photosynthetic taxa, including the cyanobacterium *Synechococcus*, and eukaryotes including the red alga *Cyanidium*, the green alga *Chlamydomonas*, and the mixotrophic protist *Euglena*. Cyanobacteria are ancient organisms that first invented oxygenic photosynthesis, so are likely to have been prominent prior to the formation of the banded iron formations. The other three organisms are already in culture in Dr. Rothschild's lab. The *Cyanidium* is critical because it is found in and around the Iron Spring in Yellowstone. Dr. Rothschild has 10 years experience working with the primitive alga *Cyanidium* both in the lab and in the field. *Chlamydomonas* and *Euglena* are well known, easily grown, large and so can be easily seen in the microscope as distinct from the iron grains. Additionally, various mutants including those defective in DNA damage repair, are available in Rothschild's lab. *Euglena* is a mixotroph, in other words, it can either function as a heterotroph or as an autotroph.

Solar radiation experiments will be conducted by adding aliquots of freshly prepared media culture to several iron oxide/clay sample suspensions, letting them grow in the indoor incubator to mature cultures, then exposing them to natural solar radiation. Note that because the media used contain very minor amounts of organics (e.g., vitamin supplements) they themselves do not attenuate UV.) Samples will be enclosed in water-tight plastic bags, and floated in a constant temperature water bath cooled to 25 °C for several hours under direct sunlight. The total UV-A (mJ/cm2, 320 to 400 nm) and UV-B (µJ/cm2, 290 to 320 nm) exposure of the samples will be measured during these experiments using UV meters. Following the solar treatment the sample bags will be wrapped in opaque foil (to prevent further exposure to UV, visible or IR radiation) and returned to the incubator until the following exposure period. A temperature-controlled water bath is operating on the roof of our building under the direction of Dr. Rothschild. This system is designed for growing microbes in a constant temperature/solar radiation environment, and will be used for these experiments. Absorbance spectra will be measured periodically in order to monitor the growth of the organisms in the incubator. Samples will be collected following UV exposure period for measurement of spectral absorbance and determination of cell counts under the microscope.

These organisms will be grown first in suspensions of the iron oxide minerals imbedded in clay matrices available from previous studies (e.g. Bishop et al. 1995). Additional growth experiments will be performed using the freshly-prepared ferric oxide minerals and the organisms described above. In these experiments the organisms will be grown in the presence of solar radiation and suspensions of the iron oxide minerals without clays or other silicates.

Synthetic ferric oxide/ oxyhydroxide/ oxyhydroxysulfate minerals will be prepared in the lab using techniques similar to those outlined in Schwertmann and Cornell (2000) and Cornell and Schwertmann (1996). These reactions will be performed by Dr. Bishop and the student/lab tech as in prior studies (Bishop et al. 1993, 1995). Synthesis of ferrihydrite, schwertmannite, goethite and hematite are planned initially. Depending on which minerals are identified in the field studies of Task 2, additional ferric oxide-bearing minerals will be synthesized.

The iron oxide/oxyhydroxide minerals will be characterized and their purity will be verified using visible/ infrared reflectance spectroscopy, bulk chemistry, and other techniques. The samples will be sent to the NASA-supported RELAB facility at Brown University under the direction of Carle Pieters for reflectance spectroscopy. These synthetic minerals will be sent out for chemical (X-ray Fluorescence) and mineralogical (X-ray Diffraction) analysis as necessary. As fine-grained samples of these minerals age with time, it is important to synthesize fresh minerals for experiments where the mineral structure and crystallinity are factors. Suspensions will be prepared with these freshly prepared iron oxides and the UV, visible and NIR absorbance spectra will be measured with a scanning spectrometer.

Task 2. Growth experiments will be performed *in situ.* The first site tested will be Iron Springs at Nymph Creek, Yellowstone, where iron oxide-bearing minerals are present in the water (Rothschild and Mancinelli 2001). The objective of these experiments is to determine how effective the local ferric oxides are in shielding UV radiation for the *Cyanidium*. These experiments will entail growing the local *Cyanidium* in their local water and nutrient environment in UV transparent containers: one set of containers will be solar UV-screened while the other will be exposed to the normal solar UV radiation. Visual inspection at the experiment site will provide qualitative analysis of the organism growth.

Several other sites that are known to be high in iron are being considered for further studies. One is the Rio Tinto river in southwestern Spain (e.g., Davis et al. 2000). Discussions with Juan Mercador of the Centro de Astrobiologia in Spain have begun that will lead to our analysis of the iron in Rio Tinto in collaboration with the Spanish affiliates of the NAI. The other is Iron Mountain in northern California, a site that has been studied extensively with respect to its microbiology (e.g., Edwards et al. 2000). Bishop is currently funded to study alteration processes of volcanic material in Iceland (through MFRP), and could cost-effectively perform field experiments at the Landmannalaugar hydrothermal site (e.g. Bishop and Murad 2002) for this project as well.

Aliquots of each experiment will be collected for UV-VIS-NIR absorbance measurements with the field spectrometer in order to monitor activity and determine the mineralogy of the iron species. Based on these measurements, samples will be selected for quantitative analysis in the lab via cell counts and mineral characterization. These samples will be sent out for chemical analysis and to the NASA-supported RELAB facility at Brown University for visible/infrared reflectance spectroscopy. It is likely that a mixture of ferric oxide /oxyhydroxide/ oxyhydroxysulfate minerals is present in the water in Nymph Creek and the adjacent Iron Spring. If the experiments show that the local ferric oxide-bearing minerals are highly effective in shielding UV radiation, while allowing penetration of the necessary visible region light, then the combination of minerals identified in this natural system will be employed in the latter experiments in Task 1.

Additional growth experiments will be performed *in situ* at Nymph Creek, Yellowstone (and selected other sites) using combinations of ferric oxide / oxyhydroxide / oxyhydroxysulfate minerals that are successful in the experiments in Task 1. The objective of these experiments is to determine the relative success of imported ferric oxides (from the lab studies) vs. the local ferric oxide minerals in shielding UV radiation for the *Cyanidium* in their local water and nutrient environment. These experiments entail setting up one batch of experiments with the *Cyanidium* in a closed environment and another set of experiments by removing the local ferric oxides and replacing them with the imported ferric oxides. Both sets of experiments will be exposed to the normal solar UV radiation. Visual inspection and spectral absorbance measurements using the field spectrometer at the experiment site will provide qualitative analysis of the organism growth. Aliquots of each experiment will be collected for quantitative analysis in the lab via cell counts and detailed spectral measurements.

Task 3. The spectral character of the synthetic iron oxides and iron-bearing components of mats from Nymph Creek, Yellowstone, will be compared in the UV, visible and near-infrared regions for the spectral absorbance in solution. Spectroscopic analyses will also be performed on the reflectance spectra of bulk powders for the successful sunscreening agents from the lab and field studies in order to develop methods for remote detection of these on other planets including Mars. Differences in the spectral and chemical factors of the experiments run in Tasks 1 and 2 will be evaluated with respect to the organisms included in these experiments and the evolution of photosynthesis. Determining the optimal spectral and chemical environments for two different photosynthetic organisms will help us understanding the likelihood of a connection between photosynthesis, banded iron formations and oxygen.

4.6 Investigative Work Plan

Co-Investigator Janice Bishop will be the leader for the proposed projects in this section. This includes sample preparation and characterization, spectroscopic analysis, lab and field experiments, data interpretation and publication of results. The intended work commitment for Dr. Bishop is 0.2 per year for Years 1-5.

Collaborator Lynn Rothschild is a senior research scientist at NASA-Ames Research Center whose expertise is in algae and the influence of UV radiation on microorganisms. Because Dr. Rothschild is a NASA employee no cost is assigned for her salary on this project. The intended work commitment for Dr. Rothschild is 0.05 per year for Years 1-5.

A staff technician at the SETI Institute, Dana Rogoff, will work with Drs. Bishop and Rothschild at NASA-Ames Research Center on this project. The intended work commitment for the student/technician is 0.3 per year for Years 1-5.

4.7 Timeline

Task 1 is primarily lab work and will be initiated first. Task 2 is field work that will begin in year two. Task 3 involves analysis of the results of Tasks 1 and 2 and increases towards the end of the project. The combined tasks in this project will be carried out over a five-year period. Depending on the results of each task, some iterations in the experimental details may be necessary. Tasks 1 and 2 contain the bulk of the work and Task 3 will produce the results of the study.

5. Effect of High UV on Life in High-Altitude Lakes: Analogs to Mars

Data returned from the Mars Global Surveyor (MGS) spacecraft support the hypothesis that liquid water and geothermal energy may still be present on Mars. Fresh gullies (Malin and Edgett 2000), and lava flows could be less than 10^6 Myr old (Hartmann et al. 2000). Mars Odyssey Gamma-Ray spectrometer shows the presence of abundant hydrogen that could be related to up to 50% per weight of water-ice in the subsurface depending on latitude. Recent ice-covered lakes (Cabrol and Grin 2001, Moore and Wilhems 2001), rock glaciers and possibly debris-covered glaciers (Cabrol et al. 2002, Baker et al. 2001, Baker 2001, Kargel 2001) form a dense population of pristine landforms covering Mars from -30^o to -60^o latitude and $+27^o$ to $+50^o$ latitude (Cabrol et al. 2001a, 2002). If life arose on Mars in the past, the presence of both energy and water in recent times increases the odds of finding oases (McKay et al. 1992a,b, Farmer and Des Marais 1994, Farmer 1995, Farmer and Des Marais 1999, Wade et al. 1999, Farmer 2000,) However, in order to survive on Mars, life (if any) needed to adapt constantly almost from the very beginning to increasing environmental stress. Critical changes included the thinning atmosphere and loss of surface water escaping into space, and migrating and freezing into the subsurface.

At this early stage in our understanding of how life originated, the search for evidence that life might have evolved on Mars is necessarily guided by our knowledge of the range of environmental niches that can be successfully occupied by terrestrial life forms. Geologic and atmospheric models suggest that Mars was more habitable during the first 500 Ma of its history, (Kasting 1991, Haberle 1986, 1998, Jakosky et al. 1993, Squyres and Kasting 1994, Carr 1996, Baker 2001). Rivers and lakes (Carr 1996, Cabrol and Grin 1999, 2001), possibly an ocean (Parker et al. 1993, Head et al. 1999, Parker et al. 2001, Baker 2001) which had formed earlier started to decline around 3.5 Ga. There is evidence that they may have occurred again in later geological periods (Cabrol and Grin 2001) but only episodically and as lower magnitude events, their formation possibly driven by magmatic pulses (Dohm et al. 1999) and/or oliquity changes (Jakosky et al. 1995, Haberle et al. 2001, Cabrol and Grin 2001).

This project focuses on environmental conditions for life in terrestrial lakes located at extreme altitudes providing a unique analogy to Martian paleolakes of this transitioning period 3.5 Ga ago. Paleolakes have been identified on Mars in topographic lows (De Hon 1992), impact craters (Newsom et al. 1996, Cabrol and Grin 1999, 2001) and in volcanic regions (Cabrol and Grin 2002). The environment at the time of their formation included: episodic water supply; increasing evaporation and sublimation due to the thinning of the atmosphere which led to the reduction in size and depth of the lakes, hence generating chemical, pH, and salinity changes; high-UV radiation; cooling temperatures accompanied by seasonal, then perennial, ice-cover on the lakes; and short to long-term hydrothermal processes for lakes associated with impact craters and volcanic activity (Brakenridge et al. 1995, Gulick and Baker 1990). Understanding how this set of conditions affected putative living microorganisms is of paramount importance to assess their chances of surviving a changing Mars (Chang 1988, Clark 1998). Determining what type of microorganisms and defense strategies they could have developed is also critical to better prepare future instruments, experiments, technology, and landing site selection for future astrobiological missions (Des Marais et al. 1995, DeVincenzi et al. 1998) Moreover, it will help us understand better how life survived on early Earth as for two billion years after it emerged, the atmosphere contained very little oxygen (Kump et al. 1991; Kasting 2001) thus little ozone. The mechanism used by these organisms may be very ancient and could shed light on early Earth biology.

5.1 Previous Work

Because of their astrobiological potential, various aspects of extreme lake environments have been studied as Mars analogs, such as: the physical and biological constraints on the structure and function of dry valley ecosystems in the Dry Valleys of Antarctica (Doran et al. 1998, 2000), the nature of lake sedimentary environment (Benison 2002), the geomorphology of high latitude lakes (Rice 2001), the formation of tufa (Stoker et al. 1996) the conditions of evaporite formation (Wentworth and Morris, 2001) and their remote sensing signatures (Baldridge et al. 2001), the biology of impact crater lakes in the High-Arctic (Cockell and Lee 2001, Cockell et al. 2001), and the physical environment of subglacial lakes in Antarctica (Oswald and Robin 1973, Siegert et al. 1996). Significant work has also been performed on the effects of UV in lakes and models of UV flux over time (Cockell 2000). Sunlight penetrating lake water is absorbed in different ways by particles and natural chemicals in the water: water molecules absorb red and infrared wavelengths; pigments (chlorophyll) in microscopic algae that float in the water absorb blue and red light for use in photosynthesis; and UV light is absorbed by organic material dissolved in water. Lakes showing a high content of dissolved organic material (DOM) shield organisms from UV (McKenzie et al. 1999, Rae et al., 2000). DOM acts as a natural sunscreen as it influences the water transparency and so is a determinant of photic zone depth (Reche et al. 2001). In sparsely vegetated alpine and tundra areas, lakes tend to be clearer and offer less protection from UV to organisms living in the water (Vinebrooke and Leavitt 1998). Transparent water, combined with high UV irradiance may maximize the penetration and effect of UV radiation as shown for organisms in alpine lakes (e.g., Vincent et al. 1984, Vinebrook and Leavitt, 1996). Shallow-water benthic communities in alpine lakes are particularly sensitive to UV radiation. Periphyton, which defines communities of microorganisms in bodies of water, can live on various substrates. While on rocks, they include immobile species that cannot seek low UV refuge unlike sediment-dwelling periphyton (Happey-Wood 1988, Vincent et al., 1993) or alpine phytoflagellates (Rodhe et al. 1966, Rott 1988) which both undergo vertical migration. Inhibition of algal photosynthesis by UV radiation has been documented in laboratory (Häder 1993, Vincent and Roy 1993) and shown that phytoplankton production is reduced by formation of nucleic acid lesions (Karentz et al. 1991) or production of peroxides and free oxygen radicals (Cooper et al., 1989). Most of the experiments that have demonstrated in situ suppression of algal growth by UV radiation have either used artificially enhanced UV irradiance (Worrest et al. 1978) or shallow systems (<1 cm) that lack significant natural attenuation of UV radiation (Bothwell et al., 1993, 1994).

5.2 Unique Analogs

We propose to investigate the short and long-term effects of Ultraviolet (UV) radiation in the highest lakes and ponds on Earth located in Bolivia and Chile as analogs to Martian paleolakes. Their elevation ranges from 6,046 m to 4,300 m. Two complementary experiments will test for the effects of UV radiation on periphyton: (1) the monitoring of biomass accrual, chlorophyll *a*, and species abundance on the underside of acrylit*e* plate stations; and (2) the positioning of UV dosimeters that will integrate the level of UVA (315-400 nm), UVB (280-315 nm), Photoactive Radiation PAR (400-700 nm), and temperature in the lakes. Environmental and physical data will be collected through long-term data logging. Core samples will be extracted to characterize the geologic and sedimentologic environment. Biological samples will undergo DNA extraction, chlorophyll *a* determination FISH analysis, DGGE analysis of bacteria and Archea 16S rDNA fragments. The environmental conditions (elevation, latitude, temperature, evaporation) and volcano-tectonic hydrothermal setting at these lakes provide a unique analog to Martian paleolakes 3.5 Ga ago at the time when the atmosphere became thinner on Mars and life, if present, would have been subjected to increased environmental and survival stress. This research, never performed before at such altitude, will allow to: (a) characterize life in high-altitude lakes; (b) identify the defense strategy developed by organisms living in shallow lakes against UV radiation; (c) advance our understanding of both the habitability potential of Mars and the limits of life on Earth. Results will provide critical clues to search and identify potential sites for life (extinct and/or extant) on Mars.

We will investigate the crater lakes and ponds at the summit of the Licancabur (6,017 m), Acamarachi (6,046 m), Aquas Calientes (5,924 m) dormant volcanoes as well as "laguna Verde-Blanca" (4,300 m). These lakes are located in Chile in the Atacama desert, at the border of Chile and Bolivia in volcanic and desert environments. Their geographical location (see Table 5.1) combined with their exceptional elevation provides a unique UV radiation environment. Moreover, the conditions of low oxygen, low atmospheric pressure (450 to 640 mb), low temperatures, aridity, volcano-tectonic environment, and hydrothermal activity make these lakes the closest terrestrial analogs to what we believe conditions were in early Martian lakes. Life is thriving in these lakes.

Table 5.1 Lake Characteristics

Name	Location		Elevation (m)	Temp. (^{o}c)		Lake dimensions (l•w•d)	Environment	Status Volcano
	Lat^{o}S	Long^o W		Max.	Min			
Licancabur	22.50	67.53	6,017	+4	-40	(100 x 70 x 10) m	Volcanic Hydrothermal?	Dormant
Acamarachi	23¼18	67⅓7	6,046	+4	-40	(~20 x 50 x ?) m	Volcanic	Dormant
Aquas Calientes	23¼22'	67¼1'	5,924	+5	-35	(~80 x 80 x ?) m	Volcanic Hydrothermal	Dormant
Laguna Verde	22.49	67.47	4,300	+17	-25	(7 x 1) km x 40 m	Hydrothermal	N/A

5.3 Preliminary Investigation

In 2001, Co-I Nathalie Cabrol was awarded a NASA Ames Directorate Discretionary Funds (DDF) as seed money to perform a reconnaissance at the Licancabur summit lake to assess its astrobiological potential. During the expedition at 6,017 m, the team was able to successfully deploy one acrylite plate station (see below) and data loggers (Cabrol et al., 2002). This was the first time that this experiment was taken to such high elevation. This preliminary experiment needs to be now expanded and completed (a) by the positioning of ELDONET dosimeters that will record the level of UV A, UVB, PAR, temperature at Licancabur and (b) by the deployment of acrylite stations, ELDONET dosimeters and data loggers to the other surrounding lakes in order to complete our vision of life and UV defense strategies at increasing altitudes. Their investigation will provide a unprecedented transect of shallow lakes, UV, and life between 4,300 m and 6,046m. Performing these experiments over long periods of time is critical to observe changes in the population leaving in the lakes. The approach to this is described below.

5.4 Plate Station Experiments

These experiments will test the effect of UV radiation on immobile periphyton located on shallow lake sediments. What is of primary interest for this study are organisms that live and are immobile in the water zone where the influence of UV radiation is the most severe (surface to 1 m). Upon selection of biologically promising sites in the lakes and following the technique successfully used in Licancabur in 2002, we will construct a gazer chamber formed by acrylite [Cyro indutries] submersed sheets in shallow water. The sheets will be suspended on four acrylite 30-cm long rods at ~10 cm above sediment. Each sheet will be surrounded by a mosquito nylon screen fixed on the upper part of the rods and closed by heavy rocks on the sediment. The sheets will be anchored to heavy rocks by four nylon ropes. Each station will be composed of one (60 x 60) cm x 3.4 mm OP-3 UV filtering and one(60 x 60) cm x 3.4 mm OP-4 UV transmitting sheet. The acrylite OP-3 absorbs 98% of the incident UV. The OP-4 transmits much of the radiation in the range from 260-370 nm and light between 395-1000 nm. It is specifically formulated to resist the degradation caused by continuous exposure to the high-intensity ultraviolet radiation. We will leave the stations over long periods of time and harvest their underside regularly to study the evolution of microorganisms that have been exposed and those that have been protected from UV. Harvest will happen after 1, 2, 3, and 4 years of exposure. The sheets are large enough (3600 cm^2) to allow 4 x 900 cm^2 harvest over this period for each station. The harvest will be performed using a brush and a scraper system (Aloi 1990). The results of this experiment will be directly compared to those obtained by Vinebrook and Leavitt (1996)—with whom the team is in direct contact—using the same method that they used on a small alpine lake in Canada (2,320 m). Samples of water and biomass will be collected in amber bottles and analyzed by the biologists on the team.

5.5 Physical Environment

The physical environment will be characterized by a) Mapping: Data will be collected using GPS units to determine the lakes' location, size, and altitude. We will determine their size; and will observe changes in annual water levels to extract some information about the lakes' water budget. Additionally, lake surface area is an important factor in energy budget (e.g. evaporative flux and the effect of insulation; b) Geophysics. We directly measure the air temperature, soil and water temperature as a function of depth, relative humidity, and UV flux at the lake surface and as a function of water depth. A lightweight, handheld probe will be used to record conductive heat flux from the lake bottom. We will install dataloggers (e.g. Onset Computing HOBOs) to monitor air temperature and relative humidity, and water temperature as a function of depth throughout one year. The prime focus of this task, however, is characterizing the UV environment at the lake surface and at the depth of the acrylite UV plate experiment. For this, a 3-channel (UVB: 280-315 nm, UVA: 315-400 nm, PAR: 400-700 nm) submersible, logging ultraviolet dosimeter will be installed at each site. Results from mapping (lake surface area, approximate volume) will be paired with data on geothermal flux and evaporative flux (from temperature and relative humidity) and used among other information to build an energy balance model. This model will be applied to investigate the role of geothermal heating in the lakes' existence and stability, and to better understand the relationship between the physical environment and the endemic biology. Because the optical properties of freshwater vary greatly in the UV, the deeper parts of these lakes (depths greater than ~1-2m) may receive only nominal UV dosages—similar to lower altitude surface environments. The shallow portions, however, are truly unique because they receive far greater incident UV flux than other freshwater environments on Earth and remain scientifically unexplored. Therefore, some of the most important results from the geophysical data collection effort will be the time-dependent flux of ultraviolet radiation at the shallow mounting depth of the UV sheet experiment. The dosimeter units will continuously monitor automatically the UV radiation on all three data channels as well as external temperature and pressure (depth); the former will be used to calculate total UV flux and the UV index. Optical properties in the UV for the lake water will be extracted from direct measurements of UV flux as a function of water depth. Data will be downloaded every year. Power is provided to the dosimeters through solar panels; c) Chemistry. Water samples will be taken from each site for laboratory analysis of fluid chemistry. Inorganic anion (e.g. sulfate, chloride, others) analysis will follow standard protocol (EPA Method 300.1) using Ion Chromatography (IC). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Emission Spectrometry (ICP-AES) will be employed (also following standard protocol (EPA method 200.7, 200.8) to determine trace element concentrations. Some data will be collected *in situ* using commercially available kits, which will be used to direct laboratory analysis and detect any effects of sample storage and transportation. Results from the water chemistry study (*in situ* and lab-based) will be employed to characterize the presence of geothermal fluid input to the lakes and allow us to build a more complete model of energy/hydrologic balance. Specifically, ICP methods will allow us to analyze the main rock-derived elements in volcanic lake fluids (e.g. Na, Ca, K, Mg, Fe, and Al from andesitic volcanoes). This will be paired with IC analysis of the principle anions derived from magmatic gas-hydrothermal fluid interaction (e.g. Cl, SO_4, and F) to characterize the presence, type, and extent of any hydrothermal activity in the lakes.

5.6 Characterization of Organisms

Shallow water and sediment samples will be taken from the lakes and ponds and will undergo a series of analyses: a) Organic Geochemical and Microbiological Characterization: samples will be analyzed using Gas Chromatograph-Mass spectrometry (GC-MS) to document the structure of lipids and photosynthetic/UV-screening compounds such as chlorophyll and carotenoids. This will identify specific adaptations in the structure of these molecules to high the UV environment. Genetic analyses will be conducted on DNA extracted from samples, leading to the sequencing of genes encoding from the 16S rRNA of organisms present in the samples. Fluorescent-In-Situ-Hybridization (FISH) will also be applied to identify quantitatively the communities present in the samples. Additionally, arsenic/sulphur enrichment media will be developed in order to cultivate arsenic reducing bacteria and sulphur reducing bacteria from the arsenic/sulphur sediment. Microorganisms will also be characterized by microscopy. b) Taxonomy: Abundant samples of the microorganic, bacterial, and algal communities in surface water and 1-m water will be collected and analyzed to identify the various species living in these environments. Slides will be attached to a line on a float at each lake. The slides will be separated at regular space interval down to 2-m depth. They will collect microorganisms at various depths and provide information on the distribution of the biological population.

5.7 Anticipated Results

These lakes combine many of the environmental characteristics suggested for early Martian lakes and thus constitute possibly the closest analogs ever studied. Learning how the organisms in these lakes protect themselves from UV may help us understand how life survived on early Earth - and perhaps on early Mars as well. For as long as two billion years after life emerged on Earth, the atmosphere contained very little oxygen and therefore little ozone (Kump et al. 1991, Kasting 2001). Somehow, life on Earth started without a protective atmosphere present. By studying the organisms that live in these lakes, we hope to discover clues about how early life on Earth managed to cope with high UV. The survival mechanisms employed in this environment may be very ancient. Results will provide not only clues for the search of life on Mars, but may also provide important information about the limits of life on Earth.

5.8 Expedition Safety and Risk Mitigation

This project involves high mountaineering and its associated risks, including Acute Mountain Sickness (AMS), and accidents associated with climbing volcanoes. For this reason, via the NASA Ames Research Center DDF program in 2001, the Licancabur expedition underwent a thorough safety and risk evaluation. Risks and mitigation were reviewed by an official safety panel at NASA Ames.. The review led to the production of official technical and safety reports showing risks closure and satisfactory risk mitigation. They can be provided upon request from Robert Navarro and Alexis Flippen (NASA Ames/Code Q). All team members listed in this project are veterans of the 2002 Licancabur expedition and have proven high-mountaineering achievements.

5.9 Logistics and local support

This project will benefit from the logistics set up for the ‘02 Licancabur expedition, including team transportation, a familiar and experienced team of mountain guides and porters, lodging, food, and permits. This includes support from the Chilean (Universidad Catolicà del Norte) and Bolivian (Sergeomin) Institutions. Letters and documents of support can be provided upon request. This project also builds upon a successful history of scientific collaboration between UCN and the Co-I started during the Nomad field experiment

5.10 Project Milestones

Year 1: Position dosimeter on Laguna Verde (can be reached by car). First harvest of acrylite positioned in 2002. Harvest Licancabur plate positioned in 2002. Position dosimeter. Collect samples of water at various depth and set data loggers; Climb Acamarachi and position one acrylite Station and one UV dosimeter. Perform geophysical tasks and sample water and sediment for chemical, geological and biological analysis. Year 02: Climb Aquas Calientes set one acrylite Station and one dosimeter. Perform geophysics, chemistry and biology task. Return to Licancabur, Laguna Verde and Acamarachi for acrylite harvest and retrieve data from the dosimeters. Ongoing sample analysis. Year 03 to Year 05: Return to all sites for harvests, plates and dosimeters maintenance, data retrieval, sample collection and completion of geophysical, chemical and biological tasks.

5.11 Team Member Responsibilities

Nathalie Cabrol is a planetary geologist and the project and expedition lead. She will be responsible for meeting deadlines and for the completion of the project, for its astrobiological implications and Mars analogy aspects. She was the Project PI and lead of the 2002 Licancabur expedition. Edmond A. Grin, a planetary geologist, is responsible for the UV acrylite Experiment. Andrew Hock, a Ph-D student at UCLA, will be responsible for the geophysics task. David Fike is a Ph-D student and responsible for GC-MS, DGGE, and FISH analyses; Cecilia Demergasso, a Collaborator at the Universidad Catolica del Norte, Antofagasta (Chile), will be responsible for the biology task. Guillermo Chong, Collaborator at the Universidad Catolica del Norte, Antofagasta (Chile), will be responsible for assisting in geology and logistics.

This research will address Goals 2, 4, and 5 of the Astrobiology Roadmap.

6. Planetary-Scale Transition from Abiotic to Biotic Nitrogen Cycle

Nitrogen is an essential element for living organisms, and is found in most biologically important molecules including proteins, DNA, and RNA. As a consequence, understanding the planetary nitrogen cycle is critical to understanding the origin and evolution of life on a planet. In fact, an insufficient endowment of nitrogen on a planet will inhibit the origin and evolution of life (Mancinelli and McKay, 1988). Of particular importance to prebiotic and biotic chemistry is "fixed N" (NH_3, NH_4^+, NOx, organic-N). Without fixed nitrogen the origin of life would not have occurred on Earth and would most likely not occur on any other planet. It is the chemistry of nitrogen and how it chemically reacts and combines with carbon that makes it so unique.

The transition from abiotic to biotic planetary N cycling will affect profoundly N distribution among the planetary N reservoirs—the atmosphere, lithosphere, hydrosphere and, if present, biosphere. The chemical speciation of nitrogen in each of the reservoirs or "spheres" will also change dramatically as biology takes hold. This project aims to improve our understanding of these changes in the chemical speciation and the distribution of nitrogen on a planet's surface and suggest methods for their assessment. The project will focus, specifically as a test case, on the nitrogen evolution on Mars and its present-day availability and distribution.

Besides N, the other essential major biogenic elements, H, C, O, S, P, and the bioessential trace elements are present on Mars at concentration similar to those of the Earth and their availability is not considered to be limiting for the development of life (Mancinelli and Banin, 1995: Banin and Mancinelli, 1995). Furthermore, recent observations by the Mars Global Surveyor (MGS) and the Odyssey Missions have shown that Mars is relatively rich in water and that liquid water has likely been intermittently present and active in shaping the surface up to the present (Malin and Edgett, 2000a,b; Boynton et al., 2002). This leaves the issue of nitrogen availability on the surface of Mars as a major unknown in the assessment of Mars ability to support biotic evolution and its future habitability.

According to current hypotheses, the atmospheres of planets considered habitable (i.e., in habitable zones) formed in a manner similar to that of Earth, that is, from the release of gases originally trapped in the solid interior of the planet during its final stages of accretion (Hunten, 1993). For example, Earth and Mars formed as hot, molten, and geologically differentiated objects. Geochemical and geological evidence suggest that the oxidation-reduction state and hence, the chemical composition of outgassed volatiles is determined by the composition and structure of a planet's interior (Hunten, 1993). These volatiles include water vapor, carbon dioxide, and dinitrogen. Based on data and models of the development of Earth and Mars CO_2 and N_2 were, and are, the major atmospheric constituents of planets formed in this manner. This makes N_2 from outgassing the primary source of N for terrestrial type planets in habitable zones. Additional sources of N on this type of planet include comets and meteorites that would provide reduced N (e.g. Chyba 1991). These sources and mechanisms should result in similar initial forms of N on habitable zone planets.

Nitrogen cycling occurs abiotically and, for those planets that harbor life, biotically. This results in two fundamentally different fates for N on inhabited vs. uninhabited planets. On those planets that harbor life organic-N is the dominant form, whereas, abiotic cycling favors inorganic forms, specifically HNO and N_2O in the atmosphere, if no liquid water is present on the planet's surface and NO_3^- and NO_2^- if water is present. (Although comets and moons of gas giant planets [e.g., Titan] can possess high levels of organic-N, they possess essentially no appreciable amounts of inorganic-N salts.) If a planet is geologically active an abiotic N-cycle such as that described by Mancinelli and McKay (1988) can occur. If geologic activity ceases, as appears to have happened on Mars, cycling does not occur, and the volatiles, including N_2, in the atmosphere can be depleted by impact erosion and hydrodynamic escape to space. In a planet that once had oceans on its surface, N may remain in the regolith as NH_4^+ attached to clays, and/or buried in the regolith as NO_3^- and NO_2^- salts.

6.1 Abiotic Nitrogen Cycling

Atmosphere. The most predominant series of non-biological N-transformation reactions in an N_2/CO_2 containing atmosphere occur as a result of thermal shock waves from either meteoritic/cometary in-fall, or lightning that breaks the dinitrogen triple bond. In such an atmosphere, the thermal shock produces NO (Borucki and Chameides 1984), that readily forms nitrosyl hydride (HNO), the primary end product of the reaction (Kasting and Walker 1981). Mancinelli and McKay (1988) defined the fate of HNO. Briefly, HNO is a reactive N^{+1} species. In the atmosphere it dimerizes and dehydrates to form N_2O and H_2O (Fig. 6.1a.).

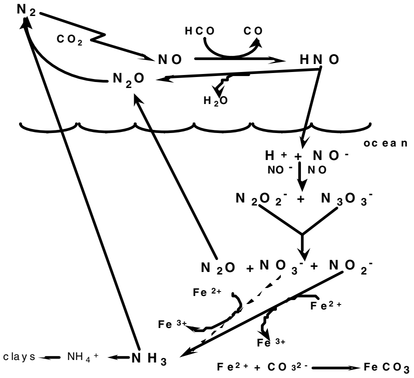


Fig. 6.1a . Summary schematic of the major pathways of the abiotic N cycle. Dashed line indicates that this reaction is less likely to occur.

Impact shock formation of nitrogen species other than NO (e.g., HCN, NH_3) have been considered (Fegley et al. 1986, Zahnle 1986). However, in a predominantly CO_2 atmosphere as thought to have existed on early Mars, early Earth and other planets in habitable zones, HCN is not produced, and any NH_3 produced photolyzes rapidly to N_2. Another potentially important form of fixed nitrogen on early Mars may have been organic-N. In a CO_2-dominated atmosphere, the formation of organic compounds is extremely difficult (Folsome, et al. 1981). Comets and meteorites, however, could have imported organic nitrogen compounds to early Mars, early Earth and possibly other planets in habitable zones (Chyba and Sagan 1992, Pierazzo and Chyba 1999).

Hydrosphere. Because the rate of dimerization of HNO is slow and it is readily soluble in water nearly all of the HNO formed falls into the ocean (on those planets that have oceans). It first dissociates into H^+ and NO^-. Once in aqueous solution NO^- reacts with itself and/or solubilized NO to form $N_2O_2^-$ and $N_3O_3^-$ and their conjugate acids. These species decay rapidly into N_2O, NO_2^- and NO_3^- (Mancinelli and McKay, 1988 and references therein). The N_2O is released to the atmosphere and is readily photolyzed to N_2. Any HNO_2 formed as a side product falls into the ocean and forms NO and HNO_3. The HNO_3 dissociates into H^+ and NO_3^-. So, if a planet did possess water on its surface then it is clear that the final product of thermal shock through the early atmosphere would produce NO_3^- and NO_2^- in the oceans.

Nitrite, but not NO_3^-, in oceans containing Fe^{2+} could be reduced to NH_3 (Zohner and Broda, 1979; Summers and Chang, 1993). These results suggest that NO_3^- would accumulate faster than NO_2^-. Most of the NH_3 that formed would be volatilized and escape to the atmosphere where it would be photolyzed to N_2. Some of the NH_3 would form NH_4^+ where it could be mineralogically fixed and stabilized by inclusion as a structural cation in the crystal lattices of certain phylosillicates replacing K^+ (reviewed by Mancinelli, 1996). The chemistry of NH^3 is the focus of section 5 of this proposal. The abiotic nitrogen cycle is summarized in Figure 6.1a.

6.2 Biological Nitrogen Cycling

The different types of fixed nitrogen, primarily organic-N, NH_3, NH_4^+, and NO_3^- are biologically useful and readily assimilated by organisms. Nitrogen is found most commonly in pools consisting of N_2, N_2O, NH_4^+/NH_3, NO_3^-, NO_{2-}, or organic-N. These pools are found throughout the various reservoirs. Reservoirs of nitrogen include the lithosphere, atmosphere, hydrosphere and biosphere. The biological and non-biological transfer of N among the various reservoirs constitutes the global nitrogen cycle (reviewed by Mancinelli, 1996; 1992) (summarized in Figure 6.1b).

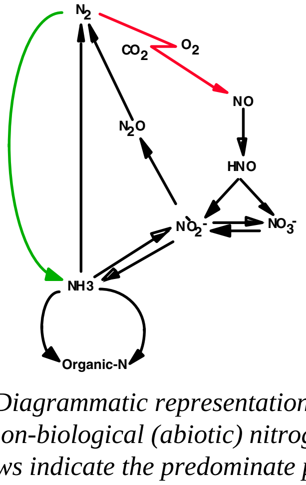


Fig. 6.1b. Diagrammatic representation of the biological and non-biological (abiotic) nitrogen cycle. The heavier arrows indicate the predominate pathways.

The biological nitrogen cycle consists of the following: Biological nitrogen fixation, the transformation of N_2 into NH_3; Ammonification, the enzymatic process of organic-N conversion to NH_4^+; Nitrogen assimilation, the conversion of NH_3 to organic-N and biomass; Nitrification, the oxidation of NH_4^+ to NO_2^- and NO_2^- to NO_3^-; Denitrification, the dissimilatory reduction of NO_3^- to N_2O or N_2.

If H_2O was on the surface of a habitable planet for extended periods, then fixed-N (especially NO_3^-) that are at least hundreds of thousands of years old. These desert areas essentially lack biological activity and leaching, which have been suggested as the reason for the NO_3^- stability (Claridge and Campbell, 1968).

6.3 Research Approach

Overview: The overall approach is to divide the research into two tasks that relate to the transition of an abiotic N-cycle to a biotic N-cycle. Task 1 concentrates on the abiotic portions of the N-cycle whereas task 2 adds the biological component. Task 1 involves understanding issues related to the chemistry, mineralogy and geology of N on a planetary basis. This specifically includes understanding and studying factors influencing the binding of N as NH_4^+ to poorly crystallized silicate minerals that are believed to be present on the surface of Mars, and the stability of nitrate mineral salts in different environments. Occurrences of nitrate accumulation on a regional scale, such as in the Atacama Desert and Antarctic soils, will be the subject of specific studies and the relevance of such accumulation of nitrate to N distribution in the Mars environment will be specifically studied using N transport simulation experiments and regional nitrogen balance modeling. In task 2, using the Atacama Desert as a study site, we will explore the biological reasons behind the stability of NO_3^- salts through geologic time on Earth. Although hypotheses have been presented for their stability, i.e., low rainfall and little biological activity (e.g., Claridge and Campbell 1968), these hypotheses remains untested. We will use the Atacama Desert in Chile as a model system. In addition, we will use the N-cycle in the microbial mat *Lyngbya aestuari* from the pacific intertidal, to model microbe-environment interactions with regard to the N-cycle as a function of organic-N:inorganic-N ratios, C:N ratios, as well as denitrification, nitrification, nitrogen fixation rates and photosynthesis and C-fixation rates (i.e., feedback effects of changing environment, including release of N_2O into the atmosphere). The results of the field, laboratory and regional modeling studies (including the results of Sec. 7 below) will be integrated into a unified framework that quantifies the partition of nitrogen into, and fluxes between, the various compartments (soils, lithosphere, hydrosphere and, if present, biosphere) in an extremely arid environment on the surface of a terrestrial, potentially habitable planet. The Atacama Desert will be our terrestrial field test site and Mars' shallow surface layers will be the target planetary site.

Task 1. Surface chemistry mineralogy and partitioning of planetary N (Dr. Amos Banin will take the lead). Nitrogen interactions with surface materials on solid-bodied planets and their distribution and accumulation in surface soils and regoliths will be studied in the following 2 ways.

The fate of N fixed and bonded as NH_4^+ in the crystal lattices of various minerals including zeolites, micas, phyllosilicates (clays) and poorly crystallized silicates (amorphous) minerals, as proposed to be present on the surface of Mars (Banin et al, 1997). We will determine the capacity of representative minerals to fix NH_4^+ under competitive conditions of high crustal K^+ (e.g. Earth), or low crustal K^+ (e.g. Mars), and the energetics of its binding. The availability of the fixed NH_4^+ to living organisms will be studied under non-oxidizing and mildly oxidizing conditions and the importance of this N-storage mechanism as a planetary sink-source to an emerging biosphere will be assessed. The ion-exchange and analytical methods to be used are described in Banin (1973) and Banin et al. (1993), respectively.

The environmental conditions and chemical-mineralogical mechanisms leading to the accumulation of soluble nitrogen as nitrate, as observed on Earth in the Atacama Desert and in Antarctic soils, will be explored. This will be done by reassessing existing observations and hypotheses on the causes and mechanisms of regional-scale accumulation of nitrates and testing the hypotheses elaborated below that such accumulation was primarily due to lack of rapid denitrification processes. The role of terrestrial plants in controlling the regional budget of nitrate/nitrogen will be quantified.

We will measure and evaluate the rates of accumulation of nitrates in soils receiving organic and ammoniacal forms of nitrogen, but where denitrification has been stopped or slowed due to high redox potential. The results will supply the basic information and data that will enable us to calculate the regional nitrate salt balance (using the approach presented by Banin and Fish, 1995) under extremely arid/high redox conditions. This sub task will be conducted in conjunction with Task 2, below.

Task 2. The Biosphere (Dr. Rocco Mancinelli will take the lead). We will focus on two systems, the Atacama desert and a microbial mat from the Pacific intertidal dominated by *Lyngbya aestuari*. (described by Rothschild and Mancinelli, 1990).

The Atacama desert is the exception rather than the rule on a wet inhabited planet such as Earth in that it is essentially a large NO_3^- salt deposit that is stable through geologic time. The surprising lack of denitrification under these conditions, apparently leading to the local nitrate accumulation, is of particular interest as an analog and model for planetary surfaces, or niches of limited biological activity. As part of a past study we have assembled a complete meteorological station in the desert that will provide pertinent data (e.g., humidity, rainfall, temperature, etc.). Preliminary denitrification data collected at one site on 3 samples during a field trip for another study in 1999 using the adetylene reduction method suggests that if denitrification occurs it is probably at a low rate. We propose to expand this preliminary data and test several sites to determine the potential for denitrification, activity in the field using standard techniques (e.g. acetylene reduction and $^{15}NO_3^-$ tracer studies). Further, to determine if denitrifiers occur in the area we will collect samples and, using probes specific for denitrifiers, probe the samples as described by Ward and Cockroft (1993) and Ward et al., (1993). Results of these tests will reveal the presence and activity, if any, of denitrifiers. These data will be correlated with the meteorological data. If denitrifiers are present and show little or no activity, this will help to determine if the lack of denitrification is due to lack of rainfall. If denitrifiers are not present (a doubtful result given their ubiquity and the broad range of prokaryotes possessing this ability) a systematic search for their inability to occupy a niche in this environment will be explored.

We have chosen an intertidal mat dominated by the cyanobacterium *Lyngbya aestuari*. This mat was chosen because cyanobacteria are important primary producers in microbially dominated ecosystems, and they likely formed the earliest recorded ecosystem of Earth (reviewed by Rothschild and Mancinelli, 2001). This mat inhabits the intertidal, so that in nature it undergoes daily drying and wetting, thus making not only a good candidate for study for varying moisture regimes, but it is easy to store in the lab, easy to grow on the roof of the laboratory building, and ideal for experiments for the terrestrial or aquatic environment. Previous work has shown that the N-cycle and the C-cycle within the mat are linked together and each exhibits a diurnal cycle (Rothschild and Mancinelli, 1990, Rothschild, 1991). N-cycling (N-fixation, denitrification, nitrification and assimilation rates) in the microbial mat will be determined using standard techniques (acetylene reduction for N-fixation and denitrification, acetylene blockage for nitrification and as well as ^{15}N tracer studies). Photosynthesis will be determined as a function of C-fixation using $^{14}C\text{-}HCO_3^-$ as described by Rothschild and Mancinelli, (1990). *Lyngbya* mat will be collected and transported to the laboratory roof artificial intertidal pool for experimentation. The effects of changes in concentrations of NO_3^- and NH_4^+ will be determined by adding various different amounts of each individually and separately to the system while monitoring rates of the various reactions of the N-cycle as well as C-fixation. Changes in rates of photosynthesis as a function of C-fixation will be correlated with changes in NO_3^- and NH_4^+ levels within the mat. Rates of N-fixation, denitrification, nitrification and assimilation will be studied as a function of changes in mat concentration of NO_3^-, NH_4^+ and rates of C-fixation. Concentrations of NO_3^- will be determined using an Ingold nitrate electrode. NO_2^- and NH_4^+ will be determined colorimetrically. Temperatures will be determined using an Omega Engineering portable temperature meter attached to a probe or a thermometer. The pH will be measured with a pH meter.

6.4 Work Schedule

Year 1: Begin laboratory nitrogen mineralogy experiments. Determine the capacity of representative minerals to fix NH_4^+ under competitive conditions of high crustal K^+, or low crustal K^+. Collect samples from the Atacama and conduct preliminary denitrification field studies. Collect microbial mat samples and set up roof experiment. Year 2: Continue laboratory nitrogen mineralogy experiments. Initiate experiments to measure the rates of accumulation of nitrates in soils where denitrification has been stopped or slowed. Continue field experiments on the Atacama; collect samples for denitrification gene probe analysis. Continue microbial mat N-cycle studies. Year 3: Complete laboratory nitrogen mineralogy experiments. Continue studies of nitrate accumulation rates in soils. Continue microbial mat N-cycle studies. Continue gene probe analyses on samples form the Atacama. Year 4: Continue microbial mat studies. Model the environmental conditions and chemical-mineralogical mechanisms leading to the accumulation of soluble nitrogen as nitrate on small scale and on regional scale. Year 5: Complete all studies and integrate the data into a unified framework and a conceptual model describing the partitioning of N on inhabited vs. uninhabited planets.

The research proposed here and in Sec. 7 addresses Goal 4 of the Astrobiology Roadmap.

7. Mars Nitrogen Simulation

Nitrogen plays an essential role in determining the habitability of a planet such as Mars. As described in Sec. 6, a prebiotic source of nitrogen is essential to the origin and early evolution of life (before the development of biotic nitrogen fixation). Nitrogen compounds also will have a significant effect on planetary habitability through its affect on such factors as climate. For example, N_2O and NH_3 both serve as greenhouse gases, N_2O is a catalyst for the destruction of ozone, and loss of N_2 from an atmosphere (and the resulting loss of atmospheric pressure) can have a catastrophic effect on a planet's climate leading to the inability to support liquid water, another essential element of life. The loss of atmospheric nitrogen on Mars may have been by fixation and sequestration in the regolith (Grady et al. 1995; Mancinelli 1996) or through loss by impact erosion, although nitrogen in the regolith would have been protected (Chyba 1990; Melosh and Vickery 1989) or by both processes.

Understanding the planetary nitrogen cycle is critical to understanding the origin and evolution of life on a planet. One planet whose habitability may have been significantly affected by the cycling of nitrogen is Mars. We propose to study directly the reactions of nitrogen that would have occurred in the early Martian atmosphere, seas, and crust by modeling the abiotic reactions experimentally. Experiments will examine the chemistry and photochemistry of a variety of proposed atmospheres, with and without water and model Martian minerals, and measure the products formed.

The predominant series of known N-transformation reactions in an N_2/CO_2 containing atmosphere occur as a result of thermal shock waves that produce NO. NO is thought to be converted (by photochemical and thermal reactions) to HNO and N_2O. In presence of water further conversion (through NO^-, $N_2O_2^-$, and N_3O_3) into non-volatile (or "fixed nitrogen") species such as N_2O, NO_2^- and NO_3^- can occur. In presence of aqueous solutions or suspensions of Fe(II) these species can be reduced to ammonia (Summers 2003; Summers and Chang 1993). It isn't known if such reactions can be support by thin layers of adsorbed or condensed water or if standing liquid water is required. The direct reduction, by Fe(II), of species such as HNO, NO, and N_2O has also not been studied. Some or most of the NH_3 that formed would be volatilized and escape to the atmosphere where it would be photolyzed to N_2. (The presence of water will keep some of the ammonia dissolved and reduce this process) Some of the NH_3 would be in the form NH_4^+ where it could be mineralogically fixed and stabilized by inclusion in certain clays. Nitrogen in the regolith (NO_2^-, NO_3^-, and NH_4^+ in clays) will protected from impact erosion & hydrodynamic escape but, if no processes exist to revolatilize it, may become permanently locked in the crust.

Our current understanding of the conversions between the product of shock heating (NO) and other forms of nitrogen is based on theoretical models (Kasting and Walker 1981; Levine and Augustsson 1985; Levine et al. 1982; Mancinelli and McKay 1988; McConnel and McElroy 1973; Yung and McElroy 1979). This has several unavoidable limitations. One is that a model can only include those chemical pathways which an investigator is aware of. For example, early models neglected the reaction between nitric oxide and hydrogen radicals (McConnel and McElroy 1973; Yung and McElroy 1979). Also, comprehensive models must take rate data from wide variety of sources. Most of the experiments that produced these data were conducted for other reasons and under variety of different experimental conditions. Often data must be extrapolated and sometimes good data is lacking and assumptions need to be made. These models can only provide estimates based on chemistry that one would expect to see and the data available.

These models also only considered the reactions that take place in the atmosphere, while separate experimental work considered reactions that may have occurred in condensed phases (Summers 2003; Summers and Chang 1993). Some of the questions remaining to be addressed in this area are particularly relevant to Mars. Could nitrogen have been fixed only in periods where bulk liquid water was present, or could the adsorption/condensation of thin layers of water allowed nitrogen fixation and/or ammonia formation? Would ammonia in clays be protected from UV photolysis? Lastly, how these reactions are coupled to atmospheric reactions is not completely understood. It has been considered by only one steady-state model (Summers 1999) and by no experimental studies.

We propose to study directly the reactions of nitrogen in an early Martian atmosphere, ocean, and crust by modeling abiotic reactions experimentally. Experiments will examine the chemistry and photochemistry of an atmosphere with a variety of compositions, with and without water and model Martian minerals, and measure the products formed. We will study the reactions of nitrogen from the initial shock heating product, NO, to the formation of nitrite, nitrate, and/or ammonia in the aqueous phases. Work will start with a simple model and experimental situation, and move to more complex situations. Work will investigate if a thin layer of water absorbed or condensed onto the surface of various minerals is sufficient to promote the formation of nitrates, nitrites, and (with ferrous minerals) ammonia. Direct illumination of clays will be conducted to study how well ammonium is protected from photolysis.

This work will increase our understanding of issues related to the chemistry, mineralogy and geology of N on a planetary basis and how these factors contribute to, or hinder, a planet’s habitability. It will help us understand the habitability of Mars in the past and how the cycling of nitrogen contributed to its current state of habitability. It will help us understand how the presence/absence of reduced nitrogen may have set the stage for, or inhibited, the formation and evolution of life on early Mars. It will provide us a better understanding of how these reactions may have lead to loss of atmospheric nitrogen through sequestration in the crust or, conversely, how sequestration maybe have helped protect nitrogen from impact erosion and/or hydrodynamic loss. It will help us understand how these processes changed over various stages of Martian history with different amounts of liquid water. Nitrogen is an essential element to life, both directly and indirectly, and if we are to understand a planet’s habitability, we must be able to understand the cycling of nitrogen on that planet. These results can be combined with other data from observations of Mars and modeling of its processes to give a broader understanding of the planet’s history and how these factors affect the habitability of planets in general.

7.1 Methodology

We will look at atmospheres made up of variable amounts of N_2, CO_2, H_2O and minor species such as H_2, CO, H_2S and SO_2 at a variety of pressures. Wall effects can be studied by looking at variations in the size of the flask. Initial work will be with a "one box model” situation (two counting the aqueous phase) where the gas is irradiated at one temperature and pressure. A portion of the gas will be passed through water to allow species to "rain out" and react in the “sea”. . We will look at what effect added species in water phases, like those that might be been present in a prebiotic sea, may have had (see; Summers and Chang 1993; Summers 2003) and at variable amounts of Fe(II) species. Analysis of gas samples will be by IR spectroscopy or by GC/MS. Analysis of aqueous samples will use nitrite/nitrate and ammonia sensitive electrodes supplemented by ion chromatography and colorimetric methods (Verdouw et al. 1978). If necessary, water will be trapped out of the return gas to simulate a cold trap on the atmosphere.

Depending upon initial results, subsequent work may begin to look at more complex simulations. For example, a second "box" where gases are irradiated at two different temperatures and pressures, such as those present in the stratosphere and the troposphere. The results from the first setup will allow us to make an informed decision as to whether the optimal use of time would involve a more complex experimental apparatus or whether spending more time running experiments with a simpler setup.

To understand whether nitrogen may be fixed in the absence of water, we will investigate reactions where the water is replaced with minerals that are typically found in the basalt and/or andesite lithologies identified on Mars (Bandfield et al. 2000; Christensen et al. 2000; McSween Jr. et al. 1999). Work will also investigate if a thin layer of water absorbed or condensed onto the surfaces of minerals is sufficient to promote the fixation/reduction reactions. . (The mineral surfaces may help keep thin layers of adsorbed water from “freezing”). Direct illumination of clays will be conducted to study how well they protect ammonium from photolysis. Mineral surfaces will be analyzed be washing with water (after reacting gases have been removed) and the washes will be analyzed (with appropriate controls to check for reaction during washing). Work can be later expanded to consider interaction of abiotic cycling with biotic sources by adding the appropriate inputs of biogenic species and/or trapping out specific species. Other areas of later study are to look at the input of amounts of organic nitrogen such a may have been delivered by comets.

This work will provide us with a better understanding of the reactions of nitrogen (and of the conditions associated with it, such as habitability of planets). It will provide us with a new understanding of abiotic cycling, contribute to our understanding of how abiotic reactions set the stage for the origin of life &early life and impact biotic cycling. It will tell us about the processes that would have gone on in the early atmosphere of Mars and what species (both nitrogen species and others) would have been present in various stages of its development.

7.2 Investigative Work Plan

Year 1: Build and test apparatus. Establish and verify optimum procedures for analysis of products. Begin to collect data under a variety of basic conditions (N_2, CO_2, CO, & water, pressure, temperature, etc). Year 2: Continue to run experiments under a variety of conditions. Test for wall effects. Evaluate where experimental apparatus needs to be improved (two box setup, etc.). Begin looking at additional sets of conditions (such as the presence/absence of water). Year 3: Expand and improve experimental set up as necessary. Test new procedures. Continue to expand range of conditions considered (such as the presence/absence of water, minerals and thin films of water) and begin to consider others (such as the photolysis of ammonia in clays). Year 4: Continue collecting data under wide variety of conditions including; photolysis of ammonium in clays and added species in water. Consider the effect of trace species such as H_2, H_2S, and SO_2. Year 5: Wrap up examination of any conditions not yet considered. Extend work to such areas as: mimicking biogenic inputs; looking at inputs of cometary type material. Compare data against theoretical models and apply data toward an understanding of the cycling of nitrogen on Mars over different eras.

This work will be conducted by Co-Investigator Dr. David P. Summers. He has been working on the prebiotic fixation of nitrogen and carbon for the last nine years and has been able to establish the reduction of nitrate and nitrite as a source of reduced nitrogen on early prebiotic planets (Summers 1999; 2003; Summers and Chang 1993; Summers and Lerner 1998). Co-Investigator Dr. Bishun Khare will also contribute expertise from many years of experience in experimentally modeling photochemical processes in reducing atmospheres.

8. Europa Geology and Astrobiology

The work proposed in Sec. 2-7 examines interactions among a world’s geology, atmosphere, oceans and biology in the evolution of that world’s surface habitability. With the recognition that Jupiter’s moon Europa likely harbors a subsurface liquid water ocean whose volume is about twice that of Earth’s oceans (e.g. Pappalardo et al. 1999), we now know that habitability in possibly entirely subsurface environments must also be examined (e.g. Sagan 1996, Chyba 1997). In the following sections, we propose work to examine the geology of Europa and its implications for the free energy sources that would be needed to power a Europan biosphere (Secs. 8 and 9). We then couple these results with terrestrial analog work (Sec. 9) and low-temperature laboratory experiments (Sec. 10) to make predictions about the possible abundance and survivability of any oceanic biomarkers that might reach Europa's surface through active geology. These results will have implications for the astrobiological exploration of Europa from either an orbiter or a surface lander.

8.1 Europa Astrobiological Overview

Jupiter's satellite Europa is a fully differentiated body with a rocky interior covered with a layer of material with the density of water. This layer is approximately 100 km thick as measured gravitationally, but such measurements do not have sufficient accuracy to distinguish between liquid water and solid water ice (Anderson et al. 1998). However, magnetic field results (Kivelson et al. 2000) strongly suggest the existence of an ocean of liquid water beneath Europa's icy surface. Liquid water is possible because Europa has a significant heat input due to tidal flexing, caused by a forced eccentricity from its resonance with Io and Ganymede (Cassen et al. 1979, 1980; McKinnon, 1999). Other lines of evidence are also consistent with a liquid water ocean (Pappalardo et al. 1999). Such water, if present, could provide an abode for life provided sufficient energy sources were available (Chyba and Phillips 2001, 2002).

A biosphere on Europa would require liquid water, appropriate biogenic elements (Pierazzo and Chyba 2002), and useful sources of free energy (Chyba 2000a,b, Chyba and Phillips 2001, 2002; Chyba and Hand 2001). Liquid water now seems a possibility, and spectral evidence suggests the existence of organic compounds (McCord *et al.*, 1999). Our work focuses on free energy sources that are independent of photosynthesis, which has long been argued to be unlikely at Europa (Reynolds et al. 1983) but remains under active investigation (Greenberg et al. 2000, 2002). Charged-particle interactions with materials at Europa's surface can produce biologically useful oxidants such as molecular oxygen and hydrogen peroxide. Irradiation of carbon-containing materials at the surface of Europa should also produce simple organics (Chyba, 2000a,b; Cooper et al. 2001; Chyba and Phillips, 2001). Oxidants and hydrogen can also be produced by processing within the ice shell due to radioactive decay of incorporated potassium-40 (Chyba and Hand, 2001). If transported downward through the ice shell to a liquid water layer, these could provide a significant amount of energy to sustain a biosphere (Chyba and Phillips 2002). However, transport mechanisms remain uncertain due to the uncertainty in formation models for Europa's surface features. That is, Europa's biosphere depends in part on the style and frequency of Europa's geological surface activity. In this research, we aim to elucidate this connection.

The work proposed in this section will examine possible environments for life on Europa. It will have two main components: (1) We will look for changes on the surface of Europa during the Galileo mission through a careful examination of the Galileo dataset; and (2) We will study various models of geological activity on Europa to determine their implications for the formation or transport of biologically useful material from the surface to the ocean, or vice versa.

8.2 Change Detection

The first aspect of our work, a search for changes on Europa's surface due to current geological activity, will follow the methods described in Phillips et al. (2000) to compare images of Europa's surface using systematic image processing techniques. Our previous study (Phillips et al. 2000) focused on comparing images of Europa's surface taken by the Voyager spacecraft with those taken 20 years later by the Galileo spacecraft. This comparison allowed a long baseline in time over which changes could occur, but was hampered by the inherently low resolution of the Voyager images of the surface of Europa. In the research proposed here, we will instead compare images of Europa's surface taken during Galileo's 5.5 years of observations in a search for current geological activity. We will have a shorter baseline in time than for the Voyager/Galileo comparisons, but we will be able to compare images at much higher resolution to allow the detection of smaller changes on Europa. Studies of the morphology of various features on Europa's surface (Greenberg et al. 1999) suggest that, given the observed size distribution of features such as lenticulae, changes are more likely to be observed in high resolution images where smaller spatial scales can be examined, even with a timeline shorter by a factor 4.5.

Any changes on Europa's surface due to current geologic activity would indicate the location and style of that activity, and would have important implications for the presence of liquid water beneath Europa's icy surface. A null result, in which no changes attributable to surface geologic activity are detected, would allow us to place a lower limit on the surface age of Europa, and an upper limit on the global resurfacing rate. These limits will depend on the details of the images compared, their resolution, and the percentage of Europa's surface that they cover.

8.3 Astrobiological Implications of Physical Models

Coupled with this search for changes on Europa's surface, we propose to evaluate the myriad models now in the literature (e.g. Pappalardo et al. 1999, Gaidos and Nimmo 2000, Greenberg et al. 2002) for the formation and evolution of various geological surface features on Europa to examine their astrobiological consequences. The questions we wish to consider for each mechanism include: (1) Does the process itself form or bury compounds of astrobiological interest? (2) Does it result in the transfer of material, formed by this or other processes, from the surface or near-surface to a subsurface ocean (i.e., as plausible electron donors or acceptors for possible life)? (3) Does the process result in the transfer of material from the subsurface / ocean layer to the surface? (i.e., does it bring up material, perhaps containing biomarkers, from the ocean to the surface, making it more accessible to spacecraft exploration?) (4) If material is transferred from the ocean to the surface, or the surface to the ocean, by any of these mechanisms, can we estimate the physical and chemical processing done on that material during the trip? Could biosignatures arrive intact?

We will examine these questions for the various mechanisms proposed for the formation of surface features on Europa, including ridges, bands, chaotic terrain, impact craters, and others. We will then consider two classes of broad results from this work: 1) What feature type, given all the different formation mechanisms, is of greatest astrobiological interest for a future lander? Which has the best overall chances of having material brought from the subsurface up to the surface intact? 2) What is the overall budget of oxidants and fuels available for a possible subsurface biosphere? (This question also connects directly with some of the simulations of radioactive decay in salty ocean models, discussed in Sec. 9.) We should be able to put upper and lower bounds on the total amount of material transferred from the surface to the ocean by considering the highest and lowest cases for each feature type.

The combination of these two lines of inquiry will allow a characterization of the possible environments for photosynthesis-independent life on Europa. If we are successful in finding surface changes due to geologic activity, we will be able to combine them with the analysis of the second part of our study to examine the consequences of this activity for the presence of a biosphere. If, for example, we were to find evidence that a domed feature on Europa's surface has increased in uplift and diameter, we would be able to focus our attention on models of the formation of these features. We would study these varying models, which range from solid-state convection to liquid water intrusions near the surface, and attempt to determine which model is best fit by the observed changes. We would also determine, from the amount of uplift, the volume of subsurface material that could have been brought closer to the surface, and from studies of the energy considerations of this process, determine what sorts of chemical processing could have taken place. These results will help us place the change detection results into an astrobiological context, to determine what implications they have for the formation of biologically useful molecules whether such materials could have been transported to the subsurface, and what quantities of subsurface material could have been transported to the surface in the process.

8.4 Preliminary Work

We have performed a preliminary analysis of the Galileo dataset to begin the search for appropriate image pairs for comparison. Ideally, such images should be matched as closely as possible in resolution, filter, viewing geometry, and lighting conditions such as phase angle. Given the sparse nature of the Galileo dataset, such "redundant" images were obviously avoided in most cases, but we have identified a number of image pairs that are sufficiently similar to perform useful comparisons, and are continuing to study the dataset as a whole to identify more possible image comparisons. There are 95 separate observations of Europa that were taken by the Galileo spacecraft over its 5.5 years of observation, and each observation consists of a number of individual frames.

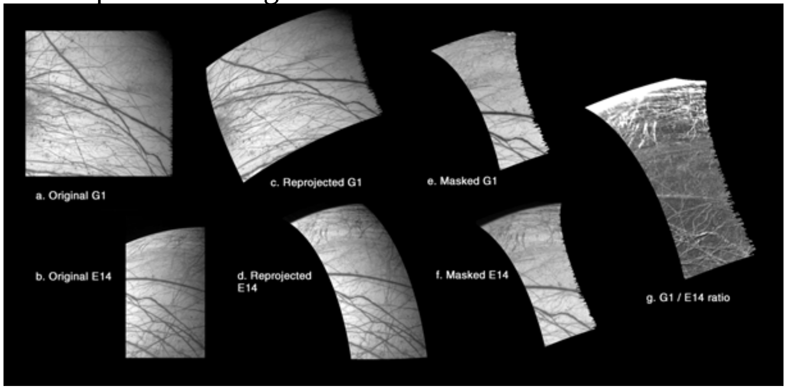


Fig. 8.1: Comparison of Galileo images taken about 2 years apart

One preliminary change detection analysis can be made between images taken on Galileo orbits G1 and E14. Fig. 8.1 illustrates the change detection procedure, with figures a) and b) showing the original images, c) and d) showing the images reprojected to the same viewing geometry, e) and f) showing the two images masked to show only the overlapping regions, and g) showing the ratio of the two images once an iterative subpixel registration procedure has been performed. The ratio image does not, however, indicate the presence of any new or changed features on Europa's surface over this 2-year period. Instead, all of the structure in the ratio image can be attributed to the difference in viewing geometry between the two images, which were taken with a difference in phase angle of almost 40 degrees. The phase angle difference, coupled with the non-linear photometric function of Europa's surface, results in apparent brightness changes of various features, which are visible in the ratio image.

Due to the non-optimized nature of the Galileo dataset, we will be forced to use non-optimal cases like this one to search for changes on Europa's surface. We are confident, based on work done with similar ratio images of Jupiter's satellite Io (Phillips 2000), that if any actual surface changes were present on Europa's surface, we could detect them. While lack of matching phase angles will make it difficult to discern changes in brightness of surface features, it will not hinder our detection of features which have changed in size or shape, and will certainly allow for the detection of new surface features. These real changes will have a completely different signature in the ratio images, and can easily be distinguished from mere brightness variations. We will also produce a new photometric function which we can use to photometrically correct the images of Europa's surface to account for the differing appearance at various phase angles. This will allow us to compensate somewhat for the changes in viewing geometry.

We have also begun the consideration of the astrobiological consequences of one particular surface process, impact gardening (the churning of the surface due to micrometeorite impacts; Phillips and Chyba 2000, 2001; Chyba and Phillips 2001). Irradiation of Europa's surface can create oxidants and organics there, but the same process also breaks down such materials if they remain exposed (Varnes and Jakosky, 1999). Material can also be removed from Europa's surface through sputtering erosion (the removal of material from the surface due to charged particle impacts). However, impact gardening will serve to mix the upper layers of the surface, and can potentially preserve surface material by moving it down below the sputtering and radiation processing depths. Sputtering erosion and surface mixing through impact gardening act together to change the preservation depth. Depending on the sputtering rate, the system may be in one of two regimes, sputtering-dominated or gardening-dominated. If sputtering dominates, oxidants and organics produced at the surface are lost before they have a chance to be preserved for future transport to a subsurface ocean layer. However, if gardening dominates, then material may be buried faster than most of it can be removed through sputtering or destroyed by further radiation processing.

Using a model of impact gardening based on studies of the lunar regolith (Phillips and Chyba 2001), coupled with new studies of the impactor population in the outer solar system (Zahnle *et al.* 1998, 1999), we have previously estimated a gardening depth on Europa of about 1 meter over a surface age of about 10 million years. It appears that, on Europa, gardening rates dominate sputtering rates, so material formed at or delivered to (Pierazzo and Chyba 2002) the surface will thereby be preserved. We are working on revising those estimates to take into account new studies of the numbers of very small craters on Europa (Bierhaus *et al.,* 2001).

Once we have a reliable, global estimate of the gardening rate on Europa, we can use this estimate, coupled with estimates of the sputtering erosion rate (Cooper *et al*. 2001), to study how material created at the surface of Europa (Chyba and Phillips 2001) through radiolytic processing is preserved and mechanically mixed beneath the surface through gardening, and to what depth this process is effective. Since gardening will have approximately the same effectiveness on different terrain types on Europa, understanding the gardening rate is a necessary first step to considering the global transport of oxidants, organics, and other compounds of exobiological interest to and from a subsurface ocean layer. Thus, once our consideration of gardening rates is completed, we can incorporate our results into the analysis of other surface feature types and mechanisms.

8.5 Work Schedule

Year 1: Image selection and analysis, including careful analysis of the full Galileo Europa dataset and elucidation of all overlapping image pairs to be used for comparison, (Phillips). Continue work on gardening (Phillips). Also full literature review (Phillips and Chyba) of all proposed mechanisms for formation of surface features. Year 2: Finish gardening model, including small-crater slope and the effect of secondaries (Chyba and Phillips). Classify feature formation mechanisms into categories based on mechanism and process (Chyba and Phillips). Determine or develop photometric function to be used for image comparisons (Phillips). Process and reproject all appropriate images (Phillips). Year 3: Begin modeling of feature formation characteristics, including creation and transport of materials of astrobiological relevance (Phillips and Chyba). Create ratio images of appropriate comparison pairs (Phillips). Year 4: Continue work on astrobiological implications of each feature formation model (Phillips and Chyba). Begin analysis of ratio images (Phillips). Year 5: Continue analysis of ratio images, focusing on careful comparison of any potential changes with the initial raw images to rule out false detections (Phillips). Use changes, or lack thereof, to compute global resurfacing rate and surface age (Phillips). Use results of feature formation analysis to determine the overall budget of oxidants and organics available for a subsurface biosphere (Chyba and Phillips). If any surface changes are detected, focus on the mechanisms for producing that surface feature type and determine the astrobiological implications (Phillips and Chyba).

This research will address Goals 1 and 2 of the Astrobiology Roadmap.

9. Salts, Radiation and the Habitability of Europa's Ocean

In Sec. 8, we briefly reviewed the evidence for a liquid water ocean under Europa's ice crust. In this section, we propose research that would improve our understanding of the chemistry and habitability of this putative ocean. Within this context we will also begin to examine the influence of Europa's extreme surface radiation environment on potential biomarkers that may be delivered to the surface via resurfacing of the ice shell—i.e., via the mechanisms that the research in Sec. 8 intends to categorize. In Sec. 10, we propose a way to move the initial modeling of biomarker survivability described here to the next level, *viz.* direct laboratory simulation.

To assess the habitability of the Europan subsurface, we must improve our understanding of the available chemical pathways and redox gradients in the ocean (Chyba & Phillips 2001; Delitsky & Lane 1997; Gaidos et al. 1999; Kargel et al. 2000). The results of these models could inform experiments and instrumentation design for future Europa missions (Chyba and Phillips 2001, Chyba 2002).

9.1 Electron Donors and Acceptors

We will begin by expanding, via a far more detailed model, our previous initial work. Chyba and Hand (2001) made order-of-magnitude estimates of the delivery of electron donors and acceptors (fuels and oxidants) to Europa's ocean; these donors and acceptors could then fuel a Europan biosphere, allowing global biomass estimates to be made (Chyba 2000a,b, Chyba and Phillips 2001, 2002). We examined the transport of radiolytic products from the surface and the production of oxidants by radioactive decay of ^{40}K isotopes in the ocean. With a half-life of 1.25 Gyr, ^{40}K decays via alpha- or beta-particle emissions that then decompose water and produce molecular oxygen and hydrogen (Draganic et al. 1987, 1991).

These results can be done far more rigorously using the CHEMSIMUL software package (Kirkegaard & Bjergbakke, 2002), for which we hold a license. CHEMSIMUL allows simulations of aqueous chemical kinetics and enables the user to incorporate the decay of isotopes and resulting radiation chemistry into the model. This software served as the basis for the analysis of terrestrial and cometary radiated aqueous systems (Draganic *et al.*, 1984; Draganic *et al.*, 1987; Draganic *et al.*, 1991; Garzon & Garzon, 2001) and it is well suited to the Europan system. Using CHEMSIMUL we will examine the steady-state redox environment of Europa's salty ocean, based on over seventy-five aqueous chemical reactions influenced by the radiation environment of decaying potassium-40 and the influx of constituents from the Europan ice shell. (Appropriate models for the latter will be further informed by the work to be done in Sec. 9.2.) The rate constants and G-values for the simulation are adjustable to the low temperature environment expected for Europa (Elliot, 1994). Our model will assume a chondritic origin (Fanale et al. 1977; Fanale et al. 2001; Kargel 1991; Kargel et al. 2000) for Europa and will incorporate available Galileo results (see Sec. 9.2) to generate the best chemical model possible to date, allowing a new estimate of the oceanic biomass that could be supported on Europa.

9.2 Salinity of the Europan Ocean

The presence of salts in aqueous solutions is known to have important consequences for the origin of life (Monnard et al. 2002). Even small concentrations of sodium chloride have been shown to substantially reduce RNA oligomerization and impede membrane self-assembly (Monnard et al. 2002). Combine this with models that indicate a salty Europan ocean (Kargel et al. 2000; Zimmer et al. 2000; Zolotov & Shock 2001) and the prospects for the origin of life on Europa—a question that is distinct from the habitability of its ocean for extant life—becomes intimately tied to the type and concentration of salts on Europa. Rather than relying on models, here we propose using the conductivity data measured by the Galileo spacecraft to calculate possible concentration levels for plausible oceanic salts. Surprisingly, this has not yet been done. Our results will serve as checks on published models, probe the prospects for the origin of life on Europa, and establish initial conditions for chemical and biological simulations of Europa's ocean.

Jupiter's time-varying magnetic field induces an electric field within Europa's ocean (Colburn & Reynolds 1985; Colburn & Reynolds 1986). Based on Galileo magnetometer measurements (Khurana et al. 1998; Kivelson et al. 2000; Kivelson et al. 1997), the conductivity of Europa's ocean has been calculated to be between 58 mS m^{-1} and 2.75 S m^{-1} (Zimmer et al. 2000). The conductivity of aqueous solutions depends upon the quantity and nature of the salt content, as well as temperature (Calvert et al. 1958; Poisson 1980; Washburn & Klemenc 1936). Most of the work done in the terrestrial context has concerned sodium chloride (NaCl). This, however, is not compatible with chondritic models for Europa (Kargel 1991; Kargel et al. 2000; McCord et al. 1999; McCord et al. 2002; Zolotov & Shock 2001). The dominant salt expected for these systems is magnesium sulfate ($MgSO_4$). As a result, it could be the case that the magnesium sulfate concentration within the water is the primary factor controlling the observed conductivity. Using data available in the literature (Washburn & Klemenc, 1936, Pehybridge & Taba, 1978), we will derive $MgSO_4$ concentration estimates from the Galileo conductivity measurements, compare them with estimates from theoretical work (Kargel et al. 2000; Zolotov & Shock 2001) and use these results to constrain our ocean chemistry models. For comparison, we will also determine concentration ranges for the less realistic case where the dominant Europan ocean salt was NaCl.

9.3 Clathrate Hydrates

In addition to analyzing the composition of Europa's ocean, it is also important to examine the form and phase that constituents—in particular oxidants—may take. We will therefore also examine the role of hydrate clathrates in the ice shell and ocean. We have studied clathrates in the context of Antarctic subglacial lakes (McKay et al., submitted). This research has focused on the stability and density of clathrates in Lake Vostok, Antarctica. Here we propose extending our work on clathrates to the case of Europa.

Given the pressure and temperature environment of Europa's subsurface, the formation of various hydrate species may be expected in both the ice shell and in the ocean (Crawford & Stevenson 1988; Seigert et al. 2001; Sloan 1998). In the shell, clathrates may play a role in determining both the physical and electromagnetic properties of the ice. Structure I and II clathrates—those known to form with CO_2, O_2 and short hydrocarbons—have dielectric constants and bulk modulus parameters considerably different than those of pure water ice (Sloan, 1998). In addition, it is important to consider the fate of hydrate crystals in the ocean. Models typically predict that the Europan ice-water interface will be at roughly 270 K and 10-15 MPa (Crawford & Stevenson 1988; Kargel et al. 2000). At these conditions, clathrates of oxygen gas could be stable. Therefore, ice sheet processes such as basal melting and fracturing may introduce oxygen in the form of clathrates that then remain in crystal form in the ocean. Depending on the density of these clathrates relative to the salty ocean (which in turn depends on plausible salt concentrations, which we will work to constrain via the work in Sec. 9.2), they may form a hydrate layer at the base of the ice shell or sink to the ocean floor and form a layer of hydrate sediment. Furthermore, as a result of ^{40}K radiolysis, O_2 will form at depth in the ocean. Here the pressures are considerably larger than at the ice-water interface (>35-40 MPa), so hydrate formation is expected. It is possible than an oxygen-rich layer will form at the base of Europa's ocean, with implications for the metabolic styles that would be permitted in that environment.

9.4 Surface Biomarkers on Europa

No direct analysis of Europa's ocean is likely in the near term (Chyba 2002; Cooper et al. 2002; Space Studies Board 1999). The coming decades, however, should see orbiters and possibly landers capable of analysis of the surface ice down to several meters in depth (NASA 1999; Space Studies Board 1999). This emphasizes the importance of evaluating the survivability and detectability of biomarkers in the Europa's near-surface ice. Were life to exist in Europa's ocean, it is possible (see Sec. 8) that geological activity would sometimes deliver microorganisms to the surface of the ice shell. Once there, the organisms would be subject to the extreme radiation environment resulting from Jupiter's magnetic field (Cooper et al. 2001; Delitsky & Lane 1997, 1998; Paranicas et al. 2001). Consequently, surface evidence for sub-surface life would depend strongly on the extent to which biomarkers would be destroyed by this radiation. Understanding this process and being able to predict the potential steady-state population of biomarkers on the surface of Europa has critical implications for future missions that may search, from orbit or *in situ*, for signs of life (Space Studies Board, 2002).

In this section we propose an empirical study of the survivability of plausible biomarkers on Europa, extrapolating from the survivability of biomarkers on Earth. In Sec. 10, we will complement this work with, and test against it, the results of laboratory simulations.

Summons et al. (1999) and Brocks et al. (2001) have shown that hydrocarbon evidence of biological lipid membranes can be used to date terrestrial life back to 2.5-2.7 Gyr. These hydrocarbons, mostly hopanes and steranes, are the preserved molecular remnants of cyanobacteria and early eukaryotes. We will use these results to estimate survivability of these molecules against radiative degradation, and hence their lifetimes in the Europan surface environment.

A lower limit of these molecules' radiation survivability can be obtained by integrating the estimated radiation background from the time of their formation to the present. The resulting total radiation dose can then be compared to that of the surface environment of Europa and a limit for the survival time of biomarkers on the surface can be calculated. A radiation vs. depth profile for the ice can be used to estimate the survivability of these biomarkers with ice depth (Cooper et al. 2001; Kminek et al. 2002; Space Studies Board, 1999). We will then incorporate gardening rates predicted for the surface of Europa (Chyba & Phillips, 2001), updated by the work in Sec. 8 above, and determine how long it would take for potential biomarkers delivered to the surface to be buried to a given depth. In addition to informing searchers for possible Europan surface biomarkers, these results will be germane to issues of planetary protection (Space Studies Board, 2000).

9.5 Personnel and Timeline

The work described in this section will form a component of the Ph.D. thesis work of Mr. Kevin Hand, now a first-year graduate student in Geological and Environmental Sciences at Stanford University, being advised by Dr. Christopher Chyba, the PI on this proposal. Dr. Chyba will work closely with Mr. Hand as he pursues the following investigations: (1) Analysis of relationship between Europan ocean conductivity and magnesium sulfate, fall 2003; (2) Calculations for extrapolating terrestrial biomarker survivability to Europan surface conditions, spring 2004; (3) Analysis of clathrate hydrate production and distribution in the Europan ice shell and ocean, fall 2004 (Hand hopes to take an intensive geobiology course in summer 2004); (4) Modeling of the Europan ocean chemistry using CHEMSIMUL, spring 2005; (5) Thereafter, continued work, still being defined, toward the completion of Hand's Ph.D. in astrobiology will be pursued.

This section and Sec. 10 address Goals 1, 2 and 7 of the Astrobiology Roadmap.

10. Irradiation of Biomarkers on Europa—Experimental Investigations

In this segment of the proposal we focus on the formation, detection, and fate of organic molecules similar to those seen in living things, but arising abiotically on icy surfaces of planets, comets, and the interstellar grains from which all Solar Systems form. We are interested in these important species under these unusual circumstances for two reasons, both central to astrobiology: First, it is important to identify and understand the chemistry of organic materials on the surface of planets in order to assess their pre-biotic potential. Second, it is imperative to characterize such life-like organic compounds that arise *non*-biotically so as not to mistake them for biomarkers when they are found, for example, on Mars or satellites of Jupiter and Saturn. Through this work we will advance NASA's Astrobiology goals of improving our knowledge of prebiotic chemistry and signs of life elsewhere in our Solar System (Objectives 2.1 and 2.2) and to recognize signatures of life on other worlds (Objective 7.1).

10.1 Organics on Europa

Astronomical observations demonstrate that organic materials are common throughout the universe (Ehrenfreund et al 2001). The appearance of molecules in space almost always differs greatly from that on Earth so, the detection and identification of compounds in space depends on them having been studied in the lab under conditions germane to the extraterrestrial environment in question. In the past we have successfully performed such work on interstellar ices (Hudgins et al 1993; Bernstein et al 1997, Bernstein & Sandford 1999). To advance the remote detection of pre-biological (or biological) molecules in the Solar System we intend to collect laboratory data on relevant compounds and conditions for comparison to astronomical spectra. We propose to reproduce ices of the potentially pre-biologically interesting Europa in the lab, measure infrared (IR) spectra at 50-100 K. From this we will generate refractive indices (*n*, *k*) that can be used to fit reflection spectra of Solar System ices. We will include molecules known to be present, such as CO_2 (Carlson 2001), and those we predict to be present, such as small cometary carbon compounds (CH_3OH, H_2CO, CO, and CH_4). Of course, many beautiful *mid* IR spectra of H_2O ice(s) have been recorded at lower (interstellar) temperatures, and *near* IR spectra of some ices have been measured at higher (Solar System) temperatures. However, our coverage of near- and mid-IR and emphasis on mixtures and temperatures that are germane to the Galilean satellites, means our measurements will complement and extend, not repeat, previous work. To our knowledge, few lab spectra exist for H_2O ices with carbon-containing molecules under these conditions and they will be well suited to fit reflection spectra of outer Solar System objects from ground based observatories that now extend out to 5 µm, and data from planned space borne infrared observatories.

We also contend that Solar System ices must contain larger, exogenously delivered, molecules as well, for example polycyclic aromatic hydrocarbons (PAHs). PAHs and closely related carbon-rich materials are abundant in our Solar System and are delivered to planet surfaces by carbon-rich meteorites and cometary and asteroidal dust. Our previous *interstellar* PAH-ice experiments produced prebiotically significant species, such as quinones, with structures similar to important biochemical intermediates (Bernstein et al. 1999, 2001). We propose to extend this work on the reactions of PAHs to Solar System conditions and radiation types.

One type of PAH central to the origin of life that remains largely overlooked in are PAHs with nitrogen atoms in the rings: aromatic nitrogen heterocycles (ANHs). From key metabolic agents to the nucleobases in the backbone of DNA, ANHs play a prominent role in modern biochemistry (Figure 10.1, below).

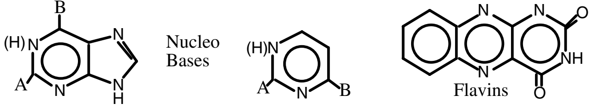


Figure 10.1, generalized structures of the purine and pyrimidine bases in DNA and RNA, and flavinoids, all aromatic nitrogen containing hydrocarbons (ANHs). Members of these classes of compounds have been extracted from meteorites.

Moreover, while the familiar nucleobases of modern biochemistry—adenine, uracil, guanine, cytosine, and thymine—are certainly of interest, they are not alone. It is plausible (if not likely) that alternative bases might have played a role in the origin and early evolution of life. Although there have been many suggestions of prebiotic alternative bases (Robertson & Miller 1995), all are ANHs. Interestingly, many of these ANHs are known to be present in meteorites. For example, xanthine, guanine, hypoxanthine, (alternative nucleic acid bases) and substituted pyrimidines were detected in Murchison (van der Velden, and Schwartz 1977) as have purines and triazines (Hayatsu et al 1975). Purine and pyrimidines have also been detected in the Jilin meteorite (Shi 1978). However, almost no work has been done on exogenous synthesis and modification of these molecules, or the impact they may have had on the evolution of life.

In addition to nucleobases, other, non-nucleic acid N-heterocycles are fundamental to biochemistry. These include folate, flavins, nicotinamides, porophyrins, and the amino acids tryptophan and histidine as well as the amino acid functional groups imidazole and indole, the latter two for which there is currently no compelling prebiotic synthesis (Keefe, Lazcano, and Miller 1995). In view of the central role these species play in modern biochemistry, and the fact that they are exogenously delivered, we propose to study the spectra and chemistry of these molecules under both interstellar and outer Solar System conditions, as we have done with PAHs (Bernstein et al. 1999, 2001, 2002a, 2003).

10.2 Pseudo Biomarkers

Over the next several years there will be numerous missions (e.g. Cassini, Rosetta, Mars NetLander) to explore Mars, Europa, Titan, and other bodies. One of most interesting objectives of these probes is the search for biomarkers–chemical evidence of extant or extinct life produced by biology. However, as we have mentioned of meteorites, extraterrestrial samples often contain organic compounds from abiotic processes that look like those from biology. It could be possible to be fooled by molecules that we think of as typically biological if one did not know that they could arise non-biologically under these unusual conditions.

For example, we have recently demonstrated the formation (under extraterrestrial conditions) of amino acids (the "building blocks" of proteins; Bernstein et al. 2002b) amphiphiles (molecules that form membrane-like structures; Dworkin, et al. 2001) quinones (ubiquitous co-enzymes; Bernstein et al. 2001) and a range of substituted aromatics, including some of the same class as those invoked as potential biomarkers in a Martian meteorite (McKay et al 1996). All of these compounds have been detected in meteorites.

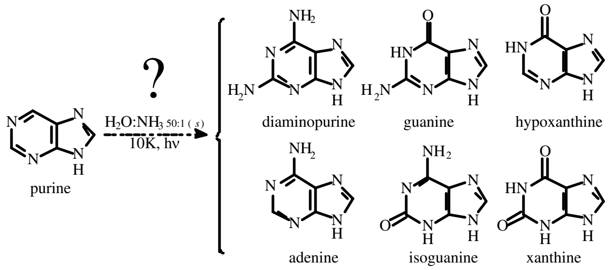


Fig. 10.2 by analogy with our previous work (Bernstein et al. 1999, 2002a, 2003) we predict the reactions of meteoritic compounds in Europan ice will lead to many biologically interesting molecules. For example, shown here are probable alternative nucleobases that would form from purine, a component of the Murchison and Jilin meteorites.

But molecules we will encounter in our exploration of the Solar System will not simply be those seen in meteorites but rather will depend on the specific conditions there. Would "biomarkers" even survive on the surface of Europa, and for how long? Our work on amino acids (Ehrenfreund et al 2001) suggests that they would be rapidly destroyed on exposure to the UV and ionizing radiation. Very little work has been done on assessing the stability and fate of larger molecules of the type that would be delivered to the Europan surface (Pierazzo and Chyba 2002). We expect based on our work on the oxidation of PAHs, however, (Bernstein et al. 2002; 2003) that the processing of meteoritic compounds such as purines in ice would yield other biologically important compounds, including alternative bases (see preceding Fig. 10.2).

10.3 Investigative Timeline

Year 1. Measure the IR spectra of nitrogen containing aromatics in argon as spectroscopic baselines for mixed molecular ice experiments. Expose to radiation to determine stability in inert Ar matrix. Year 2. Measure IR spectra of nitrogen containing aromatics in H_2O ice, at known concentrations for smaller more volatile ANHs for determination of Ns and Ks. Expose to radiation, measure rates of disappearance of starting materials. Compare IR spectra of ANHs in Ar matrix to astronomical observations of gas phase PAHs to set abundance limits. Year 3. Begin mass spectral analyses of ANH/H_2O irradiation experiments to determine products. Compare IR spectra of ANHs in H_2O to astronomical observations of ices to set abundance limits. Year 4. Begin chromatographic analyses choosing starting materials based on observations from previous years. Begin IR and mass spectral analyses of ANH irradiation experiments involving other ice components as indicated by astronomical observations. Year 5. Wrap up mass spectral and chromatographic analyses of ANHs irradiation experiments involving non-H_2O ice components. Isotopic (D_2O) labeling experiments if time allows. This research will be led by Dr. Max Bernstein, supervising a post-doc supported at the 45% level by this proposal.

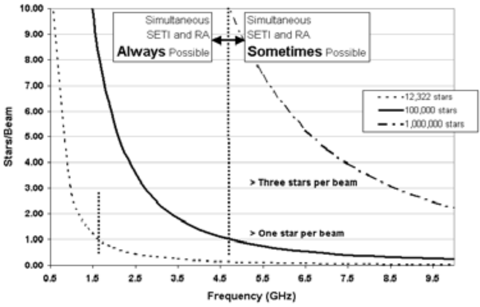
11. Expanding the List of Target Stars for Next Generation SETI Searches

SETI attempts to take advantage of extraterrestrial technical intelligence in order to detect extraterrestrial life. The most commonly used characteristic to distinguish between astrophysics and technology (the SETI biosignature) is the product of the time duration (τ) and frequency bandwidth (B) of any detected signal. The classical uncertainty relation requires that the product $B\tau$ exceed about 1 (e.g. Elmore and Heald 1969). 21st century human technology often approaches this lower bound for reasons of economy (large signal to noise ratio at low cost), but natural emissions, even line-narrowed masers, have values of $B\tau >>1$. Since 1960, there have been over a hundred SETI searches reported in the literature. They have utilized a number of different strategies, and today are conducted at both optical and microwave frequencies, seeking narrowband, continuous signals as well as very short broadband pulses. While this may seem like a significant exploration, in fact it hardly begins to probe the 9-dimensional parameter space within which electromagnetic evidence of extraterrestrial technologies might be found (3 space, 1 time, 1 frequency, 2 polarizations, 1 modulation, and 1 signal strength). The most sensitive SETI searches must compete for time on observing facilities built and operated for other science, and therefore at any given moment these searches are usually off the air (Tarter 2001). This is about to change.

The SETI Institute has partnered with the UC Berkeley Radio Astronomy Laboratory to design and prototype the Allen Telescope Array (ATA) for both SETI and more traditional radio astronomy. When completed in 2005, this instrument (an array of over 350 6 m dishes) will be dedicated to a targeted SETI search of nearby stars while simultaneously being used to do traditional astronomical surveys and research (see Ekers et al. 2002, Tarter et al 2002). The key to this dual-use strategy is a large list of target stars that represent credible abodes for technological civilizations—i.e. that are "habitable" from the point of view of complex life. The ATA will have a very large instantaneous primary field of view (PFOV) (because the array is constructed with small 6 m telescopes) and, if the target list is big enough, then on average several SETI target stars will be contained in the PFOV. The ATA will have a unique signal processing architecture permitting multiple SETI stellar targets to be observed while the PFOV is also being imaged for astronomical studies. The work being proposed in this section will concentrate on the scientific question of what constitutes 'Habstars' (those stars most likely to be suitable hosts for habitable planets), criteria for recognizing them, and in particular, the long-standing debate over whether M-stars should be considered among them. These results will be directly relevant to expanding existing target lists to 10^5 and eventually 10^6 stars that are good candidates for SETI observations from the ATA.

Turnbull and Tarter (in press, May 2003) have recently published a catalog of 17,129 'Habstars' based on the point source catalog from the Hipparcos mission. Selection of suitable stars was based on their spectral type, luminosity class, age, nature of any companions, metallicity, and flare activity. 12,322 of these stellar targets are visible from the northern California (Hat Creek) site of the ATA. In most instances, more is known about the physical attributes of the stars than about how these attributes actually influence the origin, evolution, and technical maturation of life in their vicinity. As illustrated in Fig. 11.1, a much larger list of candidate stars must be developed if SETI searches with the ATA are to be pushed to higher frequencies while still maintaining the ability to conduct SETI and traditional radio astronomy observations simultaneously. On average, for any direction on the sky, at frequencies below 1.5 GHz the current 'Habstar' list with 12,322 stars visible from the ATA (dotted curve) will yield at least one viable SETI target star within the PFOV. The 'quiet' terrestrially observable microwave window on the universe extends from ~1GHz to 10 GHz. Dual-use observing of the higher frequencies (at which the PFOV shrinks) will require a larger target list. Fig. 11.1 also illustrates the average number of stars within the PFOV as a function of frequency for two other cases; 100,000 visible stars (solid line), and one million visible stars (dash-dot line). It is apparent that a list of a million target stars provides at least two SETI targets within the PFOV at all frequencies up to 10 GHz. For a target list containing 100,000 stars, simultaneous SETI and radio astronomy observations will routinely be possible only below 4.5 GHz.

Figure 1 - Stars per PFOV Beam --- with SETI target star list of 12,322 or 100,000 or 1,000,000 stars visible from Hat Creek



The FAME spacecraft (cancelled in 2001) would have provided astrometric distance measurements of ~40 million nearby stars, from which an expanded catalog of 'Habstars' could have been built. In the absence of these distance measurements, we will develop an expanded list of target stars in stages, by using the existing catalogs of point sources, and those that are now becoming available from ground-based observations. As a first step, the 'Habstar' results from the Hipparcos catalog will be augmented by stars selected from the All-Sky Compiled Catalogue of 2,501,968 stars (Karchenko 2001) that includes ground-based proper motion catalogs as well as data from the Hipparcos and the Tycho-1 and –2 catalogs (constructed from data collected by the Hipparcos star mapper during the Hipparcos extended mission). Poorer astrometric precision for this catalog (7 milliarcsec *vs*. 1 milliarcsec) and less accurate photometry for the non-Hipparcos stars will lead to greater uncertainty in distances and therefore in the intrinsic properties of the selected stars, but a list of ~10^5 targets should be achievable. To increase the list to ~10^6 stars will require combining entries in the recently released USNO B1.0 catalog of more than 10^9 objects (including proper motion measurements), with J,H,K color data from the 2MASS survey, and the emerging color information from the Sloan Digital Sky Survey (u',g',r',i',z') in order to construct color-color relationships to determine stellar spectral types. The list will evolve over the lifetime of the ATA. Early on, it will inevitably be plagued by confusion between distant giants and nearby dwarfs, but the list will improve as distance measurements from future astrometric spacecraft missions (e.g. SIM in 2009 or GAIA in 2012) become available.

Of particular importance for the construction of the million target star catalog, is the selection (or not) of M stars since they comprise about 70% of the nearby stellar population (Henry et al. 1999). This is the SETI M-star dilemma. It is expected that the research conducted in a number of other sections in this proposal (e.g. Secs. 2, 3, 4, 7), as well as by other colleagues in the NASA Astrobiology

Institute, will inform the decision on which, if any, M stars should be included as 'Habstars'.

11.1 Do M Stars Have Habitable Planets?

Since the beginning of observational SETI programs, M stars have been excluded from most searches for three reasons—yet all three can be questioned. The habitable zone is so close to an M star that any planets would be locked into synchronous rotation (with potentially dire consequences for any atmosphere), the flaring activity of these stars during the first few Gyr of their lives would provide an untenable UV environment for the development of complex life on the planetary surface, and star spot activity would lead to unsuitable fluctuations in the total stellar luminosity. The "just right" requirements for complex life argued for by Rare-Earth proponents Ward and Brownlee (1998) reinforce this view, but other researchers refute it. Joshi et al. (1997) demonstrated that an atmosphere of 0.1 bars of CO_2 would be adequate to circulate heat to the planetary dark side, and prevent freeze-out of the atmosphere, while a CO_2 atmosphere as thick as 1.5 bars would permit temperatures compatible with the existence of liquid water at the sub-stellar point. Doyle and McKay (1991) argued that the flares from young M stars would increase atmospheric ozone production and provide protection for planetary surfaces, while Heath et al. (1999) calculated that atmospheric attenuation would prevent most UV flux shortward of 290 nm from reaching the surface and that damaging UV-B radiation would be comparable to solar fluxes on Earth. These authors also concluded that the luminosity variation from starspots would not impose undue stress.

Contradicting Heath et al. (1999), Scalo et al. (2002 preprint) claim that atmospheric reprocessing of ionizing X- and gamma-rays from M star flares transfers about 1% of the flare energy to the planetary surface, in the form of biologically damaging UV. However, instead of writing off planets around M stars as a result of these calculations, Scalo et al take the view that the strongly fluctuating UV environment due to stellar flares (on time scales of 100 hours for young M stars compared to 1000 years for the Sun), superimposed on a galactic-event background with a time scale of 10^6 years, may be ideal for forcing evolutionary turnover and innovation through mutation and sterilization (niche-emptying). A case can be made for the habitability of planets orbiting M-stars, but much work remains to be done to support it. In constructing the 'Habstar' catalog, Turnbull and Tarter (2003) opted to exclude any M star whose flare activity was sufficiently strong to be observed by Hipparcos, and retained ~ 600 M stars that met all the other culling criteria.

Deinococcus radiodurans (the gold-standard for radiation resistance among bacteria (Levin-Zaidman *et al* 2003) could possibly survive the radiation regime on a planet orbiting in the continuously habitable zone of an M star, but what does this really tell us about whether organisms might originate and evolve to intelligence there? We know that the high fluxes of ultraviolet light that radiated the surface of the early Earth (see Secs. 4 and 5 of this proposal) were obviously not inhibitory to the origin and early evolution of life. The effects of solar UV radiation on microbial life and evolution have been studied and reviewed extensively (e.g., Rothschild and Mancinelli, 2001). It has been well established that killing of cells by UV radiation is due primarily to its action on DNA, so that UV radiation near 260 nm is an effective lethal agent. The several defects in DNA caused by radiation include the formation of pyrimidine dimers, pyrimidine(6-4)pyrimidone photoadducts, DNA protein crosslinks and strand breaks.

More recently it has been reported that damage and plasmid inactivation increase with increasing photon energy. *D. radiodurans* possesses multiple copies of genes and is one of the most efficient organisms at repairing DNA damage, but these repair mechanisms are hardly universal and are thought to be incidental to its desiccation resistance (Mattimore and Battista 1996; Battista 1997). Microbes containing carotenoid pigments (e.g., Halobacteriaceae) and scytonemin (certain Cyanobacteria) are more resistant to solar UV radiation in the Earth's atmosphere than unpigmented species (Mancinelli and Shulls, 1978) because these pigments absorb UV radiation. Perhaps this is the key to evolutionary fitness on an M-star planet. The results on the sunscreen efficacy of iron compounds being studied in Sec. 4 of this proposal will help answer this. Research conducted in Sec. 5 of this proposal on UV resistance in bacteria living in Earth's highest altitude (and therefore highest UV) lakes should yield entirely new insights into this question, further informing this work. The organic molecules and aerosols that may survive in certain environments within the early atmospheres of M-star planets could also impact the UV environment on the surface, and the chemical modeling being proposed in Sec. 4 could help in evaluation of their habitability. The topic discussed in this final section will therefore serve to bring many of our team members together in a collaborative investigation that draws on much of their work. This work addresses Goals 1, 4, 5, and especially 7 of the Astrobiology Roadmap.

11.2 Work Plan: Bringing the Team Together

The work proposed here falls into two categories: (1) expanding the list of SETI target stars to ~10^6 using the most recent sky survey catalogs; and (2) once having approximately distinguished between the dwarf and the giant M stars on the basis of color-color relations (more easily accomplished for M's than for the F and G stars), decide which of the M dwarfs, if any, offer promising environs for the evolution of life—at first for life of any kind, and ultimately intelligent life. This proposal will partially fund Dr. Peter Backus, the SETI Observing Programs Manager, to accomplish the task of enlarging the target star list. Regrettably, nobody knows quite how to accomplish the second task. Therefore we propose a series of two focused workshops separated by 12 to 18 months to permit tangible results to appear from work done during the interval. The workshops will be held during the second and fourth years of this proposal at the SETI Institute, and be co-chaired by Dr. Tarter, the Director of the Center for SETI Research, and Dr. Mancinelli, a Co-I on this proposal (Sec. 6) with extensive research experience in environmentally induced stress in organisms. Dr. Cabrol, Co-I lead for Sec. 5, will participate, as will Drs. Rothschild (Secs. 2 and 4), Bishop (Sec. 4), Freund (Sec. 2), and Bakes (Sec. 3). Co-I Dr. Peter Backus, who will be preparing the target star catalogs and PI Chyba will round out the members of this proposal team whose expertise will be brought to bear on this problem. The remainder of participants will be invited from outside the SETI Institute, with an emphasis (but not exclusively so) on members of the Astrobiology Institute. In this way we will also reinforce ties between our astrobiology node and projects and those at other centers.

The workshops will be by invitation, include around two dozen scientists with specialties in particular microorganisms or atmospheric and planetary modeling, and will last 2.5 days each. Travel and per diem will be paid from this grant. The first workshop will be delayed until the second year of this proposal, in order to permit initial results from the Co-I's investigations to be included, and to allow advance preparation of the most complete description of the environment of putative M-star planets. Participants will be presented with the most recent "climate" calculations by Joshi et al. and others for a planet within the continuously habitable zone of an M star as well as the temporally varying biologically relevant UV surface fluxes calculated by Scalo and collaborators. The participants will be challenged to validate or refute these environmental conditions and to show whether the organism or radiation-damage repair mechanism in which they specialize would be viable under these conditions; work done in Secs. 2 and 4 of this proposal will be directly on point for these discussions. Results from the first workshop will feed into the second workshop held during the fourth year, at which participants will attempt to predict mutation rates and sensitivity to extinction. The goal of this latter exercise is to derive possible constraints on the frequency, duration, and magnitude of M star flaring events that can be used to answer the important question of whether M-star planets—which if they exist could be the most abundant planets in the galaxy, since 70% of stars are M-type—provide credible sites for life or even intelligent life.

These results will in turn have direct implications for determining observational strategy for the next generation SETI searches.

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The mission of the SETI Institute is to explore, understand and explain the origin, nature and prevalence of life in the universe.

SETI Institute Strategic Plan

Astrobiology is the study of the origins, evolution, distribution and future of life in the universe.

Astrobiology Roadmap

***Strengthening the Community*: The SETI Institute's 18 -Year Commitment to Astrobiology**

The SETI Institute is at the vanguard for understanding the nature of life, the search for life beyond Earth, and for communicating science and technology research to students, teachers and the public. The SETI Institute has become a premier example of an institution forging effective private/public partnerships. In 2002, the Committee on the Origins and Evolution of Life (COEL) of the Space Studies Board, National Research Council published *Life in the Universe: An Examination of United States and International Programs in Astrobiology* at the request of Congress. This report specifically cites the work of the SETI Institute, and its leadership in the search for life beyond Earth:

"Perhaps the most romantic venture in astrobiology is the search for extraterrestrial intelligence (SETI)….the current efforts are almost entirely privately funded. The SETI Institute in Mountain View, California, is the nexus of such efforts in the United States, and has accomplished in a spectacular way the founding of a science institute and the procurement of stable private funding to carry on the search. Because world-class scientists lead the SETI Institute, it is an effort carefully designed and worthy of notice by the scientific community and relevant federal agencies." (COEL Report, pp. 8-9.)

"The SETI Institute is in fact two different entities: a soft-money institution for research over a range of areas of astrobiology, largely with federal funding; and a donor-financed effort to develop technologies to search for intelligent life throughout a significant fraction of the Milky Way Galaxy.

The SETI institute has done an excellent job in developing programs in both arenas, which synergistically provide scientific breadth, vigor, and the resources for conducting a search that the federal government opted out of a decade ago. The SETI Institute's leadership—Frank Drake, Jill Tarter, and Christopher Chyba—are scientists who have personally invested their careers in the science of astrobiology. Students working at SETI from the Bay Area and elsewhere contribute their own intellectual energy and have produced high quality research projects that in some cases lead to Ph.D. dissertations. Overall the scientific quality of the program, and their output, is high….The leadership of the SETI Institute has forged a unique endeavor out of private and public funds, maintained a high standard of scientific research through its peer-reviewed research activities, and articulated clearly and authoritatively the rationale for approaches to a comprehensive search for extraterrestrial intelligence." (COEL, p. 72-73.)

Over the past 18 years, the SETI Institute has effectively administered \$82.1 million from federal agencies (NASA, NSF, USGS, and others), and \$54.4 million from private donations to support scientific research and educational projects. The Institute cultivates a quality research environment coupled with a commitment to maintain rigid cost controls in all administrative arenas. The SETI Institute is a 501(c)(3) non-profit scientific and educational research organization; our current negotiated overhead rate is 20% of direct labor and other direct costs excepting subcontracts and major equipment which are subject to lower rates. In practice, the average annual overhead rate for all projects combined at the Institute is 14.4% because of the low overhead on capital equipment. As a consequence of the Institute's low-cost environment, investigators are able to apply most of the awarded funds to research projects rather than infrastructure support. The SETI Institute provides a low-cost, highly effective institutional environment for the conduct of scientific research and education/outreach projects related to that research. In March, 1994, the SETI Institute was awarded a NASA Public Service Group Achievement Award "For meritorious service to NASA in carrying out research and education in areas of life in the universe and the search for extraterrestrial intelligence."

The Institute is governed Board of Directors, a leading group of individuals from science and private industry. The Board includes Nobel Laureate Dr. B. Blumberg and four members of the National Academy of Sciences: Drs. F. Drake, B. Blumberg, S. Faber, and W. Welch.

Board Member	Affiliation
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Dr. Charles Townes	University Professor, University of California
Dr. William Welch	Watson and Marilyn Chair for SETI at UC Berkeley

Center for the Study of Life in the Universe: Dr. Christopher Chyba, holder of the endowed Carl Sagan Chair for the Study of Life in the Universe, leads the SETI Institute's Center for the Study of Life in the Universe (LITU). Under his leadership, leading researchers in the field of astrobiology conduct a wide variety of fundamental research projects funded by NASA, NSF, USGS, and private sources. Over sixty-four employees, more than half of them principal investigators on their own peer-reviewed research grants, are supported through the Center. The LITU science team explores a wide set of disciplines ranging from observing and modeling the precursors of life in the depths of outer space to studies of Earth, where we are attempting to learn more about how life began and how its many diverse forms have survived and evolved. Each LITU research project is related in some way to understanding the origin and evolution of life, and the extent to which life may be present beyond Earth. Appropriate to the sweeping scope of this research, the Center has many partners in our LITU work including NASA, NSF, and several major universities. In preparation for the science section of this proposal, LITU scientists at the Instutute defined a set of new coupled research proposals especially germane to the NAI. As an NAI Center, the SETI Institute NAI Co-Investigators would build on, and draw from, this much larger base of researchers at the Institute.

Strategic Planning Group:

Over the past two years, Chyba has co-chaired with Professor Ken Nealson, University of Southern California, a Strategic Planning Group (SPG) for the LITU component of the SETI Institute. The mandate of this group has been to identify novel and important research opportunities in the field of astrobiology for which the Institute could serve as a launching platform. The SPG consists of about fifteen prominent scientists across the field of astrobiology, including Barry Blumberg (NAI), Leslie Orgel (Salk Institute), Bill Schopf (UCLA), Rick Stevens (Argonne National Lab), Eric Mathur (Diversa Corporation), Lori Marino (Emory University), Dan McShea (Duke), Simon Conway Morris (Cambridge University), Pascale Ehrenfreund (Leiden), Jay Melosh (University of Arizona), Don Lowe (Stanford), and others. The final report of the SPG is still being written.

As a part of his astrobiology work, Chyba will continue his ongoing successful collaboration with Dr. Carol Cleland, a philospher of science at the University of

Colorado, Boulder and member of the U. Colorado NAI team. Cleland and Chyba have been examining a long-standing fundamental question of astrobiology, namely the definition of life. In their first published paper on this topic "Defining 'Life' "(Cleland and Chyba *Origns Life Evol.Biosph.* 32, 387-393, 2002) they draw on the philosophy of language to argue that defining 'life' currently poses a dilemma analogous to that faced by those hoping to define 'water' before the existence of molecular theory. They conclude that in the absence of an analogous theory of the nature of living systems, which may or may not prove possible, interminable controversy over the definition of life is inescapable. Chyba is well equipped to contribute to this collaboration not only because of his background in astrobiology, but also because he holds an M.Phil. in the history and philosophy of science from the University of Cambridge

Chyba is also contributing to the upcoming graduate textbook (edited by John Baross and Woody Sullivan) to be published by Cambridge University Press. Chyba and Co-I Phillips have submitted the textbook's chapter on Europa, and Cleland and Chyba have submitted the textbook's chapter on definitions of life. Chyba is to write the final epilogue chapter for the volume.

Center for SETI Research:

The SETI Institute leads the search for intelligent civilizations beyond our own solar system through its Center for SETI Research, led by Dr. Jill Tarter, holder of the endowed Bernard M. Oliver Chair for SETI. Over the past decade, the SETI Institute has raised over $50M dollars to privately fund ongoing SETI research, future planning, and the development of the Allen Telescope Array (ATA).

SETI Science and Technology Working Group (STWG) and *SETI 2020*:

The SETI Institute convened a distinguished panel of 39 scientists and technology leaders from around the world to create a roadmap for SETI research through 2020. Bringing together leading radio astronomy researchers and technologists from the Silicon Valley resulted in a technologically innovative and futuristic roadmap for SETI research and the next generation of radio telescopes. The major recommendations were to develop (1) a dedicated SETI radio telescope, (2) optical SETI research on existing optical telescopes, and (3) an omnidirectional SETI system. The report is published as *SETI 2020* (Ekers et al. 2002). All of these recommendations have been acted upon to the extent commensurate with the maturity of the underlying technologies.

Allen Telescope Array—The Next Generation Radio Telescope:

The Institute, in partnership with the Radio Astronomy Laboratory at the University of California Berkeley, is developing the 350-antenna Allen Telescope Array (ATA). It will be the world's premier radio telescope dedicated to SETI research while simultaneously conducting traditional astronomical studies, including studies of interstellar chemistry in regions of star and planet formation relevant to astrobiology. SETI searches seek a biomarker of extra-terrestrial life by sensing the presence of extraterrestrial technology, as endorsed within the Astrobiology Roadmap’s Goal 7. High sensitivity radio SETI searches will for the first time be conducted 24 hours per day, 7 days per week when the ATA is inaugurated in 2005. As of the date of this proposal, Paul Allen, co-founder of Microsoft, and Nathan Myhrvold, former CTO of Microsoft, have contributed more than $12 million to the design and prototyping of the ATA, and additional funds for the construction of the ATA are expected in the near future. The SETI Institute’s aggressive pursuit of private funding for this project will result in a superb instrument for astrobiology research and the partnership with UC Berkeley, a minority institution, will ensure that the ATA is used as an effective tool for training the next generation of researchers.

The ATA design utilizes hundreds of small dishes that can be manufactured inexpensively by the satellite dish industry. Signals from the individual antennas are combined using components developed for modern telecommunications and commercial high speed computing. This is a departure from the large-single-dish built from custom components that is the heritage of radio astronomy, and results in significant improvements in performance and reductions in cost. NASA is currently the beneficiary of the privately-funded ATA design concept since it is the model for the prototype array for the next generation of the deep-space network.

The ATA design is also informing the design of the US concept for the future Square Kilometer Array (SKA), an international project to build a radio telescope with approximately 100 times the collecting area of the ATA. Co-I Tarter has served as the Chair for the US SKA Consortium and is currently the Chairman of the International SKA Steering Committee. Thus, ongoing, privately-funded research at the SETI Institute will directly benefit the entire astronomical and astrobiological community through the coming decades. Tarter is also the former chair and a current member of the SETI Permanent Study Group of the International Academy of Astronautics.

The SETI Institute currently conducts dual-site SETI observations covering a frequency range of 1-3 GHz using the Arecibo Observatory and the Jodrell Bank Observatory as *Project Phoenix,* the world's most sensitive and comprehensive search for extraterrestrial intelligence. Since its beginning in 1995, *Project Phoenix* has surveyed almost 1,000 candidate stars utilizing Australia's Parkes and Mopra Observatories, the National Radio Astronomy Observatory in Green Bank, West Virginia coupled with the Woodbury observing facility in Georgia, and currently the large antennas in Puerto Rico and England. *Project Phoenix* doesn't scan the whole sky. Rather, it scrutinizes the vicinities of nearby, sun-like stars since such stars are most likely to host long-lived planets capable of supporting life. Center researchers naturally include stars that are known to have planets, all of them within 200 light years distance from our own planet. *Project Phoenix* is the privately funded successor to the ambitious NASA SETI program that was cancelled by a budget-conscious Congress in 1993. *Project Phoenix* will be superseded by the targeted SETI searches with the ATA, expanding the list of stars by two to three orders of magnitude, and expanding the frequency coverage to explore the entire 1- 10 GHz terrestrial microwave window. Scientific research proposed for funding elsewhere in this proposal will address the question of the habitability (for life and for advanced life) of planets around dwarf M-class stars, which comprise ~70% of solar neighborhood stars. That research will in turn be critical to helping the ATA choose its target stars for observations.

Optical SETI (OSETI):

Dr. Frank Drake leads an OSETI project with scientists from the SETI Institute, the University of California's Lick Observatory, UC Santa Cruz, and UC Berkeley. He searches for short, pulsed signals using Lick Observatory's 40-inch Nickel Telescope with a new pulse-detection system capable of finding laser beacons from civilizations many light-years distant. Unlike other OSETI searches that utilize a pair of fast photodiodes in coincidence, this new three-photodiode experiment is largely immune to false alarms that slow the reconnaissance of target stars. This is the most sensitive optical SETI search yet undertaken. Other OSETI research is conducted at UC Berkeley, Harvard, Princeton, and in Australia. Drake's OSETI research is privately funded by the Institute.

Omnidirectional SETI System (OSS):

Given sufficient, affordable high speed computing capacity, it will be possible to construct the equivalent of a radio fly's eye capable of observing all directions above the horizon at once, over a range of frequencies from 1-3 GHz. This is the ideal instrument for finding transient signals from either extraterrestrial technology or astrophysical processes. An array of 4096 small omnidirectional elements would have a reasonable amount of collecting area and require $> 10^{16}$ ops to form all the beams on the sky and perform the signal processing for SETI. This much computing power is not affordable today, but will be in the future as a result of the exponential growth inherent in Moore's Law. Today preliminary work is being conducted by ElectroScience Lab at Ohio State University with funding from the Center for SETI Research to develop prototype technology for an OSS. An 8 element array (Argus Project) is now operational on the roof of the ESL building.

Funding New Science at the Institute:

The SETI Institute is a fertile breeding ground for new untried ideas in science through the private funding provided by the Institute's two endowed Chairs, C. Chyba and J. Tarter.

Center for Education and Public Outreach:

Through its Center for Education and Public Outreach (EPO) led by Co-I Edna

DeVore, the SETI Institute and its partners develop and conduct EPO programs supported by NASA, the NSF, and private donors. The EPO team has developed and is ready to publish an astrobiology curriculum entitled *Voyages Through Time* (VTT)*;* it's a standards-based course for a one-year high school integrated science class centered on the unifying theme of evolution. Scientists, teachers, curriculum writers, and media specialists created six modules that integrate astronomical, geological, and biological sciences. VTT was successfully field tested in more than 70 classrooms in 28 states by teachers during academic year, 2002-03. A Teacher Professional Development institute is proposed for EPO to enhance science teacher content knowledge and classroom implementation of VTT. The VTT project was led by the Institute's Dr. J Tarter and E. DeVore in close collaboration with co-investigators at NASA Ames Research Center (Y. Pendleton), California Academy of Sciences (Drs. M. Burke and S. Taylor), and San Francisco State University (Dr. K. O'Sullivan). San Francisco State University is a minority institution. Major funding was provided by the NSF IMD Grant # 9730693 ($2.3 million) with additional assistance from Hewlett Packard Company, Foundation for Microbiology, Educate America, and NASA's Astrobiology Institute and Fundamental Biology programs, other private support, and cost share. Over the 1998-2003 development period for VTT, project support totaled $ 3.3 million, a significant investment in astrobiology for students and teachers. The proposed EPO program brings this well-tested, standards-based astrobiology course to teachers and schools in our region, and offers the opportunity for other NAI sites to include their EPO staff in the training program. The Institute's manages EPO programs for NASA Flight Missions (see "Flight Missions" on page 101 below).

NOTE: The 5-page SETI Institute NAI-EPO Proposal appears at the end of this section.

Other "Strengthening" Elements:

The SETI Institute's NAI proposal team is a diverse group of scientists and educators, led by PI, Christopher Chyba. Each member of the team brings particular scientific expertise to the proposal, and all an engaged in activities that strengthen the overall field of astrobiology whether through participation on scientific panels, organizing scientific conferences, symposia and workshops, building new facilities relevant to astrobiology (the Allen Telescope Array), teaching courses and writing books, contributing to the professional development of pre-college teachers or simply bringing the adventure of science to students and the public. Several scientists are particularly interested in encouraging girls and young women to pursue careers related to astrobiology. This discussion describes "strengthening elements" and selected examples. The CVs in Appendix A include further documentation of the proposal team's contributions to the larger community.

1. Professional Community:

As noted in the COEL Report, the Institute's scientists are recognized leaders in the search for life beyond Earth. PI C. Chyba was awarded a MacArthur Award in 2001 for his work in both astrobiology and international security. In addition to his position at the Institute, Chyba is both Co-Director of the Stanford University Center for International Security and Cooperation (CISAC) and an associate professor (research) of geological and environmental sciences at Stanford. Co-I J. Tarter was inducted as a Fellow of the AAAS in 2003. Both are frequent plenary speakers for national and international meetings related to astrobiology. For example, at the 2002 *IAU Symposium 213 Bioastronomy Conference: Life Among the Stars*, C. Chyba, J. Tarter, K. Cullers, S. Shostak, F. Drake (all of SETI Institute), were 5 of the 10 plenary speakers. Simultaneously, the *Australian-American Fulbright Symposium 2002: Science Education in Partnership*, was held, and Co-I E. DeVore was US co-chair with K. Wilmoth (NAI), and Australian co-chairs C. Oliver and L. Vozzo of the Australian Centre for Astrobiology and University of Western Sydney respectively. C. Chyba was also an invited plenary speaker at the AAS Meeting (Jan. 2002), and the NAI Annual Meeting (Jan. 2003) addressing the question of life in the universe in both venues.

Notable Publications and Advocacy:

The PI and Co-Is for the proposed work are widely published in peer reviewed scientific journals (See CVs.) We author books, and contribute chapters and articles to many reports and conference proceedings. We publish in the popular press, which continues to build support for the community through advocacy of the importance of astrobiology within the government funding cycles, as well as enhance general public literacy and interest in astrobiology.

Congressional Testimony: On July 12, 2001, Chyba testified before the Subcommittee on Space and Aeronautics, Committee on Science, of the House of Representatives at their hearing on Life in the Universe (serial no. 107-17, pp. 46-60). He continues to be consulted by staff of that committee on issues of astrobiology (including SETI) and planetary exploration missions. Chyba has personally briefed representatives Dana Rohrabacher (Subcommittee Chair, R, California), Lamar Smith (R, Texas), Zoe Lofgren (D, California), and Curt Weldon (R, Pennsylvania) on these issues.

"The Search for Extraterrestrial Life: A Core Mission for NASA" by C. Chyba in *Space Policy in the Twenty-First Century*, ed. W. Henry Lambright, Johns Hopkins University Press, 2002, pp. 198-231. Chyba argued in this paper that the search for extraterrestrial life provides a core theme for NASA's scientific research in the twenty-first century, and a centerpiece of its program for solar system exploration.

SETI 2020: A Roadmap for the Search for Extraterrestrial Intelligence, SETI Institute, 2002, Eds. R. Ekers, D. Cullers, J. Billingham, L. Scheffer. ***SETI 2020***, conceived by leading international scientists and technologists, it delineates the bright future of humanity's search for extraterrestrial intelligence. This distillation of four work-shops, held in the Silicon Valley from 1997 through 1999, sets forth and justifies expectations for the next twenty years in the search for extraterrestrial intelligence. A bold conceptual framework, with a liberal dose of practical engineering and financial planning, ***SETI 2020*** envisions a new path of growth.

"The Search for Extraterrestrial Intelligence (SETI)", *Annual Review of Astronomy and Astrophysics*, 2001, J. Tarter, 39:511-48. This paper places the search for evidence of extraterrestrial intelligence in the broader astronomical context of the search for extrasolar planets and biomarkers of primitive life elsewhere in the universe. A decision tree of possible search strategies is presented as well as a brief history of the search for extraterrestrial intelligence (SETI) project since 1960. The characteristics of 14 SETI projects currently operating on telescopes are discussed and compared using one of many possible figures of merit. Plans for SETI searches in the immediate and more distant future are outlined. Plans for success, the significance of null results, and some opinions on deliberate transmission of signals (as well as listening) are also included. SETI results to date are negative, but in reality, not much searching has yet been done.

"Is There Life Elsewhere in the Universe?" by J. Tarter and C. Chyba, *Scientific American*, Dec. 1999, p. 118-123. The article presents a straightforward discussion of the search for life beyond Earth in our own solar system at Mars and the moons of Jupiter. Then, the authors look forward in time to seeking evidence of life in other planetary systems by seeking chemical biomarkers and ultimately evidence of extraterrestrial technologies via SETI searches.

"Life's Far-Flung Raw Materials" by S. Sandford, L. Allamandola, and M. Bernstein (Co-I on this proposal), *Scientific American*, July 1999. This cover story suggests that the origins of life had major contributions from interplanetary and interstellar materials including the dust of comets and meteors. The complex molecules that exist in space could have peppered the primordial soup on early watery planets like Earth and Mars with the organic molecules we see in living systems today. The ubiquity of complex organic molecules across space, combined with the recent discoveries of planets around other stars, makes it more likely that the conditions conducive to life, if not life itself, have developed in other solar systems.

"Introduction to Astrobiology", textbook, for graduate students and senior level undergraduate, by Co-I E. Bakes, to be published Sept. 2005 by Johns Hopkins University Press. Astrobiology covers many aspects of physics, chemistry and biology and its subject matter ranges in diversity from the Big Bang through to the formation of galaxies, stars, planets, prebiotic chemistry concerning the emergence of RNA and DNA and the emergence of life from these complex molecules respectively. This upper division, undergraduate text will include: the big bang and the formation of the first generation of stars; supernovae and subsequent next generation star formation, the interstellar medium--the site of the first prebiotic chemistry, the formation of planets--seeding the solar system for life, the evolution of a life bearing planet, the chemistry of prebiology, the origins and evolution of terrestrial life, the potential for extraterrestrial life, colonizing our solar system, and the technology of solar system and interstellar exploration.

New Encyclopedia Articles:

Mancinelli, R. L, and L. J. Rothschild: "Extremophiles: Who, What, Where & How". *McMillian Encyclopedia of Biology*, 2002.

Rothschild, L. J. "Astrobiology". *McGraw Hill Encyclopedia of Science & Technology* 2002

Tarter, J. C. "Search for Extraterrestrial Life". *Encyclopedia of Space Science and Technology*, Wiley & Sons, (in press 2003).

Proposed Workshop and Symposia:

The Institute's scientists are members and active participants in several professional organizations affiliated with astrobiology, and contribute plenary talks, invited talks, papers and presentations at a wide-variety of meetings, including those noted earlier. A review of the CVs documents the breadth of participation. For example, the Institute is directly involved in planning or having significant participation in the IAU General Assembly (July, 2003), for the International Astronautical Congress in Berlin, Germany (2003) the Division of Planetary Sciences (2003), Bioastronomy 2004: Habitable Worlds, in Iceland, AbSciCon (all meetings). The proposal team anticipates continued participation in the face-to-face conferences and symposia of the NAI community as well as in the virtual events hosted via NAI Central. This sustained scientific leadership strengthens the astrobiology community including the radio astronomical research efforts of the worldwide SETI research community

Cross-Disciplinary Scientific Workshop on M-Star Habitable Zones:

The work proposed by J. Tarter includes a series of two focused workshops in years two and four, separated by 12 to 18 months to permit tangible results to appear from work done during the interval. The purpose of these workshops is to bring together many of the Co-I’s on this proposal and relevant experts from across the spectrum of astrobiology specialties to tackle again the question of whether any planets that might be in orbit around M stars offer a habitable environment. Inputs to these workshops will be the latest ‘climate’ models and calculated UV fluxes on the surface of a synchronously locked planet within the habitable zone, as well as a more complete understanding of the responses of terrestrial microorganisms to UV and desiccation stresses arising out of research in several sections of this proposal. The workshops will be held at the SETI Institute and co-chaired by Co-I's Dr. J. Tarter, and Dr. R. Mancinelli, who has extensive research experience in environmentally induced stress in organisms. The workshops will be by invitation, include less than two dozen scientists (whose travel and per diem costs will be paid) and will last 2.5 days each The participants will be challenged to show whether the organism or radiation-damage repair mechanism in which they specialize would be viable. Results from the first workshop will feed into the second workshop at which participants will attempt to predict mutation rates and sensitivity to extinction. The goal of this latter exercise is to derive possible constraints on the frequency, duration, and magnitude of M star flaring events that can be used to constrain the SETI target list. The workshops should be an ideal tool for bringing together the diverse set of skills and knowledge bases that are necessary to decide on whether or not to include M stars on the observing list.

Monthly SETI Institute—NAI Workshop Series

Under the auspices of this proposal, in addition to the focused workshops just described, the SETI Institute will sponsor a monthly workshop series at which the Co-Investigators of this NAI proposal will informally present their ongoing research in a constructive, problem-solving environment. These discussions will also be open, and advertised to researchers from NASA ARC, Stanford University, UC Santa Cruz and Berkeley as well as the regional California State Universities at San Francisco, Hayward, San Jose and Monterey Bay. (All of these CSU campuses are minority institutions.) They will have both the effect of strengthening the Institute's team of researchers, and also of further strengthening that team's ties with researchers in the broader scientific community.

Examples of contributions to the professional community follow on the next page.

Investigator	Examples of Contributions to the Professional Community
C. Chyba	-NASA Planetary Protection Task Force -Chair, Science Definition Team for NASA's Proposed Europa Orbiter Mission, and have continued to investigate means of detecting Europa's subsurface ocean (Chyba et al. 1998, Kovach and Chyba 2001) and possible biosphere (Chyba 2000a,b; Chyba and Phillips 2001, 2002; Chyba and Hand 2001).
E. Bakes	-*Introduction to Astrobiology*, textbook for graduate students and Senior level undergraduates, Johns Hopkins Press, published 2005. -*The Astrochemical Evolution of the Interstellar Medium* Twinpress, 1997
A. Banin	-Reviewer for *Science, Icarus, JGR-Planets* and *Origins of Life and the Evolution of the Biosphere* -Senior NRC Resident Research Associate (2001-2) -Main Scientific Organizer: The Viking Commemorative Symposium, COSPAR'96; -Editor, Proceedings of Viking Commemorative Symposium published in *Advances in Space Research*, 1997.
M. Bernstein	-COSPAR: organized sessions at multiple meetings; editor of special issues of the Journal of Advances in Space Research (conference proceedings) -Member: Origins and Geochemistry Review panels -Member: NASA Specialized Center for Research and Training (NSCORT) Panel
J. Bishop	-NASA Peer Review Panels, External Reviewer for NASA Programs: PGG, EXO, MDAP, MFRP, SBR -Reviewer for *Science, Nature, Clays Clay Miner., J. Geophys. Res, Meteor, Planetary Science, Geophys. Res. Letters, Planet, Space Sci.,* and *others.*
F. Freund	-"Origins of Life and the Evolution of the Biosphere", "Astrobiology", "PNAS", and forthcoming "Astrophysical Journal". -Participant in the workshops like "Blue Dot I and II", Laboratory Astrophysics and others.
R. Mancinelli	-Member of editorial board of International Journal of Astrobiology. -Reviewer for Nature, European Planetary and Space Science Journal, Journal of Geophysicsl Research--Planets, Applied and Environmental Microbiology and Arctic and Alpine Research -Organized 2002 COSPAR meeting: Search for Signature of Life in the Solar System, Terrestrial Analogues and Simulation Experiments: Joint COSPAR/IAC Event
C. Phillips	-Co-author of chapter on the future of Europa Exploration, as part of the DPS decadal review ad-hoc panel on planetary science; -Co-author (with Chris Chyba) of chapter on Europa in upcoming Astrobiology textbook.
L. Rothschild	-Organized 1st and 2nd & 3rd Astrobiology Science Conferences, NASA ARC -Co-editor, *Astrobiology Journal* -Editor, "Evolution on Planet Earth: the Impact of the Physical Environment, Academic Press (publication in 2003) -Advisory Board, Denver Museum of Natural Science, New York Hall of Science -Co-organized Stanford Astrobiology course with Chyba
J. Tarter	-Kepler Science Working Group -Served on SOC for Bioastronomy Conferences, 1999, 2002, 2004: provided $10k conference support for each from endowed Chair.

2. Training

The SETI Institute is a nonprofit organization conducting scientific research and education projects; it is not a degree-granting institution. Nevertheless, we are engaged in training future astrobiologists through work with regional and national university undergraduate and graduate students.

In addition to his position at the SETI Institute, PI Chyba is also a faculty member at Stanford University, which funds him at the 40% level. As an associate professor (research) in the Department of Geological and Environmental Sciences, he currently supervises three graduate student research projects, including that of Mr. Kevin Hand, support for whom is requested in this proposal. Dr. Chyba also teaches at both the undergraduate and graduate levels at Stanford. His courses—developed by him and now a regular part of the Department's curriculum—are the graduate course "The Origins of Life in the Solar System" and the undergraduate seminar "The Search for Life in the Solar System." Last year this undergraduate course had 65 applicants for 15 openings. The graduate seminar, taught the previous year, drew graduate students from six different university departments, creating exactly the kind of interdisciplinary mix astrobiology requires. Chyba's research group joins employees of the SETI Institute with Stanford graduate students in a transparent manner.

Working with Stanford colleague Professor Don Lowe, Chyba has been instrumental in the creation of an astrobiology and planetary sciences concentration within the Department of Geological and Environmental Sciences. This concentration has been approved by the faculty and is starting this academic year, built around a core of four (including Chyba's) new astrobiology and planetary sciences courses.

Chyba has also supervised summer undergraduate projects. This past summer he supervised a Swarthmore College undergraduate, Aaron Goldman, who joined Chyba's group at the SETI Institute and is coauthoring a paper with Chyba and Hand on the salts in Europa's ocean. Goldman has already lectured on this work in his department (the Department of Biology) at Swarthmore College.

Training Students:

At the Institute, we specialize on involving and training younger students, motivating them with the limitless possibilities of astrobiology, the search for life beyond Earth. Because we are very conscious of the potential multi-generational nature of much of our research, we take the job of training the next generation of scientists seriously. For that reason, we develop curriculum products around astrobiological themes for elementary, middle and high school students, and conduct an extensive education and outreach program (see Table 4). We mentor students over long periods of time, and assist them in entering the best graduate schools in order to earn the degrees that enable them to contribute to the field in the way that best suits their particular talents. Over the years, without any formal, funded undergraduate program or project at the Institute, we've been successful in bringing bright young people into the field. (See Table 1 for current students.) For example, Dr. Z. Webster, now Professor at CSU San Bernadino was mentored by J. Tarter through undergraduate work at UCSC, and PhD at UC Berkeley.

Name (Gender) (Investigator)	First Contact	Current Work	Scientific Focus
Amy Barr, (F) (J. Tarter)	6th grade	Graduate studies, U CO at Boulder	Liquid ocean on Europa
Sam Laroque, (M) (J. Tarter)	Undergraduate, UCSC	Graduate studies, U of Chicago	Cosmology & building instruments for CARMA
Josh Tasman, (M) (J. Tarter)	Computer science Brown U.	Graduate Studies	Psychology
Laura Langland-Shula, (F) (J. Tarter, E. DeVore)	High school; undergraduate UCLA	Graduate Studies, UC Santa Cruz	Astrophysics
Maggie Turnbull, (F)	Undergraduate, U. of	Graduate studies,	CATTS Fellow,

(J. Tarter)	Wisconsin	U of Arizona	Astrobiology
Nia Imara, (minority F) (J. Tarter, E. DeVore)	Undergraduate, Kenyon College	Graduate studies at UC Berkeley	Astrophysics Cosmology
John Keller, (M) (E. DeVore)	NASA ARC	Graduate studies U of Arizona	Astronomy, and Astronomy Education
Andrew Hock, (M) (N. Cabrol)	NASA ARC, Astrobiology Intern	Graduate Studies, UCLA	Geophysics
Vanessa Lancaster (F) (F. Freund; L. Rothschild)	Arizona State University	Graduate Studies, Arizona State Univ.	Detoxifying enzymes
Kevin Hand (M) (C. Chyba)	Stanford	Graduate Studies, Stanford University	Europa
Jamie Elsila (F) (M. Bernstein)	Undergraduate	Graduate Studies Stanford University	Chemistry
Ren Ping, (F) (A. Banin)	Hebrew University	Graduate Studies, Hebrew University	Weathering & soil formation on Mars
John Scoville (M) (F. Freund)	NASA Ames Research Center	Graduate Studies, Stanford University	Large scale computer modeling
Charles Apel (M) (M. Bernstein)	UCSC	Post-doc from UC Santa Cruz	Membrane biophysics
John Chaklader (M) (M. Bernstein)	Colgate University, Prof. Karne Harpp	Undergraduate research project	Parent body aqueous alteration
Aaron Goldman (M) (C.Chyba)	Swathmore	Undergraduate research project	Salt in oceans of Europa (paper in preparation)
Metages Sisay (B. Khare)	Santa Clara Univ.	Graduate Studies, MS	Physics
Patrick Wilhite (M) (B.Khare)	Santa Clara Univ.	Undergraduate	Physics
Hiroshi Imanaka (B. Khare)	Univ. of Tokyo, Japan	Graduate Studies	Physics
Brian Grigsby, (M) (N. Cabrol, E. DeVore)	Planetarium Director, Shasta Co. Schools	Graduate Studies MA CSU Chico, Sci.Ed.	Lincancabur expedition virtual field trip
Gretchen Walker (F) (E. DeVore)	High School Teacher	Graduate studies, U. of Maryland, MS	Astronomy

Table 1: Current Students and Post-Doctoral Students (F=female; M=Male)

SETI Institute's NAI team members are mentors for students in NASA's SHARP (summer high school minority interns), the Astrobiology Academy at NASA ARC, and at San Jose State University (SJSU), a minority institution for graduates and undergraduates.

3. Teaming with Minority Institutions:

As discussed in the Institute's proposed EPO program, the teacher professional development summer institute will be developed in collaboration with Dr. K. O'Sullivan, Professor of Science Education at San Francisco State University (SFSU), a minority institution. Continuing education credit for participants will be arranged either through SFSU, or San Jose State University, another regional minority institution.

The SETI Institute is also interested in working with the NASA Astrobiology Institute Minority Institution Involvement Program to support the Faculty Sabbatical program, pending our membership in the NAI. E. DeVore investigated this program at the NAI meeting at Arizona State University (2003), and will facilitate the Institute's participation. Our scientists work at the Institute's Mountain View offices, NASA ARC, in the field, and in partnership with the UC Berkeley Radio Astronomy Laboratory. We look forward to hosting faculty sabbaticals through this program.

As noted earlier, the Institute's NAI Monthly Workshops will be open to faculty from regional minority institutions.

4. Staff and IT:

At the SETI Institute, PI Dr. C. Chyba holds the endowed Carl Sagan Chair for the Study of Life in the Universe; and Co-I, Dr. J.

Tarter, holds the endowed Bernard M. Oliver Chair for SETI. Both are permanent positions, fully funded; their time in this proposal is a matching contribution to the Institute's NAI work. As described earlier, the Institute's mission is congruent with astrobiology, and the Institute's existence precedes the NASA Astrobiology Institute by many years. The entire scientific research program and the EPO program at the Institute (both those activities included in this proposal, and those that are separately funded) support the Goals and Objectives of the Astrobiology Roadmap, 2002.

The Institute's indirect costs provide the administrative support for our PI-led, NASA funded projects. This includes institutional management, procurement and contracts, business services, grant management, human resources, and information technology services. For Co-I's located at the Mountain View site, common IT services are provided from indirect costs; for Co-I's located at NASA ARC, IT services are provided via the ARC Division's subcontractors. The IT department at the Institute is staffed with 3.5 FTE's plus consultants. At the SETI Institute headquarters in Mountain View, a basic teleconference and videoconference system exists in the administrative conference room, a heavily used facility. At present, the Institute has one T-1 line for all internet based communications. In support of the Institute's NAI membership, it would be highly desirable to install higher speed communications, and a separate teleconference and videoconference system in the large conference room at the Center for the Study of Life in the Universe to insure ready access for the Institute's NAI team.

5. Information Technology:

Dr. E. Bakes is the Co-I responsible for "Titan, Photochemical Haze, and the Oxidation of Early Earth" (p. 17 and forward). In her work, she will develop code that models aerosols and photochemical evolution of large molecules. She will make a user-friendly version of the charging routines and the infrared spectral model available for analysis of Cassini/Huygens data. This is a concrete contribution to the larger community in the area of information technology tools.

6. Flight Missions:

Mars Exploration Rover: Dr. N. Cabrol is one of 28 scientists chosen by NASA for participation for the 2003 Mars Exploration Rover (MER) Mission. Since joining the SETI Institute, Cabrol has focused her research primarily on planetary geology and automated, human exploration of Mars. In the upcoming MER mission, Cabrol will be studying the traces left by water activity at the landing sites and wherever the rovers explore. Cabrol's investigation is divided into 4 primary tasks: (1) the geological and morphological identification of aqueous sedimentary landforms and deposits combining the analysis of PanCam and MI images at the MER sites with MOC and MOLA for insight into the local and regional geology and recommendations for preferred directions in which to send the rover; (2) the morphometrical and statistical analysis of PanCam and MI images to deduce properties of sediments, characteristics of emplacement, and nature of the transporting agents and depositional environments; (3) the generation of graphical and statistical material that will allow easy access and combination of the results of this investigation with those of other instrument teams and science investigators, and their archival in the Planetary Data System (PDS); (4) the active participation in the planning of science sequences and rover traverses, and the completion of tasks associated to the position in the Athena Science Team for which the principal investigator will be designated, and (5) the active participation to the EPO program of the Mars Exploration Program (JPL) and Center for Mars Exploration (ARC). It is critical that this project be performed *during* the Mars Landed Operations: (a) From the science perspective, it will ensure that appropriate images are acquired by both instruments to address issues that are key to this investigation and (b) From the rover operation perspective, it will assist the planning of science targets and traverse sequences by optimizing the understanding of the aqueous history of the MER sites, and assist the rover mobility by providing projected trafficability information as inferred from context images and experience acquired from terrestrial analogues. Finally, (c) Cabrol has acquired leading experience in the management of science teams and data, the generation of command cycles, science sequences, and rover traverses during several field experiments.

Mars Reconnaissance Orbiter: Dr. J. Bishop is a current Co-I on the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument for the 2005 Mars Reconnaissance Orbiter (MRO). CRISM is a visible/near-infrared imaging spectrometer that will produce global hyperspectral images of Mars at ~200m spot size, as well as increased spectral and spatial resolution images for selected regions. She is the lead for spectral identification tasks related to hydrated minerals and surface alteration. These are of particular interest to astrobiology on Mars in that remote identification of water and aqueous processes may be connected to the potential for habitability. Dr. Bishop participated in the Marsokhod rover tests at Silver Lake, CA, in 1999 as a remote scientist during rover field activities. This test was designed to assess techniques needed for rovers, such as the Mars Exploration Rovers that are launching in the coming months. She assisted in spectral analyses of visible/NIR and thermal IR data collected from the mission that resulted in three publications. Dr. Bishop was a member of the Pathfinder mineralogy Science Operations Working Group (SOWG) from 1997 to 1999. She performed spectral analyses of Martian rocks and soils based on lab spectra of analogues and assisted the team with analysis of the spectral, magnetic and chemical data.

Galileo Imaging Team: Dr. C. Phillips assisted the Galileo imaging team in planning observations of Europa and Io, including target selection, observation design, and technical delivery of observation information to JPL. She performed initial image processing and mosaic construction of those observations.

EPO Programs for NASA Flight Missions: The Institute manages EPO programs for NASA missions that conduct research complementary to our mission and that of astrobiology: (1) As a member of the Universities Space Research Association's consortium, and in partnership with the Astronomical Society of the Pacific, the Institute conducts the EPO program for NASA's *SOFIA,* the Stratospheric Observatory for Infrared Astronomy. *SOFIA* is the next-generation airborne observatory, featuring a 2.5 meter telescope mounted in a highly modified Boeing 747SP. *SOFIA* is home-based at NASA Ames Research Center, and begins observations in late 2004, flying research missions for 20 years. As an infrared astronomical observatory, SOFIA is especially suited to astrobiological research: the chemical composition of the interstellar medium, the ecosystems of galaxies, the nature of planetary atmospheres, and the formation of stars and planetary systems. For EPO, *SOFIA* offers the unique opportunity to train and integrate educators into the research environment on board the observatory. (2) The Institute is also a partner for the NASA Discovery Mission *Kepler* that will seek evidence for Earth-sized planets in orbit about sun-like stars. Observing approximately 100,000 stars simultaneously with extreme photometric precision, *Kepler* data will allow scientists to characterize the nature of other planetary systems, and determine the prevalence of terrestrial planets in the habitable zone. *Kepler* is on the central pathway toward space-based missions that seek evidence of life on other worlds. The 9-year *Kepler* EPO program will be conducted by experienced educators at the Lawrence Hall of Science at UC Berkeley, and the Institute. SETI Institute scientists are directly involved in *Kepler*; J. Tarter is a member of the *Kepler* Science Working Group; J. Jenkins is a *Kepler* Co-I and leads the data analysis team, and E. DeVore is a *Kepler* Co-I with responsibility for the EPO component

ESA Sponsored Missions: R. Mancinelli was the PI for the European Space Agency(ESA) sponsored BIOPAN3 "Survival of Osmophiles in Space" experiment. Since 1998, he has been the PI the ESA sponsored EXPOSE Experiment for the Space Station. 1994-1995, he was the Co-I for ESA sponsored BIOPAN 1-2 Survival Experiment. For the NASA ARC NAI CAN proposal for this same cycle, R. Mancinelli proposes space flight research. It is not disclosed to this proposal team.

7. Linkage to Other Agencies:

The PI and Co-Is receive current support and anticipate future support from other federal agencies, primarily the National Science Foundation (NSF), and a variety of private foundations. A representative sample of this linkage to other support appears below and in the Appendix B

Investigator	NASA Organization or Other Agency
C. Chyba	-Carl Sagan Chair for Life in the Universe, Endowed chair at SETI Institute -MacArthur Award, 2001 -Stanford University
N. Cabrol	-Director's Discretionary Fund: NASA ARC: Exploring Lincancabur (2002-03) $80K or 90K -Collaboration from the Universidad Catolicà del Norte which contributes 10% of a biologist work-year on this project equivalent to $10,000, and the logistical support from G. Chong (3 weeks full time) equivalent to about Sergeomin in Bolivia provides assistance in the field; dosimeters from other funding. Total contributed funding: $37,000 -National Geographic Society The project explores the Licancabur lake, including diving, to collect (1) critical astrobiological information about the limits of life in this unique extreme environment, (2) scientific clues about potential planetary analogs, and (3) elements to design science mission strategies for planetary exploration. $20,800
J. Tarter	-Bernard M. Oliver Chair for SETI Research, endowed by SETI Institute -NSF IMD Grant # 9730693: Voyages Through Time (completed) -Major private funding for SETI research from: David Packard and the Packard Foundation, William Hewlett, Gordon Moore, Paul Allen, Nathan Mhyrvold, and many other donors. -NSF requested white paper prepared indicating intention to apply for NSF annual funding to operate the Allen Telescope Array over 30 years..
R. Mancenilli	-NASA's Life Sciences, Planetary Protection, and NAI at Ames Research Center -Sole US PI on ROSE experiements; oversees the work on prokaryotes and testing all organisms in the Space Simulation Facility at the DLR in Germany; will co-coordinate flight experiments.
M. Bernstein	NASA's Origins, Planetary Geolog, Exobiology & NAI at Ames Research Center
F. Freund	NASA Goddard Space Flight Center Earth Sciences, and the Geophysical Laboratory at Carnegie Institution of Washington (Dr. G. cody & Dr. Y. Fei)
C. Phillips	Collaborated with USGS researchers; trained in using ISIS image processing software by USGS Flagstaff, and continue to assist them in the construction of a base map for Europa, as well as planetary nomenclature issues.
E. DeVore	NSF IMD Grant # 9730693: Voyages Through Time (completed) SOFIA EPO via USRA Prime Contract with NASA Kepler EPO, NASA ARC Grant #NAG 26066 NAI & Fundamental Biology, Grant # NAG 26051

Table 2: Examples of Linkage to Other Agencies

Other—Strengthening the participation of young people in Science: Dr. Janice Bishop volunteers as a Trustee for the Summer Science Program, Inc., an accelerated astronomy program for advanced high school students. This is a college-level astronomy program that teaches students from a variety of ethnic and social backgrounds about math, physics and astronomy. The curriculum has a strong hands-on component and each student spends many nights observing and developing plates, and many days calculating the orbit of their asteroid.

Dr. Cynthia Phillips authored *The Everything Astronomy Book*, an introduction to astronomy including a chapter on astrobiology, written for a general audience (Adams Media, 2002). She ran a website on Space & Astronomy for Kids from 1997-2001, at About.com providing weekly articles, annotated links, chat room and bulletin board, and answered questions from kids from around the world. She continues to provide occasional articles about Europa, and its potential for water and life for website Space.com as part of SETI Thursday.

Dr. J. Tarter is a high-profile figure for the media. As the role model for the Eleanor

Arroway character in Carl Sagan's *Contact*, she is often on camera or in press. She accedes to many media requests because she wishes to encourage the next generation of female scientists. One recent example of this commitment to young people is the book *Looking for Life in the Universe* by Ellen Jackson (2002). This book is a biography of Dr. Tarter written in a style that is intended to portray a career in science as rewarding and exciting. Tarter is also featured on *The Tech Club* a CD-ROM based collection of interviews with 54 women of science, engineering, mathematics and technology intended to provide positive female role models.

Dr. Nathalie Cabrol was awarded an IDEAS (Initiative to Develop Education through Astronomy and Space Sciences) one-year grant: to conduct a virtual field trip from Lincancabur for students, teachers and the public. Partnered with SETI Institute and the Shasta County Office of Education (rural schools in northeastern California), Cabrol's team and educator Brian Grigsby developed a web site, and interacted with students and the public during the 2001 research expedition. The project is the subject of Grigsby's MA in Science Education (2005); Cabrol anticipates integrating the activity into future research expeditions.

The SETI Institute's Proposal for NAI Education and Public Outreach (EPO):

Understanding the origins, evolution, distribution and future of life in the universe engages students, teachers and the public in the great adventure of 21st century science. Our Education and Public Outreach (EPO) program goal is to share the cutting-edge research and discoveries of astrobiology with educators and the public in order to inspire students to pursue careers related to astrobiology and to enhance science literacy.

The EPO program for the SETI Institute's "Planetary Biology, Evolution, and Intelligence" our NAI proposal focuses on these key audiences: (1) high school science teachers at schools with underserved students in urban, rural and minority communities; (2) science museum visitors--students, teachers, and families; and (3) the general public.

The SETI Institute's EPO programs have a long and successful history of engaging our scientists and educators with these key audiences in formal and informal education, and public outreach. Today, we have a broad and active EPO program. (See Table 4 below). The NAI-EPO activities we propose here will integrate into the Institute's ongoing programs to take advantage of natural synergies with existing projects and engage with the networks of people and institutions that have been developed by the Institute's EPO team over the past dozen years. This will substantially leverage NASA's investment in NAI-EPO. The Institute's proposed NAI-EPO program is comprised of five major activities:

- Conduct professional development for high school science teachers implementing *Voyages Through Time(*VTT*)*, and make VTT a resource available to the entire NAI
- Collaborate with the California Academy of Sciences for exhibits and outreach
- Facilitate education outreach, media opportunities, and public events that feature the Institute's NAI scientists
- Participate in the NAI EPO network and NASA OSS and Education Activities

The Institute's NAI EPO program will be developed and conducted in compliance with the OSS EPO guidelines described in *Partners in Education (1995)* and *Implementing the Office of Space Science Education/Public Outreach Strategy (1996)* as are the other NASA-funded EPO programs conducted by the SETI Institute.

The Institute's NAI EPO program will be directed by Co-I Edna DeVore (5%), Director of Education and Outreach at the Institute, with Pamela Harman (15%), Education Manager. Dr. Kathleen O'Sullivan, Professor of Science Education at San Francisco State University (SFSU) joins the team for her sabbatical in spring 2004 at no cost to the program. DeVore is an experienced educator and has more than a decade of experience developing and directing EPO programs for NASA missions and the SETI Institute. Like DeVore, Harman is an experienced classroom and NASA EPO educator, most recently presenting a teacher professional development workshop at the 2003 NAI Meeting at ASU.

Professional Development & *VTT*

*Voyages Through Time (*VTT*)* is an astrobiology curriculum for integrated high school science. It is a standards-based course centered on the unifying theme of evolution, that is delivered on CD-ROMs plus printed readers. Over a period of five years at a cost of $3.3 million, the SETI Institute brought together scientists, teachers, curriculum writers, and media specialists to create six modules that integrate astronomical, geological, and biological sciences. They are:

- *Cosmic Evolution*: origin of the universe, life cycles of stars, & formation of planets
- *Planetary Evolution*: study of Earth, Venus and Mars, & what makes a planet habitable
- *Origin of Life*: origin hypotheses, common chemistry, life on Earth, multicellular life
- *Evolution of Life:* the great diversity & diversification of living things
- *Hominid Evolution*: processes & events in hominid evolution
- *Evolution of Technology:* technologies that meet human needs, evolution & impact of technology

Individually, the modules are appropriate as supplementary materials for Earth Science, Biology, Life Science, Astronomy, and Space Science courses. Together, the six modules comprise one year of science for grades 9 or 10. The VTT curriculum is based upon the *National Science Education Standards* and *The Benchmarks for Science Literacy*. The goals and objectives of these two key documents are specifically referenced and stated throughout the curriculum materials at both the module and lesson levels.

VTT's themes, goals and objectives align closely with the Fundamental Questions and the Goals and Objectives of NASA's astrobiology program (The Astrobiology Roadmap, 2002) and introduce students to astrobiology early in their education. VTT's goal is to engage students in understanding that evolution is the result of cumulative changes over time; that it occurs in all realms of the natural world; and that various processes underlie evolving systems and organisms as reflected in the differing time scales and rates of change. The intent is that students understand connections and relationships across these realms of change, and learn that science is a process of advancing our understanding of the natural world, rather than a set of final answers. The major overarching questions posed in each module are: What is changing? What is the rate of change? What are the mechanisms of change?

The VTT project was led by J. Tarter (PI) and E. DeVore (SETI Institute); M. Burke and S. Taylor at California Academy of Sciences (CAS), K. O'Sullivan at SFSU (a minority institution), and Y. Pendleton at NASA ARC. The NSF IMD Grant #9730693 provided major funding with additional assistance from the Foundation for Microbiology, Hewlett Packard Company, Educate America, and NASA's Astrobiology Institute and Fundamental Biology programs. The SETI Institute (a non-profit organization) is publishing VTT in partnership with *Learning in Motion*, a woman-owned small business that develops and publishes software products for K-16 education. VTT will be available commercially in summer, 2003.

The proposed VTT Teacher Professional Development (VTT-PD) will feature a 5-day, summer institute for 20 teachers plus NAI EPO participants each year. (Total is 100 teachers plus NAI participants over 5 years.) Other NAI EPO teams will be invited to participate in the VTT-PD with funding from their home institution. One VTT-PD institute will be held each summer, calendar year 2004 -2008. As recommended by the *National Science Education Standards*, the VTT-PD teachers will participate in science content training led by scientists from the Institute's NAI team, NASA ARC, and other collaborating organizations such as CAS, hands-on training with curriculum materials, planning time for classroom use, and on-going, school-year online-mentoring via the VTT-PD web site at the SETI Institute. The VTT Online Community web site will be separately developed by the Institute and *Learning in Motion* to support VTT implementation and represents cost-share on this proposal.

Each VTT-PD teacher will receive a set of the 6 VTT modules, and a stipend to be used for additional materials or continuing education college credit. We anticipate holding the VTT-PD institutes at various regional sites in the San Francisco Bay Area and greater Northern California. Potential venues are regional high school districts, NASA ARC in Santa Clara County, CAS in San Francisco, Chabot Space and Science Center in Alameda County, CSU Monterey Bay in Monterey County, The Tech Museum in Santa Clara County, and Shasta County Office of Education which serves rural northeastern counties. These sites represent an extension of the collaborations that developed the VTT curriculum as well as a network of other organizations working with the Institute's current EPO projects. Continuing education credit for participating teachers will be offered via SFSU or San Jose State University (SJSU), both minority institutions well-known for training science teachers, and universities with existing relationships with the Institute's EPO programs. Dr. K. O'Sullivan, Professor of Science Education (SFSU) will spend one semester on sabbatical at the Institute spring 2004 to collaborate on planning the VTT-PD institute, and additional dissemination strategies and proposals for VTT. Dr. O'Sullivan's participation is evidence of ongoing collaboration of the VTT development team, and represents institutional commitment of both SFSU and the Institute. Teachers will be recruited for VTT-PD specifically from school districts dominated by minority and under-served students with the goal of assisting these teachers and schools to effectively implement a tested, research-based, standards derived curriculum for freshman or sophomore science. As California is a minority-majority state, and the schools of California reflect great ethnic and cultural diversity, we expect to achieve this goal. The VTT-PD time-line appears in Table 3.

The VTT-PD institute program will be evaluated by the participants and over duration of the 5-year program and will be tracked via regular communication with the teachers and schools to understand the implementation of the curriculum in the classrooms. Evaluation tools will be developed with the assistance of Dr. O'Sullivan during her sabbatical. O'Sullivan's participation is cost shared.

VTT-PD Events	**Summer 03**	**School Yr. 03-04**	**Summer 04**	**School Yr. 04-05**	**Summer 05**	**School Yr. 05-06**	**Summer 06**	**School Yr. 06-07**	**Summer 07**	**School Yr. 07-08**	**Summer 08**
NAI proposal awarded	▨										
VTT Published	▨										
Build *VTT* Online Community		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Recruit teachers & schools		▨		▨		▨		▨		▨	
Plan workshop		▨		▨		▨		▨		▨	
Conduct workshop			▨		▨		▨		▨		▨
Evaluate & Report to NAI			▨		▨		▨		▨		▨

Table 3: VTT-PD Timeline

Collaboration with CAS

The California Academy of Sciences (CAS) is the oldest scientific institution in the West and houses one of the largest natural history museums in the world, attracting about 1 million visitors each year. The CAS Education Division serves over 400,000 participants, many of them from urban, disadvantaged backgrounds. While the main museum in Golden Gate Park is undergoing major renovation beginning January 2004, a temporary facility with exhibit and aquarium facilities will be open in downtown San Francisco. Over the 4 years of construction, the Institute's EPO team will collaborate with CAS by providing scientific and educational expertise, and by co-sponsoring and participating in CAS EPO activities. In addition to collaboration for VTT-PD, the Institute's scientists will act as scientific and educational advisors for CAS in planning and developing exhibits for the new facility on the theme of "Earth and its Place in the Universe." Because CAS scientists are primarily involved in systematic and organismal biology, the Institute's expertise will complement existing resources and enrich the physical science and astronomical components of the new exhibitry. The Institute will work closely with Drs. M. Burke and C. Tang (a CAS astrobiologist and educator) to coordinate efforts. This will be collaborative work that grows from the long-term relationship between the Institute and CAS which has been both collegial and formal as partners in the development of curriculum materials, presentation of courses and workshops, and lectures at CAS. Beyond advising on future exhibits and programs, the Institute will be a co-sponsor for select CAS education outreach programs. The opportunity for continued and ongoing collaboration with CAS's education group effectively leverages NASA's EPO funding through NAI. The Institute will participate in and provide financial support (see Table 5) for the CAS education program as follows:

(1) ScienceNow, museum exhibit: The Institute NAI EPO program will contribute scientific information, images, and expertise for the development of two ScienceNow panels each year for public display. The panels will also be featured and archived on the CAS web site.

(2) New Exhibit Development for "Earth in its Place in the Universe": The Institute's EPO team will identify and support NAI team members as advisors and reviewers for development of exhibits and classroom materials providing scientific and educational expertise. Included is support for new exhibit prototyping and "road testing" of materials for both exhibits and curriculum.

(3) Public Education: Institute scientists and educators will be speakers and presenters for educator (teachers, docents, staff and interns) workshops, the BioForum series, and other public lectures such as Member's Lectures, the Planetarium's Dean Lecture series, the Leakey Series, book signings, and other Special Forums. Support for these events is provided in the Institute's proposed EPO budget. A letter of support from CAS affirming the collaboration appears in Appendix C.

Education Outreach, Media Opportunities and Public Events: As detailed in Table 4, the Institute has an active and far-reaching EPO program supported by the EPO team and the Institute's Public Information Office that often works in close coordination with NASA's Public Information Office with media contacts for our PIs and Co-Is. The Institute's NAI team on this proposal has been involved in our Public Outreach Program activities, and we plan to facilitate additional opportunities for them over the next 5 years. Further, the Institute's EPO team conducts an active program of workshops and short courses at regional and national science teacher meetings; NAI-EPO workshops and short courses will be proposed and conducted as a part of our overall outreach for educators..

NAI EPO Network Participation

The Institute expects to participate fully with other NAI members in the NAI EPO virtual network to share successful EPO programs and projects. For example, other current NAI members have already expressed interest in conducting VTT workshops or institutes at their sites. The Institute's planning and strategies will be shared openly; Institute staff could be available to assist at other NAI sites as appropriate. The SETI Institute expects to provide activity reporting in a timely and accurate way to NAI Central. Because of the experience as the NASA EPO lead on other projects, the Institute's EPO team understands the requirements for such reporting. The Institute anticipates participation in the OSS Origins Forum, and other NASA programmatic activities related to EPO in concert with the Institute's other NASA EPO program requirements.

Curriculum Projects for Formal Education
• *Voyages Through Time, (VTT)* a standards-based, astrobiology curriculum for high school integrated science centered on the unifying theme of evolution • *Life in the Universe Series (LITU Series)*a supplementary series of six science teaching guides for grades 3-9 on the theme of the search for life in the universe
Outreach & Professional Development for Science Educators
• *Australian-American Fulbright Symposium 2002: Science Education in Partnership*, E. DeVore US co-chair with K. Wilmoth, NAI, and C. Oliver and L. Vozzo of the Australian Centre for Astrobiology and University of Western Sydney; held simultaneously with the *IAU Symposium 213 Bioastronomy Conference: Life Among the Stars*, July 2002 • *Educator Day for Division of Planetary Sciences*, Institute EPO staff are the lead organizers for the DPS day-long teacher workshop, Sept. 2003 • *Short Courses for Science Teachers*, professional development courses for *SOFIA*, *LITU Series*, *VTT*, and others at major regional and national science teacher meetings, 10 over past 2 years

• *Workshops for Science Teachers*, 1-2 hour workshops regional and national science teacher and astronomy meetings, 130 over the past 6 years • *Invited Talks*, SETI and astronomy including SOFIA and Kepler, teaching astrobiology and evolution, and teacher professional development at American Association of Physics Teachers, American Geological Institute, and several different State Science Teacher Associations
Online, Science Museum & Planetarium Projects for Informal Education:
• *Other World's, Other Beings*: interactive science museum exhibition and 2 planetarium programs developed by Pacific Science Center; Institute advised on all exhibits; the Institute's SETI scientists were featured in interactive kiosks; and the Institute's EPO team produced the two planetarium programs (1997-present: on exhibition) • *Cosmic Origins:* interactive science museum exhibition under development by the Space Science Institute involves SETI, NAI, *SOFIA*, *Kepler*, *VTT* and the *LITU series* (NSF & NASA funded) • *SETI*, an animated, video planetarium program developed with the National Space Center, UK • *NASA's QUEST* and *Women of NASA* feature several Institute projects and scientists • *Virtual Field Trip to Lincancabur*, an IDEAS project led by Co-I N. Cabrol that supported a virtual field trip for students and the public during her exploration of the world's highest lake, Fall 2002, in cooperation with Shasta County Schools, a rural underserved community
NASA Mission Education & Public Outreach Programs
• *SOFIA*, NASA's Stratospheric Observatory for Infrared Astronomy; EPO program that trains and integrates K-14 educators into the research environment onboard *SOFIA* (1996-current) • *Kepler*, NASA's Discovery Mission that seeks evidence of Earth-like planets in habitable orbits around Sun-like stars (2002-2011) • *ABE*, Astrobiology Explorer, a pending mission with a consortium of EPO groups; the Institute's participation will support dissemination of *Voyages Through Time*.(pending) • *Origins Forum*, Institute staff participate fully in OSS's Origins Forum (ongoing)
Public Outreach Program
• *Public Lectures:* Institute scientists have presented more than 100 public talks at science museums, civic organizations, colleges and universities throughout the nation and world during the past year • *Television Documentaries*: Institute scientists are often featured in documentary programs, e.g., Voyager Missions, SETI, solar system exploration, comets and meteors--all related to astrobiology • *Are We Alone?* A weekly one-hour talk radio show that emphasizes the search for life in the universe • *SETI: The Search For Life* on *Space.com*: a weekly column by Institute scientists and educators on since November 2000, more than 100 articles published on astrobiology-related topics • *SETI Institute News*: the quarterly publication of the SETI Institute • *Silicon Valley Astronomy Lecture Series*: co-sponsor with Astronomical Society of the Pacific, NASA Ames Research Center, and Foothill Community College, the host institution • *SETI Institute Web Site:* established 1994; the Institute's popular web site provides information on the scientific search for life in the universe to over 100,000 unique visitors each month. • *Astronomy & SETI Classes for the Public*: taught for California Academy of Sciences and Elderhostel • *CONTACT*: provided advice and role models for this feature film starring Jody Foster
Recent Textbooks and Popular Books:
• *Life in the Universe*, J. Bennett, S. Shostak, & B. Jarkowsky, college introductory astrobiology 2003 • *The Everything Astronomy Book*, C. Phillips (Co-I on proposal) and S. Priwer, introductory astronomy for the general public, 2002 • *Cosmic Company*, S. Shostak & A. Barnett, companion to *SETI* planetarium program, 2003 • *SETI 2020: A Roadmap for the Search for Extraterrestrial Intelligence*, Institute's report of the Science and Technology Working Group that outlines the future of SETI research, 2001

Table 4: SETI Institute's Current Education and Outreach Programs

Facilities and Equipment

Section 2.

Co-I Freund has the necessary lab space at NASA Ames including access to collaborator Dr. Rothschild's labs. These two labs are located at NASA Ames Research Center and include shared facilities with SETI PI Rocco Mancinelli. Jointly the labs have all of the basic equipment for studies of microbial physiology, DNA damage and ecology including a Zeiss Axioscope microscope with phase optics, fluorescence, DIC optics and both film and digital cameras with OpenLab software for image analysis. In addition, their labs have assorted equipment for biochemical and molecular analyses (e.g., speed vac centrifuge, thermal cycler, horizontal and vertical gel electrophoresis equipment, UV and white light boxes and cameras). Centrifuges, autoclaves, combustion oven and drying ovens are all available on the same floor. An EPA-certified analytical lab is located one floor below Rothschild’s lab. This lab uses EC-HPLC to analyze DNA that Rothschild’s lab prepares for analysis of DNA damage.

Section 3.

Co-I Bakes currently has all the facilities and computational resources necessary at NASA Ames Research Center to investigate quantum photochemical models of Titan’s haze.

Section 4.

Dr. Bishop has laboratory space at NASA-Ames Research Center (building 239, SSX Branch) for synthesis of the iron oxide/oxyhydroxide minerals as described in section 4. Collaborator Dr. Rothschild has two labs at NASA Ames Research Center and shared facilities with SETI PI Rocco Mancinelli. Jointly the labs have all of the basic equipment for studies of microbial physiology, DNA damage and ecology including a Zeiss Axioscope microscope with phase optics, fluorescence, DIC optics and both film and digital cameras with OpenLab software for image analysis. Additionally, they have a model Z1 Coulter Counter, a UV/Visible plate reading spectrophotometer and fluorometer (Molecular Devices), glassware, balance, pH meter, microprobes for pH, O_2 and CO_2 measurement, a Li-Cor model LI-185B quantum/ radiometer/ photometer with an spherical sensor, a broad band UVA/UVB meter (Solar Light Company), an underwater temperature sensor, several microfuge centrifuges, a radioisotope hood, anaerobic hood, gas manifolds, incubators, freezers, chromatography refrigerators, and assorted supplies. In addition, their labs have assorted equipment for biochemical and molecular analyses (e.g., speed vac centrifuge, thermal cycler, horizontal and vertical gel electrophoresis equipment, UV and white light boxes and cameras). Centrifuges, autoclaves, combustion oven and drying ovens are all available on the same floor. An EPA-certified analytical lab is located one floor below Rothschild’s lab. This lab uses EC-HPLC to analyze DNA that Rothschild’s lab prepares for analysis of DNA damage.

One piece of specialized equipment is described under “Iron, the Oxygen Transition, and Photosynthesis” (Bishop and Rothschild), a constant-temperature water bath on the roof. This facility was custom-built with a long, six-inch deep plexiglass container, recirculating water and a heater and cooler. Thus, organisms can be grown exposed to natural solar radiation but grown at a set temperature.

Section 5.

Co-Is Cabrol and Grin have access at to all the equipment and facilities necessary for the completion of this investigation at NASA Ames Research Center, UCLA, and Universidad Catolicà del Norte (UCN), Chile. This includes: I) General: Access to UNIX machines, Macintosh computers, color, black & white printers, map printers, and software (e.g., Statistica 4., Mathematica, Excel, Deltagraph, Kaleidagraph, Adobe Photoshop 5.1, GraphiConverter, NIH Image 1.6.1, Word, and Powerpoint) for processing of both images and data allowing mapping, modeling, and 3-D rendering of data; Video conference room of Ames as well as conference phone lines for telecons. II) for "Geophysics": computer time and CPU for analysis of logger and on site data; III) "Chemistry": laboratory (care of UCLA Dept. of Civil and Environmental Engineering) for Ion Chromatography, use of UCLA Earth and Space Sciences Inductively Coupled Mass Spectrometer; IV) For biology, use of NASA Ames Research Center lab (see Lynn's Rothschild facility description), including cold chambers for preservation of samples; Use of UCN biology laboratory; V) GPS units, RangeFinders and laser target, field flags, soil, water thermometers, soil temperature profiler (heat flux probe) + short term logger (small PC or similar), hobo environmental dataloggers (for water temp, air temp, relative humidity), ELDONET UV dosimeters, UV acrylite plates, sample containers as well as lab equipment that may be necessary at the time of analysis (flasks, additional reagents, pippettors, etc.), water sampling kits, DGGE equipments, microscopes, culture facililties.

Section 6.

Co-I Amos Banin will perform advanced soil and water research and analyses laboratory at the Department of Soil and Water Science, Hebrew University, Rehovot. Laboratories are well-equipped for advanced analyses of soils and water, using ion selective electrodes, various potentiometric methods, UV-VIS spectroscopy, pyrolytic DOC analysis and microwave analytical digestion system (CME) for controlled-conditions (temperature and pressure) digestion of organic and mineral materials. Mineralogical analyses employing XRD and DTA and TEM and SEM instrumentation. Available at the Interdepartmental Equipment Unit of the Faculty of Agricultural, Food and Environmental Quality Sciences in Rehovot are: Two advanced ICP-AES instruments (Spectro) for multi-elemental analysis in high-electrolyte matrices. A state-of-the-art ICP-MS instrument (Elan 6000, Perkin-Elmer) has in general 2 - 3 orders-of-magnitude better detection limits than the ICP-AES for trace metals in low-electrolyte matrices, enabling analyses at the ng/l (ppt) range. Pyrolytic-GC elemental analysis system (Fissons EA 1108) for analyses of C, N, H, S, O, in solids, liquids and gases has a measuring range of concentrations from 0.01% to 100%.

Co-I Rocco Mancinelli has lab space at NASA Ames Research Center and shared facilities with collaborator, Dr. Lynn Rothchild. These are described in section 4. Additionally, this team has constructed on the roof of the laboratory building an artificial intertidal facility for growing microbial mats in the open air using artificial sea water.

Section 7.

Dr. Summers has access to laboratories at the NASA Ames Research Center. His laboratory is equipped with chemicals, glassware, analytical balances sonic bath, strip chart recorders, pH meters, ovens, centrifuges, thermostatic baths, fumehoods, etc. The laboratory has a nitrogen line for purging samples and glassware. A vacuum pump is available for conversion to a schlenk line. The laboratory contains a 450 watt medium pressure mercury arc lamp, a CHEMTRIX Type 45 pH controller with Sage Inst. 341B syringe pump, and a glove box. The usual computers (PC and Macintosh) are present. Also available are a Hewlett Packard Series II Gas Chromatographs with a 5971 Series Mass sensitive Detector, a Nicolet Nexus 670 FT-IR, a Cary 3 UV-visible spectrophotometer, a Dionex Ion Chromatograph, a HP 1084 HPLC, A Technics Lab One reverse osmosis water purification system, a Hitachi 4000 FESEM with Noran Voyager EDS, and a Modified Phillips X-ray Diffraction. (All instruments are attached to suitable computers.) Co-I, Dr. Khare has much of the necessary specialized glassware already made up and has some additional gas handling equipment. Dr. Khare also has access to facilities in the Center for Nanotechnology to conduct the proposed research. Available are: Lyman-alpha source; reactor set-up; FTIR, Raman, UV-Vis-NR, NMR, SEM, TEM, AFM and STM and other characterization facilities; ion beam sputtering; general chemistry lab facilities; plasma generator.

Section 8.

At the Center for the Study of Life in the Universe at the SETI Institute (which Dr. Chyba directs), Drs. Phillips and Chyba have access to the full computational resources and imaging necessary to complete their research under section 8 of this proposal.

Section 9.

At the Center for the Study of Life in the Universe at the SETI Institute and at Stanford University where Mr. Hand is a graduate student, Drs. Hand and Chyba have access to the full computational resources necessary to complete their research under section 9 of this proposal.

Section 10.

Dr. Bernstein has all of the equipment needed to carry out the tasks described in this proposal, currently available at NASA-Ames Research Center. This includes multiple high vacuum ice simulation chambers with closed cycle helium refrigerators, IR spectrometers, various sources of UV radiation, two electron sources, and analytical techniques. More information about the scientists, the Astrochemistry Lab, ongoing projects, recent publications and pictures of the facilities can be found on line at the Astrochemistry Lab web site at http://www.astrochem.org

A. Sample Preparation

In order to reproduce the unusual conditions experienced by an ice on the surface of an icy satellite we employ a high vacuum - closed cycle helium cryostat apparatus. With this equipment we can (under a dynamic vacuum at ~10-8 Torr) hold a substrate anywhere from 12 to over 300 K. It is on this substrate that the ice analog is formed as a thin film of ice by vapor deposition. Volatile samples (such as water vapor) are introduced into the stainless steel vacuum system as gases that are previously mixed in glass bulbs using a glass manifold at room temperature. Non volatiles, such as PAHs are vapor deposited from an evacuated Pyrex tube, heated if needed. Our cryostat is mounted on a double O-ring seal so once the sample is deposited we can rotate the window to face the source of UV radiation, or electrons. We have many UV sources including mercury, deuterium and xenon lamps but typically use a microwave-powered, hydrogen flow, discharge lamp for the production of UV radiation (C.2). We have a Kimball Physics EGG electron gun which allows us to irradiate our sample with electrons tuned to any energy between ~100 eV and 10 keV, and a 20 keV electron gun extracted from a CRT. After irradiation (and spectroscopy) at low temperature we warm the sample monitoring the evolution of the ice using IR spectroscopy. Once the volatiles have sublimed away, the residual, non-volatile, organic film that remains is washed from the substrate with water and analyzed by attaching a chiral fluorescent tag to any primary amines and separation by HPLC, or by attaching a trimethylsilyl (TMS) functional group to reactive -OH and NH2 moieties followed by analysis by GC-MS.

B. Sample Analysis:

IR Spectroscopy: Our experimental set-up allows us to take infrared (IR) spectra at low temperature while an experiment in progress so we use IR spectroscopy on the low temperature ices to check the starting materials before the reaction has begun and to monitor the progress of the reaction. Also, we use our IR spectrometer to monitor volatile molecules that sublime from the ice as it is warmed under vacuum, and take spectra of the non-volatile organics that remain. We have a Nicolet 740 IR spectrometer with a spectral coverage from 12,000 to 600 cm-1 (0.83-17 mm) and a Bio Rad excalibur with a spectral range of 15,000 to 75 cm-1 (0.67-130 mm) both which have a resolution of 0.5 cm-1.

GC-MS: Identifications are based not only on the retention time but also the mass spectrum on the unknown, and this allows us to perform isotopic labeling experiments and more securely identify unknown compounds. We use an HP 5971 series II GC-MS and bis[trimethylsilyl]acetamide to derivatize the residual organic materials from our simulations.

HPLC: We use an Hewlett Packard 1100 series HPLC consisting of a ternary pump with both a diode array UV detector and a four channel fluorescence detector. This HPLC, used in conjunction with a variety of columns (reverse phase, anion, cation, etc.), is an ideal configuration for the separation and detection of a wide range of polar compounds. While many compounds can be detected via their UV absorption, fluorescence generally increases sensitivity by orders of magnitude, so we intend to use fluorescence labeling to increase our sensitivity.

Section 11.

The work undertaken by Drs. Backus and Tarter to generate an enlarged list of 'Habstars' for the SETI targeted search with the Allen Telescope Array, will involve extensive manipulation of large data catalogs. All of these will be acquired prior to the commencement date of this proposal by exchanging adequate disk storage medium with the USNO or directly from the CDS portal in Strasbourg. Construction of the new target list is expected to be feasible with the existing computational resources of the SETI Institute. If additional capacity is required, it will be acquired as a charitable donation (the SETI Institute has enjoyed consistent success with this approach), or provided from funds available in Dr. Tarter's endowed chair, and constitute additional matching funds to this proposal.